Development of Heteroanionic Metal oxide Nanostructures for Solar and Mechanical Energy Harvesting

A thesis submitted for the partial fulfillment of the degree of Doctor of Philosophy

by

Maqsuma Banoo



Department of Chemical Sciences Indian Institute of Science Education and Research Sector-81, Knowledge City, Mohali, Punjab-140306

February 2024

CERTIFICATE

The work presented in this thesis has been carried out by me under the supervision of Dr. Ujjal K. Gautam at the Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali.

This work has not been submitted in part or full for a degree, a diploma, or a fellowship to any other university or institute.

Whenever contributions by others are involved, every effort is made to indicate this clearly, with due acknowledgment of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Date

Place

Maqsuma Banoo

In my capacity as supervisor of the candidate's thesis work, I certify that the above statements made by the candidate are true to the best of my knowledge.

Dr. Ujjal K. Gautam

(Supervisor)

ii

Dedicated to my parents

from whom I learned the immeasurable value of perseverance and the importance of always giving my best when confronted with challenges.

Acknowledgments

In the name of Almighty, the most gracious and merciful, who bestowed upon me the strength and perseverance to accomplish my work to the best of my abilities, I would like to express my profound gratitude and heartfelt appreciation to my supervisor, Dr. Ujjal K. Gautam. His untiring guidance, support, and invaluable insights have been instrumental in shaping my research journey. His expertise, dedication, patience, and encouraging nature have not only enriched my understanding of the subject matter but also elevated the quality of my thesis. I appreciate all the insightful discussions, ranging from fundamental concepts to intricate scientific problems. I am greatly amazed and inspired by his remarkable ability to think innovatively and creatively, going beyond conventional boundaries. I consider myself fortunate to have been supported by a compassionate and amiable mentor throughout my Ph.D. journey. I am grateful to him for his support and understanding during the traumatic phases of my Ph.D. journey. Above all, I deeply respect him for being a genuinely good human being. Thank you sir for everything.

I would like to thank Prof. J Gowrishankar (Director, IISER Mohali), Prof. N. Sathyamurthy (former Director, IISER Mohali), Prof. Sanjay Singh (Head of the Department of Chemical Science, IISER Mohali, and Prof. S. Arulananda Babu (former HOD, DCS) for providing exceptional research facilities at IISER Mohali.

I would like to express my genuine gratitude to Prof. Sanjay Singh and Dr. Arijit Kumar De, who served as members of my thesis committee. I am grateful for their expertise and scholarly input, which have played a vital role in refining and strengthening my research work.

I am truly thankful to Prof. Sanjay Singh, Dr. Jino George, and Dr. Angshuman Roy Choudhury, my course instructors for their dedication to imparting knowledge and their commitment to creating an enriching learning experience.

I am immensely grateful to my collaborators, Dr. Goutam Sheet (IISER Mohali), Dr. Dirtha (Sanyal from Homi Bhabha National Institute), Dr. Vinod (NCL Pune), Dr. D. G. Porob (Goa University), Dr. Dibyajyoti (IIT Delhi) for their invaluable assistance and fruitful discussions.

I would like to acknowledge the Council of Scientific and Industrial Research (CSIR) India for my Scholarship.

To my wonderful labmates, Dr. Bramhaiah, Dr. Abhishek, Reeya, Raj, Komal, Supriya, Arjun, Mukul, and Sahil, I would like to extend my deepest gratitude. Each of you has played an integral role in making my time in the lab truly enriching and less daunting. I am immensely grateful for your willingness to lend a helping hand, share valuable insights, and engage in fruitful discussions. Furthermore, I want to express my heartfelt thanks for the friendly and supportive atmosphere within the lab. I deeply appreciate the moments of laughter, shared experiences, and the steady support I have received during my challenges.

I would like to extend my heartfelt appreciation and gratitude to Kaustav, Sandita, Jaspreet, Aman, and Arjun for the valuable contributions they have made to my research.

I am incredibly grateful to all my friends Garima, Komal, Saba, Sushil, Reeya, Rubiya, Sumina, Anjum, Sahila, Dilnaz, Sajida, Kaneez, Kherun, Tsering, Yogi, Sachin, Bali, Vishal, Shefali, Narender, Deepak, Arjun, and Umer for their words of motivation during the challenging times of research

I want to extend a special expression of gratitude to Garima, Komal, Saba, and Sushil for their exceptional listening skills and empathetic nature. Their support and understanding during moments of personal struggles have been a true blessing. Their willingness to lend an ear and provide comfort has been a testament to their genuine care and friendship.

Special thanks to Dr. Monikankana Sharma and Mr. Anuraj Gautam (Reon) for their kind hospitality, affection, and care.

My vocabulary utterly fails in expressing my accolade to my revered parents (Aata and Amaly) who brought me to this stage. Thank you for the endless love, support, sacrifices, understanding, patience, belief in my abilities, and countless words of encouragement. I am profoundly blessed to have parents like you in my life.

To my siblings (Achy, Nomo, Nono Javid, and Nono Imti.), my Brother-in-law (Kaka Zahir), and my adored Niece and Nephew, I am incredibly thankful for your support and unconditional love. Your presence has infused my life with joy, laughter, and a profound sense of ease.

I am immensely grateful to my maternal parents (Ajang Chopo, Ajang Parpa, Ajang Doctor, Ajang Bulu) for their unconditional support and boundless affection.

I am grateful to Kaka Anwar (Cousin) for all his motivation during my Ph.D. journey.

Thesis Synopsis

The thesis "Development of Heteroanionic Metal Oxide Nanostructure for Solar and Mechanical Energy Harvesting" presents a comprehensive investigation into the Sillen Aurivillius (SA) phase, a unique class of metal hetero-anionic oxides for utilization in solar and mechanical energy harvesting. The thesis is structured into four main parts. Part 1 elucidates the imperative for renewable energy harvesting, how it can be harnessed, and underscores the significance of Sillen Aurivillus phases as pivotal candidates in this pursuit. Additionally, it provides insights into the characterization techniques employed in this thesis Part 2 introduces the synthesis of the Sillen Aurivillius phase under ambient conditions and demonstrates its remarkable photocatalytic abilities by enabling the photocatalytic deethylation of waste Rhodamine B into the valuable pro fluorophore Rhodamine 110 and production of green and high energy density fuel i.e., hydrogen peroxide. Additionally, the study uncovers the SA phase's self-activation property, driven by surface reconstruction observed during various reactions. Part 3 explores the piezocatalytic ability inherent in the Sillen Aurivillius phase, showcasing its exceptional bifunctional property in the simultaneous production of hydrogen peroxide and hydrogen evolution. Additionally, we unravel the structural and electronic transformations that transpire under the piezocatalytic conditions using a centrosymmetric BiOBr microsphere, shedding light on the underlying mechanisms driving this universal phenomenon and extending the piezoelectric property beyond noncentrosymmetric substances. Part 4 proposes a novel wastewater treatment approach by integrating photocatalysis and piezocatalysis, demonstrating the SA phase's multifunctionality for sustainable solutions. This research underscores the SA phase's promise in catalysis, energy generation, and environmental remediation.

Part 1: General Introduction and Characterization

Chapter 1.1. describes the fundamental concepts of photocatalysis, piezocatalysis, and the innovative synergy between them, known as piezo-photocatalysis, emphasizing their collective potential to efficiently harness and conserve both solar and mechanical energy, thereby presenting a promising solution to the persistent global energy crisis. This chapter provides insights into recent developments and materials explored in this field and identifies key research gaps that warrant further investigation. Furthermore, it highlights the significance of Sillen Aurivillius phases as prospective solutions due to their unique properties, including flexible crystal structure, visible light absorbing property, ferroelectric property, and robust stability which can potentially address the limitations of existing energy conversion systems and propel advancements in sustainable energy technology.

Chapter 1.2. contains comprehensive details regarding the characterization techniques employed in this thesis and the experimental procedures adopted for performing photocatalytic, piezocatalytic, and piezo-photocatalytic processes.

Part 2: Photocatalytic Investigations of sillen Aurivillus

Chapter 2.1. elucidates the successful fabrication of composites comprising Bi_3TaO_7 and Bi_4TaO_8X (X= Cl and Br) through ambient air treatment of precursors, retaining over 60% of the halide phases and demonstrating significantly enhanced photocatalytic activity compared to pure Bi_3TaO_7 and Bi_4TaO_8X . Incorporating minute amounts of noble metals into these composites suppresses the recombination of photo-generated excitons, enhancing photocatalytic performance. The research explores the photodegradation of Rhodamine B, revealing the generation of reactive species and reaction intermediates. Remarkably, even under extreme conditions at pH 2, these catalysts exhibit outstanding stability against both

light and acid, with only a 2% reduction in activity after ten repeated cycles, promising practical applications in environmental remediation.

Chapter 2.2. introduces Rh110 as the most widely used pro-fluorophore in biological studies, and has recently gained prominence in SARS-CoV-2 research. Current commercial Rh110 production methods involve the high-temperature condensation of phthalic anhydride and maminophenol, resulting in challenges for side product separations, reduced purity, and excessive costs. In contrast, other xanthate-based dyes like Rhodamine B (RhB), structurally similar to Rh110 but with protected amino groups, are highly stable and cost-effective for industrial applications. However, their stability hampers decomposition and makes them environmental pollutants, rendering them unsuitable as pro-fluorophores. Notably, Rh110 is upto 1000 times costlier than RhB. This research demonstrates a commercially viable method to convert RhB into Rh110 using Bi₃TaO₇-Bi₄TaO₈Br heterostructures as photocatalysts. These heterostructures efficiently deprotect the amino groups of RhB to yield pure Rh110. A remarkable finding is the substantial surface reconstruction of the catalyst heterostructures during the reaction, enhancing catalytic efficiency without the typical deactivation seen in photocatalysts over cycles. This study has practical implications and holds historical significance by reviving the commercial value of Rh110 as a degradation intermediate in a sustainable manner, bringing considerable worth to this long-established reaction.

Chapter 2.3. explores the challenges facing conventional methods of hydrogen peroxide (H_2O_2) production, highlighting its significance as an industrial oxidant and emerging solar and rocket fuel. This chapter introduces a novel approach to utilizing facet-controlled Sr₂Bi₃Ta₂O₁₁Cl nanoplates of the Sillen Aurivillius (SA) phase, to achieve an impressive H₂O₂ production rate (~3 mmol/h/g) with an apparent quantum yield of ~17.5%. A noteworthy feature of this catalyst is its unique self-activation property, continuously enhancing performance over an unprecedented 15 days of continuous operation, surpassing typical

stability benchmarks. Comprehensive investigations employing various analytical techniques reveal that defect-induced enhancements, including oxygen adsorption, charge transfer, exciton separation, and a reduction in the band gap, collectively contribute to this self-activating behavior. This pioneering catalyst represents a significant advancement in sustainable and efficient H_2O_2 production, offering a promising alternative to traditional methods and catalytic technologies.

Chapter 2.4. is dedicated to the in-depth exploration of double-layered Sillen Aurivillius phase $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates, showcasing their capability in efficiently producing the profluorophore Rh110. This research is particularly noteworthy for an impressive 54% yield of Rh110 within a mere 180 minutes during the first catalytic cycle compound to 480 min observed in Bi₄TaO₈Br heterostructures in the 2nd cycle. Equally noteworthy is the observation of an unprecedented self-activation rate, yielding 100% efficiency by the 11th cycle, outperforming Bi₃TaO₇-Bi₄TaO₈Br heterostructures, thus highlighting the potential for significant Rh110 production.

Chapter 2.5. summarizes the key observations and future prospects of the studies described in Part 2.

Part 3: Piezocatalytic Investigation of Sillen Aurivillus

Chapter 3.1. describes an emerging approach to hydrogen production, namely, Piezocatalytic water splitting, which has gained significant attention for its potential to overcome the limitations of traditional methods such as photo-, electro-, and photoelectrocatalysis. Unlike photocatalysis, this method doesn't require precise band alignment with the proton reduction potential since band-bending in the catalyst naturally occurs under pressure. Similarly, it doesn't necessitate high conductive material and external voltage as in electrocatalysis since surface potential develops due to atomic displacement, enabling even low-conducting materials

to split water. This study explores the potential of structurally diverse Sillen-Aurivillius phases for hydrogen generation, with Bi₄TaO₈Cl nanoplates as a representative. These nanoplates demonstrate high efficiency in water splitting, simultaneously producing hydrogen and H_2O_2 without the need for Cocatalysts and scavengers. Impressively, these achieve a hydrogen generation rate of 1.5 mmol/g/h, which further improves with hole-trapping agents. Notably, this work marks the first-ever demonstration of seawater splitting through piezocatalysis, yielding a hydrogen production rate of 854 µmol/g/h, surpassing many oxide-based photocatalysts and piezocatalysts for pure water. These results open doors to flexible, efficient piezocatalysts, offering prospects for sustainable hydrogen production.

Chapter 3.2. introduces the exploration of piezoelectricity in centrosymmetric BiOBr. Conventionally, piezoelectric materials have required non-centrosymmetric crystal structures, posing a century-old challenge. However, we overcame this limitation by inducing polarization in centrosymmetric BiOBr through the creation of oxygen vacancies, which was confirmed by multiple studies. The piezoelectric property of BiOBr was evaluated using piezoelectric force microscopy (PFM), unveiling unexpected piezoelectric behavior with a piezoelectric constant of 93 pm/V. Furthermore, BiOBr displayed remarkable bifunctional piezocatalytic activity for complete water splitting, concurrently producing H₂ and H₂O₂ without requiring co-catalysts or scavengers. High-pressure synchrotron X-ray diffraction and theoretical investigations were conducted within a pressure range of 0.048 to 42.48 GPa, closely resembling piezocatalytic conditions, to assess their impact on the crystal and electronic structure. Remarkably, BiOBr underwent a distinctive isostructural phase transition under high pressure, accompanied by a reduction in carrier effective masses, thereby enhancing electron mobility, all while maintaining crystallographic symmetry. These findings provide opportunities to design piezoelectric materials beyond centrosymmetric ones.

Part 4: Piezo-photocatalytic Investigation of Sillen Aurivillus

Chapter 4.1. describes the piezo-photocatalytic activity of SA phases for environmental remediation. Addressing the global concern of water pollution, particularly from organic pollutants and pharmaceuticals due to rapid industrialization and pandemic situations, has proven challenging. Photocatalytic decontamination using solar energy has shown promise but faces limitations in catalyst efficiency, specificity to certain pollutants, and effectiveness at realistic pollutant concentrations. The single-crystalline Bi₄TaO₈Cl nanoplates exhibit excellent piezoelectric behavior, generating pressure-induced band-bending and crystal deformation. By combining piezocatalysis and photocatalysis, the piezo-photocatalytic approach achieves exceptional efficiency because of its synergistic effect, surpassing most single-contaminant-specific catalysts, even at real-life pollutant concentrations. Synergy varies widely among different contaminants and concentrations, highlighting the complexity of contributing factors. The study proposes a synergy generator gear-interlock concept to aid the rational design of high-synergy piezo-photocatalysts, offering a promising solution for addressing water pollution on a global scale.

Chapter 4.2. summarizes the key observations and future prospects of the studies described in Parts 3 and 4.

Contents

Certificate	i
Acknowledgment	v
Thesis Synopsis	vii
Table of Contents	xiii
Part 1. General Introduction and Characterizations	
Chapter 1.1. General Introduction	
1.1.1. Energy Crises and Clean Water Scarcity	1
1.1.2. Photocatalysis	3
1.1.2.1. Basic Principle and Mechanism of Photocatalysis	4
1.1.2.2. Type of photocatalysis	7
1.1.2.2.1. Homogenous Photocatalysis	7
1.1.2.2.2. Heterogenous Photocatalysis	7
1.1.3. Piezocatalysis	8
1.1.3.1. Fundamentals and Mechanism of Piezocatalysis	9
1.1.4. Piezo-photocatalysis	11
1.1.5. Application of photo, piezo, and piezo-photocatalysis	12
1.1.5.1. Environmental Remediation	12
1.1.5.2. Sustainable Fuel Generation	13
1.1.6. Photo, piezo, and piezo-photocatalyst and its development	16
1.1.7. Sillen Aurivillus phase	23
1.1.8. Concluding Remark	27

Bibliography

-	-
1.2.1. Materials	40
1.2.2. Characterization Techniques	41

Part 2: Photocatalytic Investigation of sillen Aurivillus

Chapter 1.2. Materials and Characterization techniques

Chapter 2.1. Synthesis of Bi₃TaO₇–Bi₄TaO₈Br composites in ambient air and their high photocatalytic activity upon metal loading

2.1.1. Introduction	48
2.1.2. Scope of the present investigation	49
2.1.3. Methods	50
2.1.3.1. Synthesis of Bi_3TaO_7 - Bi_4TaO_8X (X = Cl, Br) composite	50
2.1.3.2. Loading of co-catalysts onto the composite	50
2.1.3.3. Photocatalytic Experiments	50
2.1.4. Results and Discussion	51
2.1.4.1. Photocatalytic RhB Degradation	53
2.1.4.2. Photodeposition of noble metal on Br Composite	56
2.1.4.3. Enhanced activity by noble metal loading	58
2.1.5. Conclusion	64
Bibliography	

CHAPTER 2.2. A 'self-activating' Bi₃TaO₇-Bi₄TaO₈Br photocatalyst and its use in the sustainable production of pro-fluorophoric Rhodamine-110

2.2.1. Introduction	72
2.2.2. Scope of the present investigation	72
2.2.3. Methods	74

2.2.3.1. Catalyst Synthesis	74
2.2.3.2. Photocatalytic Reactions	74
2.2.4. Results and Discussion	76
2.2.4.1. Catalyst Characterization	76
2.2.4.2. RhB to Rh110 transformation by Bi_3TaO_7 - Bi_4TaO_8Br heterostructures	79
2.2.4.3. Mechanism of RhB to Rh110 transformation	87
2.2.4.4. Spontaneous surface evolution during improved Rh110 yield	92
2.2.4.5. Surface vacancies	92
2.2.4.6. Reconstruction led surface-charge variation for increasing	94
reactant adsorption with suitable on-surface orientation	
2.2.5. Conclusion	100
Bibliography	
Chapter 2.3. Surface reconstruction route for increasingly improved photocatalytic	
H ₂ O ₂ production using Sr ₂ Bi ₃ Ta ₂ O ₁₁ Cl	
2.3.1. Introduction	108
2.3.2. Scope of the present investigation	109
2.3.3. Methods	111
2.3.3.1. Catalyst Synthesis	111
2.3.3.2. Photocatalytic reactions	112
2.3.4. Results and Discussion	114

2.3.4.2. Photocatalytic hydrogen peroxide generation 116

114

2.3.4.3. Origin of self-Activation of SBTOC-F 121

2.3.4.1. Catalyst Characterization

2.3.5. Conclusion

Bibliography

Chapter 2.4. Massive self-activation in n=2 Sillen Aurivillus phase by vacancy associate formation for promoted photocatalytic pro-fluorophore Rh110 formation 2.4.1. Introduction 136 2.4.2. Scope of the present investigation 136 2.4.3. Methods 137 2.4.3.1. Flux Synthesis of Sr₂Bi₃Ta₂O₁₁Cl 137 2.4.3.2. Photocatalytic reactions 138 2.4.4. Results and Discussion 139 2.4.4.1. Catalyst Characterization 139

2.4.4.2. Photocatalytic RhB to Rh110 transformation by $Sr_2Bi_3Ta_2O_{11}Cl$	141
2.4.4.3. Mechanism of RhB de-ethylation	143
2.4.4.3. Origin of Enhanced Catalytic Activity	145
2.4.5. Conclusion	149
Bibliography	

Chapter 2.5. Conclusion and future outlook of part 2	152
--	-----

Chapter 3.1. Bi₄TaO₈Cl as a New Class of Layered Perovskite Oxyhalide Materials for Piezopotential Driven Efficient Seawater Splitting

3.1.1. Introduction	157
3.1.2. Scope of the present investigation	157
3.1.3. Methods	158
3.1.3.1. Catalyst Synthesis	158
3.1.3.2. Photocatalytic reactions	159
3.1.4. Results and Discussion	160
3.1.4.1. Catalyst Characterization	160
3.1.4.2. Piezocatalytic Hydrogen Generation	166
3.1.4.3. Seawater Splitting Prospects Using Piezocatalysis	170
3.1.4.4. Mechanism of Piezocatalysis and Influencing Factors in Seawater Splitt	ing 172
3.1.5. Conclusion	174
Bibliography	
Chapter 3.2. Unusual structural phase transition in BiOBr under high pressure a	nd
ultrahigh bifunctional fuel generation efficiency under piezocatalytic conditions	
3.2.1. Introduction	183
3.2.2. Scope of the present investigation	183
3.2.3. Methods	185

3.2.4. Results and Discussion	186
3.2.4.1. Piezocatalytic Hydrogen Generation	190
3.2.4.2. Structural Change at high pressure and	
origin of efficient piezocatalysis	195
3.2.5. Conclusion	200

Bibliography

Part 4: Piezo-photocatalytic Investigation of sillen Aurivillus

Chapter 4.1. Universal piezo-photocatalytic wastewater treatment at realistic pollutant feed-stocks by Bi₄TaO₈Cl: Origin of high efficiency and adjustable synergy

4.1.1. Introduction	209
4.1.2. Scope of the present investigation	209
4.1.3. Methods	211
4.1.3.1. Catalyst Synthesis	211
4.1.3.2. Photocatalytic reactions	211
4.1.4. Results and Discussion	212
4.1.4.1. Catalyst Characterization	212
4.1.4.2. Synergistically improved piezo-photocatalytic	
the efficiency of Bi ₄ TaO ₈ Cl nanoplates	217

4.1.4.3. Band-bending, exciton separation as the origin of synergy	220
4.1.4.4. Universality, diversifying synergy, and high	
concentration contaminant degradation efficiency	223
4.1.4.5. Deviation from expected behavior and the key	
synergy generator parameters	228
4.1.5. Conclusion	231
Bibliography	
Chapter 4.2. Conclusion and future outlook of parts 3 and 4	246

Part 1

General Introduction and Characterizations

CHAPTER 1.1.

Introduction

1.1.1. Energy Crises and Clean Water Scarcity

Energy crises and clean water scarcity are interconnected issues that have significant implications for global sustainability and well-being. Despite water covering 70% of the Earth's surface, the availability of freshwater, essential for drinking, agriculture, and other activities, is limited. Only 3% of the world's water is freshwater, with much of it inaccessible due to being locked in frozen glaciers and contaminated by industrial pollutants.^{1,2} Lack of access to safe drinking water affects approximately 25% of the global population, while nearly half lack proper sanitation services. Tragically, approximately two million individuals, primarily children, die each year from waterborne diseases caused by consuming contaminated water.³ Additionally, around two-thirds of the global population experiences severe water scarcity for at least one month annually, a problem worsened by climate change-induced water flow unpredictability.⁴ Clean water scarcity poses a significant challenge for the energy sector as well. Water plays a crucial role in electricity generation, fossil fuel extraction, and biofuel production. The global energy system heavily relies on freshwater resources, consuming approximately 370 billion cubic meters in 2021, or 10% of global freshwater withdrawals.⁵ The over-reliance on non-renewable fossil fuels like natural gas, oil, and coal (Figure 1.1.1.) has contributed to both energy crises and water scarcity. Projections indicate that global energy consumption will reach 778 Exajoules by 2035, highlighting the urgent need for sustainable and environment-friendly energy sources. The scarcity of energy and clean water has farreaching socio-economic consequences and geopolitical tensions. To address the challenges of energy crises and water scarcity, a comprehensive approach is required. The use of renewable energy resources, such as solar and mechanical energy from wind, ocean waves, and tides, plays a crucial role in diversifying the energy mix, reducing dependence on finite fossil fuels, and mitigating environmental impacts. Solar energy, with an average solar irradiance of approximately 342 Wm⁻², is abundant on Earth's surface. However, only around 70% (approximately 239 Wm⁻²) of this energy is available for human consumption, as the rest is scattered or reflected back into space.⁶ The utilization of solar energy for human use presents challenges, but various technologies exist to overcome these obstacles. One popular approach is photocatalysis, which enables the capture and storage of solar energy in chemical bonds.

This process addresses the challenge of efficient energy storage, making solar energy a viable option for meeting energy demands.



Figure 1.1.1. Global primary energy supply 2019. Adapted with permission from [9]

However, solar energy is intermittent and diurnal, necessitating the exploration of other renewable energy resources too. In this regard, an emerging process called piezocatalysis has gained attention. Piezocatalysis harnesses mechanical energy and converts it into chemical energy, offering a complementary approach to the utilization of solar energy. By combining these two processes, renewable energy can be harnessed from multiple sources simultaneously, ensuring a more consistent and reliable energy supply.^{7,8} Photocatalysis and piezocatalysis can be utilized for the treatment of wastewater, enabling the removal of contaminants and the production of clean water. These approaches not only address water scarcity but also contribute to the sustainable production of fuel.^{9,10}

1.1.2. Photocatalysis

Photocatalysis is a highly promising and eco-friendly process that utilizes one of the most abundant and renewable energy sources available to us: sunlight. This process involves driving a chemical reaction in the presence of a photocatalyst, a substance that absorbs light energy and transfers it to other chemical species in the system, without being consumed in the reaction itself.¹¹ The inspiration for photocatalysis comes from the natural process of photosynthesis, in which plants use sunlight as their sole energy source to convert atmospheric CO_2 into chemical fuels, while also employing the H₂O/O₂ cycle.¹² The concept of photocatalysis was first

introduced by Edmond Becquerel in 1839, but it did not gain mainstream attention until 1970 when Honda and Fujishima discovered the UV light-induced photo-assisted decomposition of water into hydrogen and oxygen over a titanium dioxide photoanode in an electrochemical cell.¹³ Since then, modern researchers have dedicated significant time, energy, and intellect to further developing and fully utilizing this concept.

Photocatalysis offers a perfect technique for the current global pursuit of a more sustainable world. It holds great promise for a wide range of applications, including environmental remediation, energy production, and chemical synthesis. With its potential to harness the vast energy of sunlight and drive chemical reactions cleanly and sustainably, photocatalysis is poised to play a critical role in shaping a brighter, more sustainable future.

1.1.2.1. Basic Principle and Mechanism of Photocatalysis

To achieve efficient photocatalysis, optimize catalyst design, and unlock its full potential, it is crucial to understand all the steps involved in photocatalysis and the associated time scale. Takanabe *et.al.* categorized photocatalysis into six different steps with different time scales (**Figure 1.1.2**).¹⁴

- 1) Photon absorption: In the first step of photocatalysis, the photocatalyst absorbs photons from a light source, such as sunlight or artificial light. Photon absorption and exciton generation are crucial processes that occur within femtoseconds. The electronic structure of the photocatalyst primarily determines this step.¹⁵ For effective absorption, the energy carried by photons must match or exceed the bandgap energy of the photocatalyst material, allowing electrons to transition from the valence band (VB) to the conduction band (CB) and generate electron-hole pairs. Besides the bandgap, other factors influencing photon absorption include the catalyst's absorption coefficient, band gap type (direct or indirect), band positions, optical penetration depth, refractive index, and light scattering and reflection.¹⁶ To enhance photon absorption various strategies have been employed including doping the photocatalyst with different elements, altering the crystalline structure or particle size of the photocatalyst, or utilizing composite materials.¹⁷
- 2) Exciton separation: Following successful photon absorption and the consequent generation of excitons, the excitons (electron-hole pairs) need to be separated to generate excited electrons and holes (free carriers) or else recombine readily. The separation of the excitons typically occurs when it suppresses the exciton binding energy determined by the electronic structure. The value of binding energy is determined by effective mass

and dielectric constant. The curvature of the electronic structure in the conduction and valence bands determines the effective masses of the electron and hole, respectively.¹⁸ Additionally, the electronic dielectric constant is also influenced by the electronic structure of a material. Photocatalysts with high dielectric constant, such as perovskite structures, are often known for their excellent performance.



Figure 1.1.2. Parameters associated with photocatalysis along with the time scale of reactions. Adapted with permission from [14]

3+4) *Carrier Diffusion and Transport:* Carrier diffusion and transport are other crucial steps involved in photocatalysis. It takes place on a microsecond time scale. Carrier diffusion refers to the movement of charge carriers, within the photocatalyst material typically driven by concentration gradients or electric fields. The efficiency of carrier diffusion is influenced by various factors, including the material's crystal structure, defects, and doping.¹⁹ And carrier transfer involves the transfer of charge carriers between the photocatalyst and other species, such as reactants or co-catalysts. This transfer can occur through surface reactions or by electron hopping between different sites on the catalyst material. Efficient electron transfer is essential for facilitating the desired chemical reactions and avoiding undesirable charge recombination.²⁰

5) Catalytic efficiency: Surface reactions involve the interaction of photogenerated charge carriers (electrons and holes) with adsorbed species or reactants at the surface of the photocatalyst. These reactions typically occur on a time scale longer than microseconds. Electrons at active sites function as reducing agents, transferring their excess energy to electron acceptors like oxygen molecules (O_2) or organic compounds, thus reducing the acceptor species. Conversely, holes act as oxidizing agents, accepting electrons from electron donors such as water molecules (H₂O) or organic molecules, resulting in the oxidation of the donor species. Surface reactions can follow various pathways depending on the specific reactants, properties of the photocatalyst, and reaction conditions. Factors like the nature of the adsorbed species and the accessibility of reactive sites on the photocatalyst surface can influence the selectivity of the photocatalytic process, including the preference for specific products or reaction pathways. The surface properties of the photocatalyst, such as composition, morphology, and surface functionalization, have a significant impact on surface reactions.²¹ Surface modifications such as doping the photocatalyst with different elements, introducing co-catalysts, or optimizing surface area and structure can enhance photocatalytic activity and selectivity by promoting specific surface reactions.²²

6) *Mass Transfer:* In photocatalysis, mass transfer refers to the movement of ions or molecules, including reactants, products, and intermediates, within the reaction medium or across the catalyst surface. Efficient mass transfer is crucial in photocatalysis to ensure an adequate supply of reactants to the catalyst surface and the effective removal of products to maintain reaction rates. Factors such as concentration gradients, species diffusivity, viscosity, and effective ion size influence mass transfer in photocatalysis. For instance, the presence of pore structures or surface coatings can hinder the diffusion of ions, impacting overall reaction efficiency.²³ Optimizing mass transfer is essential to enhance the accessibility of reactants to the catalyst surface and improve the overall performance of the process.

1.1.2.2. Type of Photocatalysis: There are two different types of photocatalysis.

1.1.2.2.1. Homogenous Photocatalysis

In homogeneous photocatalysis, the catalyst and reactants exist in the same phase, typically a liquid solution, offering advantages such as high reaction rates and selectivity due to efficient interactions and rapid energy transfer. Various compounds, including organic dyes like Eosin

Y, Methylene Blue, and Rose Bengal, as well as organometallic complexes such as ruthenium tris (2,2'-bipyridine) and fac-tris(2-phenylpyridine)iridium(III), along with polyoxometalates, are recognized and widely utilized as homogeneous photocatalysts.^{24–26} Homogeneous photocatalysis plays a significant role in the chemical industry, contributing to approximately 20% of its processes. It finds applications in important reactions like alcohol oxidation, (where catalysts like ruthenium-based complexes efficiently convert alcohols into aldehydes or ketones.) water-splitting reactions for hydrogen and oxygen generation, as well as in C-C bond formation reactions like Negishi, Suzuki, or Heck reactions.^{27,28} However, homogeneous photocatalysis faces challenges such as catalyst separation and recovery, as well as limitations due to catalyst solubility in the reaction medium.

1.1.2.2.2. Heterogeneous Photocatalysis

Heterogeneous photocatalysis emerges as a promising alternative, extensively employed in industrial catalytic reactions. In contrast to homogeneous photocatalysis, heterogeneous catalysis involves a catalyst that exists in a different phase (typically a solid, such as metals, metal oxides, zeolites, etc.) from the reactants (usually gases or liquids). In this process, the reactants come into contact with the catalyst and adhere to its surface, forming reactive intermediates. These intermediates then undergo chemical reactions through an alternative pathway with lower activation energy, resulting in increased reaction rates and the formation of products.

Heterogeneous photocatalysis offers several advantages over homogeneous photocatalysis. One of the primary advantages is the ease of catalyst separation from the reaction mixture, which simplifies the process and reduces costs. Unlike homogeneous catalysis, where catalyst separation can be complex and expensive, heterogeneous photocatalysis allows for straightforward physical separation techniques such as filtration, sedimentation, centrifugation, or magnetic separation. The solid nature of heterogeneous catalysts also enables their use in fixed-bed reactors or supported catalyst systems, where the catalyst is immobilized or supported on a solid material. This immobilization facilitates easy handling and separation, as the reaction mixture passes through the catalyst bed and the products can be collected separately from the catalyst.^{29–31}

Another advantage of heterogeneous photocatalysis is the ability to recycle and reuse the catalyst. After the reaction, the recovered catalyst can be regenerated and employed for subsequent cycles, reducing the need for frequent catalyst replacement and minimizing waste generation. This recyclability adds to the cost-effectiveness of heterogeneous photocatalysis

and makes it a sustainable option for industrial-scale processes. The solid nature of heterogeneous catalysts also allows for easy scalability of the reaction system. Industrial-scale processes can be readily implemented since the catalyst can be easily scaled up without significant challenges. This scalability, combined with the other advantages of heterogeneous photocatalysis, makes it an attractive option for various industrial applications. The benefits of heterogeneous photocatalysis make it a valuable technology with numerous applications.

1.1.3. Piezocatalysis

Piezocatalysis is a rapidly advancing and emerging field of research that shows great potential for applications in clean energy conversion, organic synthesis, and wastewater treatment. This technology harnesses mechanical energy from various sources such as ocean waves, vibrations, friction, wind, and tidal energy, using the distinctive properties of piezoelectric materials. Piezoelectric materials, which possess non-centrosymmetric crystal structures, were discovered by French physicists Jacques and Pierre Curie in 1880.^{32–34} they observed the accumulation of electric charges in these materials when exposed to mechanical stress and coined the term "piezoelectric materials" to describe them. Piezoelectric materials have traditionally been employed in electronic devices, such as transducers, actuators, and sensors, to introduce mechanical displacement and bias.³⁵ The concept of piezocatalysis, however, is relatively recent. It emerged in the early 2000s when researchers began exploring the potential synergy between piezoelectric materials and catalytic processes. An influential study by Wang's group in 2006 demonstrated the idea of piezocatalysis by utilizing aligned zinc oxide (ZnO) nanowires to harvest electricity from mechanical energy.³⁶

Despite being a relatively new field, piezocatalysis has attracted significant interest due to its potential for sustainable and efficient catalytic processes. By combining the principles of piezoelectricity and catalysis, piezocatalysis offers exciting opportunities for both scientific exploration and practical applications.

1.1.3.1. Fundamentals and Mechanism of Piezocatalysis

Piezocatalysis is analogous to conventional electrocatalysis, where electron transfer reactions are facilitated by applying electrical potential from an external power source. However, in piezocatalysis, the need for an external power source is eliminated as the driving force is provided by the piezoelectric potential resulting from piezoelectric polarization.³⁷ This

potential arises when a piezoelectric material undergoes mechanical deformation. The opencircuit voltage (Vp) generated across the piezoelectric material during mechanical deformation can be quantified using the following equation 1:^{38,39}

$$V_p = \frac{W_3 T_3 d_{33}}{e_0 e}$$
 eq1

Where, W_3 represents the thickness of the piezoelectric material, T_3 corresponds to the applied stress exerted on the piezoelectric material in the c direction. The term d_{33} refers to the piezoelectric coefficient, which characterizes the material's response to mechanical strain. Additionally, e_0 denotes the permittivity of free space, and e_r represents the relative permittivity specific to the c dimension.



Figure 1.1.3. Schematic diagram of ultrasonic cavitation bubble formation, growth, and the fluctuation of pressure because of the implosive collapse of a cavitation bubble. Adapted with permission from [40]

There are various methods of applying mechanical stress to piezoelectric materials. These include: i) vortex-induced shearing force: It involves the generation of a shearing force on the material through the creation of vortices or rotational fluid motions. ii) Physical bending: in this method, the piezoelectric material is physically bent or deformed, causing strain and stress within the material. iii) ultrasonic cavitations: ultrasonic cavitation refers to the formation, growth, and collapse of small gas-filled cavities, known as cavitation bubble, in a liquid medium when high-frequency ultrasound waves are applied. This phenomenon occurs due to rapid pressure fluctuations, resulting in the creation of low-pressure regions where dissolved gases come out of solution and form bubbles. The rapid collapse of the bubbles creates intense localized energy in the form of high temperatures (~10000) and pressures (~10^8 pa). This energy acts as a "hammer" on the catalyst present in the solution, potentially enhancing catalytic reactions (**Figure 1.1.3**)^{7,40-42}

In the field of electrocatalysis, the application of potential gives rise to two distinct possibilities: Firstly, the potential can induce oxidation of a species. This occurs when the applied potential reduces the energy levels of unoccupied states within the electrode, causing them to become lower than the highest occupied molecular orbital (HOMO) of a species in the solution. As a consequence, electrons transition from the HOMOs in the reactive species to the unoccupied states within the electrode, leading to its oxidation (center panel of **Figure 1.1.4. a**). Secondly, the potential can trigger the reduction of the solution. If the applied potential raises the energy levels of occupied states within the electrode above the lowest unoccupied molecular orbital (LUMO) of the species, it facilitates the transfer of electrons from the occupied states in the electrode to the LUMOs in the active species, resulting in its reduction (right panel of **Figure 1.1.4. a**).

Similarly, in piezocatalysis, the piezoelectric potential brings about changes in the energy landscape of the valence band (VB) and conduction band (CB) across the piezoelectric material (band bending). This alteration can significantly impact the material's interaction with its surrounding environment. When the energy levels of the VB approach those of the LUMO, it becomes energetically favorable for electrons to exit the VB and enter the LUMO (center panel of **Figure 1.1.4 b**). Likewise, if the energy levels of the CB approach those of the HOMO, it becomes energetically favorable for electrons to leave the HOMO and transition into the CB (right panel of **Figure 1.1.4 b**).⁴³



Figure 1.1.4. Energy diagrams describing the electrochemistry and piezocatalysis process. (a) The effect of applying a sufficient positive or negative bias to an electrode is to increase anodic and cathodic currents, respectively. (b) In the case of a piezoelectric, conduction and valence bands act as the reservoirs for electrons donated or accepted from molecules in solution. The piezoelectric polarization (P_{PZ}) applies a variable bias across the material, lifting and lowering valence band and conduction band energies. Adapted with permission from [43].

Piezoelectric materials possess the remarkable ability to generate exceptionally high potentials when subjected to varying degrees of strain. When the electrode potentials surpass a threshold potential numerous chemical reaction can become thermodynamically feasible.

1.1.4. Piezo-photocatalysis

Piezo-photocatalysis, which integrates the principles of both piezocatalysis and photocatalysis, presents a promising solution to overcome the limitations encountered in solitary photocatalysis and piezocatalysis. Both photocatalysis and piezocatalysis face specific challenges that impact their efficiency. Photocatalysis suffers from rapid charge recombination, leading to a decrease in quantum efficiency. On the other hand, piezocatalysis requires a high built-in electric field, resulting in low efficiency.

The integration of piezocatalysis and photocatalysis in piezo-photocatalysis offers several strategies to address the issue of low quantum efficiency. The application of mechanical stress generates a piezopotential on the surface of the catalyst, effectively separating the charges

generated during the photocatalytic process. Moreover, the catalyst, which may be inactive in piezocatalysis due to a low built-in electric field, becomes active in a photocatalytic manner. The combination of mechanical stress and light energy also exhibits a synergistic effect, leading to an improvement in the overall catalytic efficiency. This approach allows for the efficient utilization of multiple energy sources, enabling improved quantum efficiency and expanding the range of potential applications.^{44–47}

Ongoing research and development in the field of piezo-photocatalysis aim to further optimize the system design, explore novel piezo-photocatalyst materials, and deepen the understanding of the underlying mechanisms. These efforts contribute to the advancement of efficient and sustainable catalytic processes across various fields.

1.1.5. Application of Photo, Piezo, and Piezo-photocatalysis

1.1.5.1. Environmental Remediation

Photocatalysis, piezocatalysis, and piezo-photocatalysis provide an effective, sustainable, and environmentally friendly approach to the removal of pollutants. Industries such as textiles, dyeing, printing, and pharmaceuticals generate wastewater containing complex and persistent dyes and drugs that pose a threat to aquatic ecosystems and human health. Conventional removal methods like physical adsorption and chemical oxidation often fall short of achieving complete and efficient degradation.^{48,4950,51} Photocatalysis and piezocatalysis offer a sustainable solution by utilizing light energy and mechanical energy to generate electron-hole pairs and piezopotential on the catalyst surface respectively, which react with molecular oxygen and hydroxyl groups on the catalyst surface, producing various reactive oxygen species such as hydroxyl radicals ('OH), superoxide radicals ('O²⁻), and protonated reactive species according to the following equations. (O_2) _{ads} represents adsorbed molecular oxygen.^{40,51–55}

<i>Catalyst</i> + $hv \rightarrow e^- + h^+$	eq2

$(O_2)_{ads.} + e^- \rightarrow {}^{\bullet}\mathrm{O}^{2-}$	eq3
$h^+ + H_2 O \longrightarrow H^+ + {}^{\bullet}OH$	eq4
$h^+ + {}^-OH \leftrightarrow \bullet OH$	eq5
$\bullet O_2^- + H^+ \to \bullet OOH$	eq6
$\bullet OOH + \bullet O_2^- + H^+ \longrightarrow O_2 + H_2O_2$	eq7
$H_2O_2 + \bullet O_2^- \to \bullet OH + {}^-OH + O_2$	eq8

These reactive species then attack the chromophoric groups and chemical bonds within the dye or drug molecules, resulting in their degradation and eventual mineralization. The degradation efficiency can be significantly increased by simultaneously applying light and mechanical energy to a piezo-photocatalyst, such as ZnO, BiOBr, etc., through piezo-photocatalysis. Li *et. al.* synthesizes a composite of BiOCl/ NaNbO₃ for RhB degradation through photo, piezo, and piezo-photocatalysis and the proposed mechanism is shown in **Figure 1.1.5.**⁵⁶



Figure 1.1.5 Schematic showing photo, piezo, and piezo-photocatalytic organic pollutant degradation over BiOCl/NaNbO₃ Composite. Adapted with permission from [56]

1.1.5.2. Sustainable energy production

The quest for sustainable and clean energy sources has spurred significant interest in developing innovative approaches for fuel generation. Among the emerging technologies, photo, piezo, and piezo-photocatalytic processes have shown immense promise in harnessing renewable energy and driving efficient fuel production. These cutting-edge methodologies leverage the synergistic effects of light, mechanical energy, and catalysts to initiate and enhance chemical reactions, opening up new avenues for sustainable fuel generation. The two important reactions studied in this field are i) water splitting and ii) hydrogen peroxide production.

a) Water Splitting: Photo, piezo, and piezo-photocatalytic water splitting represent groundbreaking approaches in the pursuit of sustainable fuel generation. Water splitting is a highly desirable reaction as it produces hydrogen, a clean and high-energy-density (120–142 MJ kg⁻¹) fuel while yielding oxygen as a valuable byproduct. Notably, hydrogen stands out as

a zero-emission fuel, as its utilization in fuel cells or combustion solely yields water vapor as a byproduct, devoid of any greenhouse gas emissions or harmful air pollutants. The overall process of water splitting can be summarized in two half-reactions:^{55–57}

Reduction:

$$4H^{+} + 4e^{-} \rightarrow 2H_{2}, \quad E^{0} = 0 \ V \ vs. \ NHE \qquad eq9$$

Oxidation:
$$H_{2}O + 2h^{+} \rightarrow O_{2} + 2H^{+} + 4e^{-}, \quad E^{0} = 1.23 \ V \ vs. \ NHE \qquad eq10$$

To initiate the water-splitting process, in the case of photocatalysis, it is necessary for the band positions of the catalyst to be appropriately aligned. Specifically, the bottom of the CBs should have a more negative potential than the reduction potential of hydrogen ions (H^+) to hydrogen gas (H₂), which is 0 V vs. Normal Hydrogen Electrode (NHE) at pH = 0 (eq. 9) Additionally, the top of the VB should have a more positive potential than the oxidation potential of water to oxygen (O₂), which is 1.23 V vs. the NHE at pH = 0 (eq.10). This proper alignment of band positions is crucial for facilitating the efficient splitting of water into its constituent elements. On the other hand, in the case of piezocatalysis, no proper band alignment is needed. When mechanical stress is exerted on the catalyst, it induces strain or lattice defects, resulting in the generation of piezopotential at the catalyst's surface, resulting in sufficient band bendings that facilitate the dissociation of water molecules into hydrogen and oxygen. The precise mechanism of piezocatalytic water splitting is still an active area of research, and different catalyst materials may exhibit unique pathways. For instance, a study by Hong et al. demonstrated that ZnO nanofibers, when subjected to ultrasonic waves, develop sufficient electric potential on their surface. This electric potential triggers the redox reaction of water, as depicted in Figure 1.1.6.⁵⁸⁻⁶²



Figure 1.1.6. Schematic diagrams showing the charges developed on the ZnO fiber surface through bending with ultrasonic vibration and its participation in water splitting. Adapted with permission from [58].

Moreover, the coupling of photo and piezocatalysis i.e., piezo-photocatalysis can enhance the reaction rate and kinetics even further by promoting the movement of charge carriers, suppressing their recombination, and increasing their availability for water-splitting reactions. These combined effects make piezo-photocatalysis a powerful approach for improving the efficiency and performance of water splitting.^{63–65}

b) Hydrogen peroxide Production: Hydrogen peroxide (H_2O_2) is a chemically significant compound with wide-ranging applications in various industries. It also has the potential to serve as a clean and advantageous fuel source due to its low transportation costs. However, the current predominant method of H_2O_2 production, the anthraquinone process, has negative environmental implications along with many other limitations.^{66–69} Therefore, the utilization of renewable energy sources through photo, piezo, and piezo-photocatalysis is a meaningful contribution to sustainable objectives. H_2O_2 production can occur through three main pathways: oxygen reduction, water oxidation, or both (Two channels), each involving distinct reactions. In the oxygen reduction pathway, electrons generated by an external energy source (such as light, ultrasound, or both in the case of the photo, piezo, and piezo-photocatalysis, respectively) can reduce molecular oxygen (O₂) to superoxide radicals ($\cdot O^{2^-}$). These superoxide radicals can then react with protons (H⁺) to produce H_2O_2 according to the following equations:^{70–72}

$$O_2 + 2e \rightarrow O^{2-}$$
 eq11
2H⁺ + 2e $\rightarrow H_2O_2$ eq12

In the water oxidation pathway, water molecules undergo oxidation, resulting in the generation of hydroxyl radicals (•OH), which subsequently combine to form hydrogen peroxide. The reactions can be described as:

$$2H_2O \rightarrow 2 \cdot OH$$
 eq13
 $2 \cdot OH \rightarrow H_2O_2$ eq14

As shown in **Figure 1.1.7**., the study conducted by. Bai *et al.* showcased the "two-channel" photocatalytic hydrogen peroxide production utilizing a $g-C_3N_4$ coated CuO nanorod heterojunction, which incorporates both the water oxidation and oxygen reduction pathways. ⁷³ However, it is crucial to note that the specific pathway and relative contribution of each pathway to H_2O_2 production can vary based on the experimental conditions and catalysts utilized. The production of hydrogen peroxide through photo, piezo, and piezo-photocatalysis has gained significant attention due to its versatility and its potential to advance hydrogen peroxide synthesis while minimizing environmental impacts.


Figure 1.1.7. Schematic showing two-channel photocatalytic H_2O_2 production over C_3N_4 coated CuO nanorod heterojunction. Adapted with permission from [73].

1.1.6. Photo, Piezo, and Piezo-photocatalyst and its development

Photocatalyst: The groundbreaking discovery made by Fujishima and Honda, which involved the splitting of water using a TiO₂ electrode under light, is widely recognized as a pivotal moment that sparked the exploration of different semiconductor-based photocatalysts. Extensive research has been dedicated to understanding the fundamental principles of TiO₂ photocatalyst, improving its efficiency, and expanding its range of applications. However, TiO₂ exhibits limited performance in solar photocatalysis due to its wide bandgap (3-3.2 eV), which restricts its ability to effectively utilize a significant portion of the solar energy available on Earth's surface. As a result, substantial efforts have been devoted to discovering alternative photocatalysts.^{74–76}

Numerous metal oxides containing d⁰ and d¹⁰ transition metals such as WO₃, ZnO, Cu₂O, and SrTiO₃, have been explored as a possible alternative to TiO₂. Despite progress, the efficiencies of these photocatalysts remain unsatisfactory because of insufficient light harvesting. Over the past decade, significant efforts have been devoted to exploring complex metal oxides as novel photocatalytic materials. This includes the investigations on metal hetero-anionic photocatalysts such as metal oxynitrides, oxysulfides, and oxyhalides. The availability of multiple anions in these materials provides an opportunity for the development of visible light-absorbing efficient photocatalysts through electronic and crystal structure engineering. In

contrast to metal oxides, metal hetero-anionic photocatalysts exhibit narrower bandgaps (<3 eV) due to the inclusion of non-oxide anions with lower electronegativity, enabling absorption of visible light. In most metal hetero-anionic materials like MO_xN_y (metal oxynitrides), $M_xO_yS_z$ (metal oxysulfides), and MOX (metal oxyhalides), the valence band maximum (VBM) is primarily composed of non-oxide p orbitals such as nitrogen 2p, sulfur 3p, or halogen np. These electronic structures present a challenge because when photogenerated holes (h⁺) are produced, they can potentially react with non-oxide anions at the valence band maximum (VBM) leading to the photo corrosion of the material. This problem can be overcome by a new class of hetero-anionic materials i.e., *Sillen Aurivillius* phases which possess a distinctive electronic structure in which the p orbitals of the anions are embedded within the O 2p orbitals. This unique arrangement contributes to their enhanced photo durability compared to the above metal hetero-anionic photocatalysts (discussed *vide infra*). The electronic structure of these materials is shown in **Figure 1.1.8.**,^{77,78} illustrating the origin of high stability.

In addition to the synthesis of new materials, various other strategies such as heterostructure formation, Co-catalyst loading, defect creation, and doping have also been made to control the key steps of photocatalysis and improve the efficiency of these materials.



Figure 1.1.8. Schematic representation of the electronic structure of (a) metal oxide (MO_x) (b) metal hetero-ionic $(MO_xN_y, M_xO_yS_z, and MOX)$, and (c) *Sillen Aurivillius* (Bi_4MO_8X) . Adapted with permission from [77].

Heterostructure Formation: Heterostructure formation involves creating interfaces or junctions between different semiconductor materials within a photocatalyst. These heterojunctions are formed by carefully matching the band structures and energy levels of the materials involved. There are three primary types of heterojunction structures based on their band alignment.^{79–81}

a) Type-I heterojunction (**Figure 1.1.9 a**): In Type-I heterojunction, material A has a smaller band gap compared to material B. This configuration enables the transfer of electrons and holes from material B to material A, facilitating efficient charge separation and enhancing photocatalytic activity.

b) Type-II heterojunction (**Figure 1.1.9 b**): Type-II heterojunction exhibits an asymmetric band alignment. Material B has a more negative conduction band position, while material A has a more positive valence band position. This arrangement allows for the transfer of electrons from material B to material A and holes from material A to material B, establishing effective charge separation. Type-II heterojunction can also establish a Z-scheme configuration, where electrons from material A's conduction band combine with holes from material B's valence band, further enhancing catalytic reactions.

c) Type-III heterojunction (**Figure 1.1.9 c**): Type-III heterojunction shares similarities with Type-II heterojunction but has a larger energy disparity between the valence band and conduction band of the materials involved. This difference creates a stronger driving force for charge transfer, resulting in superior photocatalytic performance. In Type-III heterojunctions, electrons generated in material A combine with holes in material B, while electrons from material B and holes from material A participate in reduction and oxidation reactions, respectively.



Figure 1.1.9. Schematic showing the band alignment for three different types of heterojunctions.

These distinctive heterojunction structures offer significant potential for enhancing photocatalysis by facilitating efficient charge separation, maximizing light absorption, and optimizing electron-hole transfer. By carefully designing the band alignment and selecting appropriate semiconductor materials, heterostructures can be precisely tailored to significantly boost the overall photocatalytic activity of the system.⁸¹

Co-catalyst Loading:

Co-catalysts are frequently utilized alongside photocatalysts to enhance their efficiency and selectivity. In many cases, the addition of a suitable co-catalyst is necessary to achieve high activity and reasonable reaction rates in photocatalysis. Co-catalysts play a crucial role in regulating the kinetics of redox reactions by acting as electron or hole sinkers and facilitating the transfer of charge carriers. Furthermore, co-catalysts can modify the surface properties of the photocatalyst and provide active sites for desired reactions. There are two types of co-catalysts: oxidation co-catalysts and reduction co-catalysts. Oxidation co-catalysts, such as RuO₂ and IrO₂, promote oxidation reactions, while reduction co-catalysts, such as noble metals (Pt, Pd, Rh, Au), facilitate reduction reactions.

Among all noble metals, Pt is considered as best co-catalyst for photocatalytic hydrogen evolution. The efficiency of a reduction co-catalyst largely depends on its ability to effectively trap electrons from the light-absorbing semiconductor. This trapping capability is primarily determined by the work function of the co-catalyst. Pt has higher work functions compared to many semiconductors. Trasatti's research revealed a volcano relationship between the exchange current for H₂ evolution and the strength of the M-H bond (where M represents a transition metal). Platinum occupies the peak of this volcano, exhibiting the lowest activation energy for H₂ evolution. Hence, due to its electronic and catalytic properties, platinum is generally considered the most suitable co-catalyst for facilitating H₂ evolution in photocatalytic water splitting. However, one limitation of noble metals as co-catalysts is their tendency to catalyze the reverse reaction, leading to the formation of water from H₂ and O₂. This restricts their effectiveness as co-catalysts for overall water splitting.

To overcome this limitation, various methods have been developed to inhibit the undesired reverse reaction. One such technique involves coating the surface of the co-catalyst with a hydrated Cr_2O_3 nanolayer. This nanolayer prevents the migration of O_2 to the co-catalyst's surface while still allowing access to reactants such as H+ and H₂O. As a result, the co-catalyst selectively promotes the forward reaction of water splitting while inhibiting the reverse reaction. An example of this approach is demonstrated in **Figure 1.1.10.**, where Damain and co-workers successfully coated Rhodium (Rh) with Cr_2O_3 to create a core-shell

co-catalyst structure on GaN:ZnO, leading to enhanced photocatalytic overall water splitting.^{22,57,82}

These considerations highlight the need to explore catalysts or methods that can efficiently produce hydrogen without relying on co-catalysts. Developing such catalysts and methods could have significant implications for advancing photocatalytic water splitting as a sustainable means of hydrogen production.



Figure 1.1.10. (a) illustrates the process of Cr_2O_3 deposition through the reduction of Cr (VI) ions, where electron donor (D) and acceptor (A) are indicated. The high-resolution transmission electron microscopy images in (B) show GaN:ZnO with Rhodium (Rh) photodeposited onto its surface. The left image represents GaN:ZnO with Rh before the photodeposition of a Cr_2O_3 shell, while the right image shows the same material after the Cr_2O_3 shell is formed. (c) Plot showing the time course of overall water splitting over Rh@GaN: ZnO (left) and core/shell-structured Rh/Cr₂O₃@GaN: ZnO (right). Adapted with permission from [82]

Defect creation: Defects, even in minute quantities, play a crucial role in determining the properties of semiconductors. The type, concentration, and distribution of defects significantly influence the photocatalytic behavior of the semiconductor material. Therefore, optimizing defect concentration and understanding their impact on the material's electronic structure, surface chemistry, and charge transfer processes are vital for achieving enhanced

photocatalytic performance. Several commonly used methods for creating defects in semiconductors are as follows:^{83,84}

Doping: The intentional introduction of impurity atoms during the synthesis or fabrication process creates defects and modifies the electronic structure of the semiconductor. Doping with elements of different valence states generates additional energy levels within the bandgap, facilitating the absorption of a broader range of photons and enhancing photocatalytic activity.⁸⁵

Annealing and Thermal Treatment: Thermal treatments, such as annealing, promote the diffusion and rearrangement of atoms, resulting in defect creation as otherwise controlled heating and cooling cycles enable the creation and stabilization of specific defect types, such as oxygen vacancies or interstitials, which influence the photocatalytic performance of the material.^{86,87}

Chemical Etching: Etching processes selectively remove specific atoms from the semiconductor surface, inducing surface defects. By carefully controlling the etching conditions, such as the etchant concentration and temperature, surface defects like steps, terraces, or roughness can be created. These defects enhance light absorption and increase the active surface area for photocatalysis.^{88,89}

Furthermore, the in-situ creation of defects during the photocatalytic reaction can hold significant potential for advancing the field. This spontaneous defect formation will occur without the need for any special external energy sources or additional fabrication steps. Harnessing the dynamic formation of defects during the photocatalytic process represents an intriguing avenue for tailoring semiconductor materials with enhanced photocatalytic properties. In situ-created defects can act as active sites for catalysis, promoting desired reaction pathways and improving overall photocatalytic efficiency.

Piezocatalysts: In the mid-20th century, the practical applications of piezoelectric materials which can generate an electric charge in response to applied mechanical stress or, conversely, to deform or generate mechanical strain when an electric field is applied to them started to emerge. These materials are used in various devices, such as transducers, sensors, actuators, and resonators. The focus during this period was mainly on the functional properties of piezoelectric materials rather than their catalytic capabilities.⁹⁰ The idea of utilizing piezoelectric materials for catalytic applications gained attention in the early 21st century. It was observed that mechanical stress could modulate the energy landscape of a catalyst, influencing reaction kinetics and product distribution.⁷ Up to now various materials have been introduced to piezocatalysis. Initially, 1D wurtzite ZnO and BaTiO₃ were developed for

environmental remediation and to solve energy shortage problems. Further research introduces 2D morphology or 3D hierarchitectures also. Wang et al. in 2014 reported the strain-sensing capabilities of single-atomic-layer MoS_2 . ⁹¹ This discovery paved the way for the exploration of 2D materials (MoS_2 , $MoSe_2$, and WS_2) for efficient piezocatalysis. Additionally, bulk piezoelectric perovskite materials and layered Bi-based materials have been investigated as well for their suitability in piezocatalysis. For instance, Huang and co-workers reported the synthesis of the rhombohedral phase of BiFeO₃ nanosheets for piezocatalytic hydrogen production, utilizing sodium sulfate as a sacrificial agent for holes. The researchers demonstrated that when the BiFeO₃ nanosheets were subjected to ultrasound, they exhibited bending behavior, leading to the generation of piezopotentials on their surfaces. This piezopotential created a favorable energy landscape for hydrogen production (**Figure 1.1.11**).³⁹



Figure1.1.11. (a) Atomic structure of BiFeO₃ nanosheets (b) The diagram depicting the generation of piezoelectric surface charges when the material experiences mechanical vibration, and their involvement in the piezocatalysis hydrogen evolution reaction. (c) Energy band diagram in the absence of mechanical vibration and (d) the tilting of energy bands under the influence of a strong piezoelectric field induced by mechanical vibration, along with the accompanying redox reactions. (e) Piezocatalytic hydrogen production at different vibrational frequencies and (f) mechanical power. Adapted with permission from [39].

Piezo-photocatalyst: While piezocatalysis and photocatalysis hold significant promise, they do possess certain limitations and drawbacks solitarily. Photocatalysis, for instance, suffers from challenges such as sluggish charge separation, the necessity for proper band alignment, and inefficient utilization of light energy, which can limit catalytic activity. In the case of piezocatalysis, low catalytic efficiency can result from the requirement of high built-in electric fields to enable sufficient activation for electron transfer. Moreover, in piezocatalysis, a considerable fraction of the catalyst particles may not experience the necessary pressure due to inappropriate orientation to cavitation bubbles.

Nonetheless, recent progress has focused on the exploration of materials capable of harnessing both light and mechanical energy concurrently. BaTiO₃, ZnO, BiOCl, etc., have demonstrated this ability. These innovative materials address the limitations of solitary photocatalysis and piezocatalysis, exhibiting improved performance. The combination of piezoelectric and photocatalytic properties leads to synergistic effects, wherein the piezo-potential developed by mechanical stress application enhances the separation of photogenerated charge carriers and also forcibly adjusts the redox potentials of the catalyst to create a favorable energy landscape for the reaction, thus enhancing catalysis. Additionally, the particles which are inactive due to partial band bending during solitary piezocatalysis can still contribute to a photocatalytic pathway.^{92,93}

The piezo-photocatalysts have garnered interest due to their potential applications in various fields like environmental remediation, organic transformation, and energy harvesting. To develop efficient piezo-photocatalysts, further exploration of suitable materials and optimization of their structural and compositional properties are necessary. Researchers are actively investigating different combinations of piezoelectric and photocatalytic materials to create effective piezo-photocatalysts with improved performance.

1.1.7. Hetero-anionic catalysts (Sillen Aurivillius Phases)

The development of solid-state materials with multiple structure flexibility and compositional features is the key to the continuous rise of modern technologies. Perovskite metal oxides laid the foundation for material synthesis during the last century. Perovskites are a group of compounds that share the same crystal structure as CaTiO₃ (ABO₃). 'A' and 'B' are two positively charged ions, often of very different sizes. Such compounds have the potential for various cation embedments in their crystal, which allows the fabrication of a variety of engineered materials. Perovskite structures can exhibit a layered arrangement where the ABO₃

structure is separated by thin sheets of intrusive material. Based on intrusive material layered perovskite can be divided into three types. 1) Dion–Jacobson phase (every n ABO₃ layer is separated by an intruding layer of alkali metal M, overall formula is $M^+A_{(n-1)}B_nO_{(3n+1)}$), 2) Ruddlesden-Popper phase (the intruding layer occurs between everyone (n = 1) or multiple (n > 1) layers of the ABO₃ lattice), and 3) Aurivillius phase.

Aurivillius phase: It is a crystal structure that was initially identified by Bengt Aurivillius, a chemist from Sweden, in 1949. This crystal structure is composed of alternating layers of fluorite ($[M_2O_2]^{2+}$) and perovskite, and its general chemical formula is represented as (M_2O_2) ($A_{n-1}B_nO_{3n+1}$). Until 1993, structures with M=Bi³⁺, [Bi₂O₂] layers have only been synthesized. Later, subsequent research demonstrated the potential for substituting Bi³⁺ with other elements such as Pb²⁺, Sb³⁺, and Te⁴⁺ whereas A = Bi, Ba, Sr, K, Ca, Na, Pb, and B = Ti, Nb, Ta, Fe, W, Mo, Ga, Cr, etc. The crystal structure of the Aurivillius phase is orthorhombic with a space group of P4/nmm as shown in **Figure 1.1.12. a**. The interest in the Aurivillius phase arises because of its ferroelectric property.^{94,95}

Sillen Phase: Back in 1931, L. Sillen described a phase having an intergrowth of (double $([M_2O_2])$ or triple $([M3O_{4+n}], n$ denotes the thickness of fluorite layer) fluorite layers separated by one or more halide layers, and named as Sillen phase. It has a tetragonal crystal structure with a space group of P4/nmm as shown in **Figure 1.1.12. b**. The general formula is $[M_2O_2]$ $[X_m]$ (where M=Bi³⁺, Pb²⁺, Ca²⁺, Sr^{2+,} etc., and X can be halogen or chalcogen X=C1, Br, I, F, Se, Te m=1,2,3). Examples of Sillen phases with different numbers of halide layers are BaBiO₂Cl (X=1), BiOCl (X=2), Ca_{1.25}Bi_{0.5}O₂Cl₃] (X=3). ⁹⁶

Sillen Aurivillius Phases: The *Sillen Aurivillius* phases is a layered bismuth oxyhalide, first reported by J. F. Ackerman and B. *Aurivillius* in 1980 and named "Bipox" (Bismuth-Perovskite Oxyhalide) later popularised as *Sillen Aurivillius* phase. *Sillen Aurivillius* phases have attracted significant attention due to their interesting structural and functional properties. They exhibit good light absorption and ferroelectric properties and are known for their potential applications in various fields, such as data storage, sensors, and catalysis. By modifying the composition and structure of *Sillen Aurivillius* phases, researchers have explored their photocatalytic, ferroelectric, and piezoelectric aiming to optimize their performance for specific applications.⁹⁷ *Sillen Aurivillius* phases consists of a regular intergrowth of the *Silleń* phase (alternating $[Bi_2O_2]^{+2}$, X⁻ slabs) and *Aurivillius* phase (alternating $[Bi_2O_2]^{+2}[MO_4]^{-3}$ slabs), generally formulated as $[M_2O_2] [A_{n-1}B_nO_{3n+1}] [M_2O_2] [X_m]$, where n and m represent the no of perovskite

and halide layers **Figure 1.1.12. c and d**. The simplest member with *n* and m = 1, Bi₄MO₈X, exhibits a non-centrosymmetric orthorhombic crystal structure with a space group denoted as P4/nmm. There are a total of eight independent oxygen sites (O1–O8) within the structure due to the significant tilting of the MO₆ octahedra of the perovskite block. O1-O4 corresponds to $[Bi_2O_2]^{+2}$ and O5-O8 present in the in-plane [MO₄] perovskite block. Due to the rotation of the MO₆ octahedra and off-centering of the octahedral cation caused by the second-order Jahn-Teller effect and displacement of Bi³⁺ ions, there are interlayer and intralayer polarizations of 0.6 μ C/cm² and 43.5 μ C/cm² along 'c' and 'a' axis respectively. The in-plane and out-of-plane polarization indicates that *Sillen Aurivillius* compounds have great potential as ferroelectric and piezoelectric materials.^{40,97,98}

Abe and co-workers calculated the density of states (DOS) and revealed that the VBM of Bi₄MO₈X is primarily composed of Bi 6s and O-2p orbitals and non-oxide halogen orbital contribute to lower energy states within the valence band, in contrast to BiOX where the VBM is mainly occupied by X np orbital. Analysis of the partial DOS reveals that Bi 6p orbital also contributes near the valence band in the case of Bi₄MO₈X. A strong hybridization occurs between the stereochemically active Bi³⁺ 6s² lone pairs and O 2p orbital, forming a bonding orbital (Bi 6s + O 2p) and a high-energy antibonding orbital (Bi 6s + O 2p) as shown in Figure 1.1.12. e. Due to crystal distortion, the high-energy antibonding orbital interacts with the vacant Bi 6p orbital. This interaction between the antibonding and Bi 6p orbital leads to an asymmetric electron density distribution over the Bi^{3+} lone pair, stabilizing the (Bi 6s + O 2p) antibonding orbitals. This stabilization raises the VBM in Bi₄MO₈X, with dispersive O 2p orbital contributing to the valence band. This unique electronic structure leads to improved photodurability by suppressing photo corrosion suggesting the Sillen Aurivillius phase as a stable and potential photocatalyst. Kato et al. utilized a theoretical calculation approach, considering the electrostatic potential generated by neighboring ions or the Madelung site potential, to investigate the presence of a dispersive O 2p orbital in the Sillen Aurivillius phase compared to its absence in BiOX. The findings revealed a distinct pattern in the energy levels of oxygen and halogen sites in Bi₄MO₈X (Figure 1.1.12. f). Specifically, most oxygen sites exhibited higher energies compared to the halogen sites, which significantly deviates from the behavior observed in BiOX. Further analysis showed that within Bi₄MO₈X, the oxygen sites (O1-O4) originating from the fluorite-like [Bi₂O₂] block were more destabilized than the oxygen sites (O5-O8) from the [MO₄] block. This unique band structure in Bi₄MO₈X was attributed to the electrostatic destabilization of oxide anions and the stabilization of X- ions.

To provide additional insights, a similar analysis was conducted for the Bi_2GdO_4X and $SrBiO_2X$ systems, which have less distorted lattices.^{40,99–101}



Figure 1.1.12. Crystal structure of (a) *Sillen* phase, (b) *Aurivillius* phase, (c) *Sillen Aurivillius* phases (*n*=1), and (d) double perovskite layered *Sillen Aurivillius* phases (*n*=2). (e) Schematic illustration showing interactions among Bi-6s, Bi-6p, and O-2p orbitals according to the revised lone pair (RLP) model (f) Ionic energy levels of each anionic site in BiOX, Bi4NbO₈X, Bi₂GdO₄X, and SrBiO₂X calculated by the sum of Madelung potential and electron affinity. Adapted with permission from [101]. The red, blue, green, and orange symbols represent oxygen, chlorine, bromine, and iodine anions, respectively.

Although the exact origin of the difference in electronic structure between undistorted BiOX and the heavily distorted *Sillen Aurivillius* phase is yet to be determined due to the complexity associated with the latter, numerous studies have established the exceptional photocatalytic stability of the *Sillen Aurivillius* phase. Abe and co-workers demonstrated the continuous

utilization of Bi_4NbO_8X for photocatalytic water splitting, employing an electron scavenger. Interestingly, no structural changes were observed after photocatalysis, and there was no increase in chlorine concentration, indicating remarkable stability against photo corrosion.^{102–108}

1.1.8. Scope for investigation or concluding remarks

The above discussion highlights the promising potential of piezocatalysis, piezophotocatalysis, and traditional photocatalysis as innovative techniques for addressing clean water scarcity and the energy crisis by harnessing renewable energy resources. Semiconductor metal oxides have been extensively studied as photocatalysts, with various strategies such as defect creation, co-catalyst loading, and the formation of heterojunctions with other semiconductors being employed to enhance their overall performance. Among these metal oxides, hetero-anionic metal oxides, particularly the sillen and sillen Aurivillus phases, have garnered attention due to their structural flexibility, stability, and ferroelectric properties.

However, for these applications to be more sustainable and effective, it is crucial to focus on improving their efficiency and durability. It would be advantageous if the catalysts could self-activate during the catalytic reaction, rather than deteriorating over time.

While piezocatalysis and piezo-photocatalysis remain active areas of research, scientists worldwide are dedicated to exploring new materials and optimizing their performance as piezocatalysts and piezo-photocatalysts. Notably, since all ferroelectric materials inherently possess piezoelectric properties, there is a compelling opportunity to investigate the piezoelectric properties of the Sillen Aurivillus phase. Furthermore, it would be advantageous to explore the introduction of piezoelectric properties in centrosymmetric materials, as non-centrosymmetry is a fundamental requirement for piezoelectricity.

By optimizing the structure, shape, size, defects, and electronic structure of the sillen and sillen Aurivillus phases, in addition to their piezoelectric properties. The detailed scope for further investigation will be discussed in subsequent chapters, providing a roadmap for advancing this exciting field of research.

Bibliography

- Kumar, R. Emerging Challenges of Water Scarcity in India: The Way Ahead. Int. J. Innov. Stud. Sociol. Humanit. 2019, 4 (4), 1–28.
- (2) Al-Tohamy, R.; Ali, S. S.; Li, F.; Okasha, K. M.; Mahmoud, Y. A. G.; Elsamahy, T.; Jiao, H.; Fu, Y.; Sun, J. A Critical Review on the Treatment of Dye-Containing Wastewater: Ecotoxicological and Health Concerns of Textile Dyes and Possible Remediation Approaches for Environmental Safety. *Ecotoxicol. Environ. Saf.* 2022, 231, 113160. https://doi.org/10.1016/j.ecoenv.2021.113160.
- Manetu, W. M.; Karanja, A. M. Waterborne Disease Risk Factors and Intervention Practices: A Review. *OALib* 2021, 08 (05), 1–11. https://doi.org/10.4236/oalib.1107401.
- He, C.; Liu, Z.; Wu, J.; Pan, X.; Fang, Z.; Li, J.; Bryan, B. A. Future Global Urban Water Scarcity and Potential Solutions. *Nat. Commun.* 2021, *12* (1), 1–11. https://doi.org/10.1038/s41467-021-25026-3.
- (5) Chow, J.; Kopp, R. J.; Portney, P. R. Energy Resources and Global Development. *Science* (80-.). 2003, 302 (5650), 1528–1531. https://doi.org/10.1126/science.1091939.
- (6) World Bioenergy Association. *Glob. Bioenergy Stat.* 2021 2021.
- Tu, S.; Guo, Y.; Zhang, Y.; Hu, C.; Zhang, T.; Ma, T.; Huang, H. Piezocatalysis and Piezo-Photocatalysis: Catalysts Classification and Modification Strategy, Reaction Mechanism, and Practical Application. *Adv. Funct. Mater.* 2020, *30* (48), 1–31. https://doi.org/10.1002/adfm.202005158.
- Li, S.; Zhao, Z.; Zhao, J.; Zhang, Z.; Li, X.; Zhang, J. Recent Advances of Ferro-, Piezo-, and Pyroelectric Nanomaterials for Catalytic Applications. *ACS Appl. Nano Mater.* 2020, *3* (2), 1063–1079. https://doi.org/10.1021/acsanm.0c00039.
- Wang, Y. C.; Wu, J. M. Effect of Controlled Oxygen Vacancy on H2-Production through the Piezocatalysis and Piezophototronics of Ferroelectric R3C ZnSnO3 Nanowires. *Adv. Funct. Mater.* 2020, *30* (5), 1–12. https://doi.org/10.1002/adfm.201907619.
- (10) Laurenti, M.; Garino, N.; Garino, N.; Canavese, G.; Hernandéz, S.; Cauda, V. Piezo-And Photocatalytic Activity of Ferroelectric ZnO:Sb Thin Films for the Efficient Degradation of Rhodamine-β Dye Pollutant. ACS Appl. Mater. Interfaces 2020, 12

(23), 25798–25808. https://doi.org/10.1021/acsami.0c03787.

- Wang, H.; Zhang, L.; Chen, Z.; Hu, J.; Li, S.; Wang, Z.; Liu, J.; Wang, X. Semiconductor Heterojunction Photocatalysts: Design, Construction, and Photocatalytic Performances. *Chem. Soc. Rev.* 2014, 43 (15), 5234–5244. https://doi.org/10.1039/c4cs00126e.
- Wang, Y.; Suzuki, H.; Xie, J.; Tomita, O.; Martin, D. J.; Higashi, M.; Kong, D.; Abe, R.; Tang, J. Mimicking Natural Photosynthesis: Solar to Renewable H2 Fuel Synthesis by Z-Scheme Water Splitting Systems. *Chem. Rev.* 2018, *118* (10), 5201–5241. https://doi.org/10.1021/acs.chemrev.7b00286.
- (13) Finegold, L.; Cude, J. L. Biological Sciences: One and Two-Dimensional Structure of Alpha-Helix and Beta-Sheet Forms of Poly(L-Alanine) Shown by Specific Heat Measurements at Low Temperatures (1.5-20 K). *Nature* 1972, 238 (5358), 38–40. https://doi.org/10.1038/238038a0.
- (14) Takanabe, K. Photocatalytic Water Splitting: Quantitative Approaches toward Photocatalyst by Design. ACS Catal. 2017, 7 (11), 8006–8022. https://doi.org/10.1021/acscatal.7b02662.
- (15) Yang, Y.; Niu, S.; Han, D.; Liu, T.; Wang, G.; Li, Y. Progress in Developing Metal Oxide Nanomaterials for Photoelectrochemical Water Splitting. *Adv. Energy Mater.* 2017, 7 (19), 1–26. https://doi.org/10.1002/aenm.201700555.
- (16) Li, X.; Yu, J.; Low, J.; Fang, Y.; Xiao, J.; Chen, X. Engineering Heterogeneous Semiconductors for Solar Water Splitting. *J. Mater. Chem. A* 2015, *3* (6), 2485–2534. https://doi.org/10.1039/c4ta04461d.
- (17) Moniz, S. J. A.; Shevlin, S. A.; Martin, D. J.; Guo, Z. X.; Tang, J. Visible-Light Driven Heterojunction Photocatalysts for Water Splitting-a Critical Review. *Energy Environ. Sci.* 2015, 8 (3), 731–759. https://doi.org/10.1039/c4ee03271c.
- (18) Thimsen, E.; Biswas, S.; Lo, C. S.; Biswas, P. Predicting the Band Structure of Mixed Transition Metal Oxides: Theory and Experiment. J. Phys. Chem. C 2009, 113 (5), 2014–2021. https://doi.org/10.1021/jp807579h.
- (19) Herz, L. M. Charge-Carrier Mobilities in Metal Halide Perovskites: Fundamental Mechanisms and Limits. ACS Energy Lett. 2017, 2 (7), 1539–1548. https://doi.org/10.1021/acsenergylett.7b00276.
- (20) Zafar, Z.; Yi, S.; Li, J.; Li, C.; Zhu, Y.; Zada, A.; Yao, W.; Liu, Z.; Yue, X. Recent Development in Defects Engineered Photocatalysts: An Overview of the Experimental and Theoretical Strategies. *Energy Environ. Mater.* **2022**, *5* (1), 68–114.

https://doi.org/10.1002/eem2.12171.

- (21) Cheng, H.; Wang, J.; Zhao, Y.; Han, X. Effect of Phase Composition, Morphology, and Specific Surface Area on the Photocatalytic Activity of TiO₂ Nanomaterials. *RSC Adv.* 2014, *4* (87), 47031–47038. https://doi.org/10.1039/c4ra05509h.
- Maeda, K.; Domen, K. Photocatalytic Water Splitting: Recent Progress and Future Challenges. J. Phys. Chem. Lett. 2010, 1 (18), 2655–2661. https://doi.org/10.1021/jz1007966.
- (23) Dai, B.; Zhou, Y.; Xiao, X.; Chen, Y.; Guo, J.; Gao, C.; Xie, Y.; Chen, J. Fluid Field Modulation in Mass Transfer for Efficient Photocatalysis. *Adv. Sci.* 2022, 9 (28), 1–20. https://doi.org/10.1002/advs.202203057.
- Wang, C. A.; Li, Y. W.; Cheng, X. L.; Zhang, J. P.; Han, Y. F. Eosin Y Dye-Based Porous Organic Polymers for Highly Efficient Heterogeneous Photocatalytic Dehydrogenative Coupling Reaction. *RSC Adv.* 2017, 7 (1), 408–414. https://doi.org/10.1039/c6ra25123d.
- (25) Cooper, A. T.; Goswami, D. Y. Evaluation of Methylene Blue and Rose Bengal for Dye Sensitized Solar Water Treatment. *J. Sol. Energy Eng. Trans. ASME* 2002, *124*(3), 305–310. https://doi.org/10.1115/1.1498850.
- (26) Hoffmann, N. Homogeneous Photocatalysis with Organometallic Compounds. *Appl. Homog. Catal. with Organomet. Compd. A Compr. Handb. Three Vol.* 2012, 1097–1133. https://doi.org/10.1002/9783527651733.ch17.
- (27) Giles, P. R.; Tsukazaki, M.; Urch, C. J.; Brown, S. M.; V, C. D. Lou; Pasteur, P. L.; V, B.-L. V; Agrochemicals, Z.; Rg, B.; Works, H.; Box, P. O. A.; Road, L.; Hd, H. Efficient, Aerobic, Ruthenium-Catalyzed Oxidation of Alcohols into Aldehydes and Ketones Istva Paramount Importance in Synthetic Organic Chemistry . 1 The This Reaction Is Testimony to Its Importance . 2 Unfortunately, One Agents Are Usually Required . 1997, 7863 (16), 12661–12662.
- Yang, M.; Yarnell, J. E.; El Roz, K.; Castellano, F. N. A Robust Visible-Light-Harvesting Cyclometalated Ir(III) Diimine Sensitizer for Homogeneous Photocatalytic Hydrogen Production. *ACS Appl. Energy Mater.* 2020, *3* (2), 1842–1853. https://doi.org/10.1021/acsaem.9b02269.
- (29) Ren, Y.; He, B.; Yan, F.; Wang, H.; Cheng, Y.; Lin, L.; Feng, Y.; Li, J. Continuous Biodiesel Production in a Fixed Bed Reactor Packed with Anion-Exchange Resin as Heterogeneous Catalyst. *Bioresour. Technol.* 2012, *113*, 19–22. https://doi.org/10.1016/j.biortech.2011.10.103.

- (30) Xu, G.; Zhang, Z.; Li, T.; Du, M.; Guan, Y.; Guo, C. Continuous High-Efficient Degradation of Organic Pollutants Based on Sea Urchin-like Fe3O4/ZnO/ZnSe Heterostructures in Photocatalytic Magnetically Fixed Bed Reactor. *Colloids Surfaces A Physicochem. Eng. Asp.* 2020, 603 (April), 125198. https://doi.org/10.1016/j.colsurfa.2020.125198.
- Wehinger, G. D.; Eppinger, T.; Kraume, M. Detailed Numerical Simulations of Catalytic Fixed-Bed Reactors: Heterogeneous Dry Reforming of Methane. *Chem. Eng. Sci.* 2015, *122*, 197–209. https://doi.org/10.1016/j.ces.2014.09.007.
- (32) Mason, W. P. Piezoelectricity, Its History and Applications. J. Acoust. Soc. Am. 1981, 70 (6), 1561–1566. https://doi.org/10.1121/1.387221.
- Wu, J. M.; Sun, Y. G.; Chang, W. E.; Lee, J. T. Piezoelectricity Induced Water Splitting and Formation of Hydroxyl Radical from Active Edge Sites of MoS2 Nanoflowers. *Nano Energy* 2018, 46, 372–382. https://doi.org/10.1016/j.nanoen.2018.02.010.
- (34) Zhang, Y.; Thuy Phuong, P. T.; Hoang Duy, N. P.; Roake, E.; Khanbareh, H.;
 Hopkins, M.; Zhou, X.; Zhang, D.; Zhou, K.; Bowen, C. Polarisation Tuneable Piezo-Catalytic Activity of Nb-Doped PZT with Low Curie Temperature for Efficient CO₂ reduction and H₂ generation. *Nanoscale Adv.* 2021, *3* (5), 1362–1374. https://doi.org/10.1039/d1na00013f.
- (35) Fath, A.; Xia, T.; Li, W. Recent Advances in the Application of Piezoelectric Materials in Microrobotic Systems. *Micromachines* 2022, *13* (9), 1–18. https://doi.org/10.3390/mi13091422.
- (36) Wang, Z. L.; Song, J. Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays. *Science (80-.).* 2006, *312* (5771), 242–246. https://doi.org/10.1126/science.1124005.
- (37) Starr, M. B.; Wang, X. Fundamental Analysis of Piezocatalysis Process on the Surfaces of Strained Piezoelectric Materials. *Sci. Rep.* 2013, *3* (1), 1–8. https://doi.org/10.1038/srep02160.
- (38) Starr, M. B.; Shi, J.; Wang, X. Piezopotential-Driven Redox Reactions at the Surface of Piezoelectric Materials. *Angew. Chemie Int. Ed.* 2012, *51* (24), 5962–5966. https://doi.org/10.1002/anie.201201424.
- (39) You, H.; Wu, Z.; Zhang, L.; Ying, Y.; Liu, Y.; Fei, L.; Chen, X.; Jia, Y.; Wang, Y.;
 Wang, F.; Ju, S.; Qiao, J.; Lam, C. H.; Huang, H. Harvesting the Vibration Energy of BiFeO₃ Nanosheets for Hydrogen Evolution. *Angew. Chemie Int. Ed.* 2019, 58 (34),

11779–11784. https://doi.org/10.1002/anie.201906181.

- (40) Wu, J.; Xu, Q.; Lin, E.; Yuan, B.; Qin, N.; Thatikonda, S. K.; Bao, D. Insights into the Role of Ferroelectric Polarization in Piezocatalysis of Nanocrystalline BaTiO₃. ACS Appl. Mater. Interfaces 2018, 10 (21), 17842–17849. https://doi.org/10.1021/acsami.8b01991.
- (41) Rooze, J.; Rebrov, E. V.; Schouten, J. C.; Keurentjes, J. T. F. Dissolved Gas and Ultrasonic Cavitation - A Review. *Ultrason. Sonochem.* 2013, 20 (1), 1–11. https://doi.org/10.1016/j.ultsonch.2012.04.013.
- (42) Khoshkhoo, M. Research Report Sustainable and Energy Efficient Leaching of Örjan Johansson, Taraka Pamidi, Mohammad Khoshkhoo, Åke Sandström. 2017, No. June.
- (43) Wang, K.; Han, C.; Li, J.; Qiu, J.; Sunarso, J.; Liu, S. The Mechanism of Piezocatalysis: Energy Band Theory or Screening Charge Effect? *Angew. Chemie - Int. Ed.* 2022, *61* (6). https://doi.org/10.1002/anie.202110429.
- (44) Singh, S.; Khare, N. Coupling of Piezoelectric, Semiconducting and Photoexcitation Properties in NaNbO3 Nanostructures for Controlling Electrical Transport: Realizing an Efficient Piezo-Photoanode and Piezo-Photocatalyst. *Nano Energy* 2017, *38*, 335– 341. https://doi.org/10.1016/j.nanoen.2017.05.029.
- Pan, L.; Sun, S.; Chen, Y.; Wang, P.; Wang, J.; Zhang, X.; Zou, J. J.; Wang, Z. L. Advances in Piezo-Phototronic Effect Enhanced Photocatalysis and Photoelectrocatalysis. *Adv. Energy Mater.* 2020, *10* (15), 1–25. https://doi.org/10.1002/aenm.202000214.
- (46) Kumar, D.; Sharma, S.; Khare, N. Piezo-Phototronic and Plasmonic Effect Coupled Ag-NaNbO₃ Nanocomposite for Enhanced Photocatalytic and Photoelectrochemical Water Splitting Activity. *Renew. Energy* 2021, *163*, 1569–1579. https://doi.org/10.1016/j.renene.2020.09.132.
- (47) Hu, C.; Chen, F.; Wang, Y.; Tian, N.; Ma, T.; Zhang, Y.; Huang, H. Exceptional Cocatalyst-Free Photo-Enhanced Piezocatalytic Hydrogen Evolution of Carbon Nitride Nanosheets from Strong In-Plane Polarization. *Adv. Mater.* 2021, *33* (24), 1–9. https://doi.org/10.1002/adma.202101751.
- (48) Ahmad, R.; Ahmad, Z.; Khan, A. U.; Mastoi, N. R.; Aslam, M.; Kim, J. Photocatalytic Systems as an Advanced Environmental Remediation: Recent Developments, Limitations and New Avenues for Applications. *J. Environ. Chem. Eng.* 2016, *4* (4), 4143–4164. https://doi.org/10.1016/j.jece.2016.09.009.
- (49) Luo, J.; Zhang, S.; Sun, M.; Yang, L.; Luo, S.; Crittenden, J. C. A Critical Review on

Energy Conversion and Environmental Remediation of Photocatalysts with Remodeling Crystal Lattice, Surface, and Interface. *ACS Nano* **2019**, *13* (9), 9811– 9840. https://doi.org/10.1021/acsnano.9b03649.

- (50) Xu, B.; Wang, X.; Zhu, C.; Ran, X.; Li, T.; Guo, L. Probing the Inhomogeneity and Intermediates in the Photosensitized Degradation of Rhodamine B by Ag3PO4 Nanoparticles from an Ensemble to a Single Molecule Approach. *RSC Adv.* 2017, 7 (65), 40896–40904. https://doi.org/10.1039/c7ra07163a.
- (51) Fu, H.; Zhang, S.; Xu, T.; Zhu, Y.; Chen, J. Photocatalytic Degradation of RhB by Fluorinated Bi2WO 6 and Distributions of the Intermediate Products. *Environ. Sci. Technol.* 2008, 42 (6), 2085–2091. https://doi.org/10.1021/es702495w.
- MacIa, N.; Bresoli-Obach, R.; Nonell, S.; Heyne, B. Hybrid Silver Nanocubes for Improved Plasmon-Enhanced Singlet Oxygen Production and Inactivation of Bacteria. *J. Am. Chem. Soc.* 2019, *141* (1), 684–692. https://doi.org/10.1021/jacs.8b12206.
- (53) Xiang, D.; Liu, Z.; Wu, M.; Liu, H.; Zhang, X.; Wang, Z.; Wang, Z. L.; Li, L. Enhanced Piezo-Photoelectric Catalysis with Oriented Carrier Migration in Asymmetric Au–ZnO Nanorod Array. *Small* 2020, *16* (18), 1–8. https://doi.org/10.1002/smll.201907603.
- Liu, D.; Jin, C.; Shan, F.; He, J.; Wang, F. Synthesizing BaTiO3 Nanostructures to Explore Morphological Influence, Kinetics, and Mechanism of Piezocatalytic Dye Degradation. ACS Appl. Mater. Interfaces 2020, 12 (15), 17443–17451. https://doi.org/10.1021/acsami.9b23351.
- Liu, Y.; Wang, X.; Qiao, Y.; Min, M.; Wang, L.; Shan, H.; Ma, Y.; Hao, W.; Tao, P.; Shang, W.; Wu, J.; Song, C.; Deng, T. Pyroelectric Synthesis of Metal-BaTiO₃ Hybrid Nanoparticles with Enhanced Pyrocatalytic Performance. *ACS Sustain. Chem. Eng.* 2019, 7 (2), 2602–2609. https://doi.org/10.1021/acssuschemeng.8b05647.
- Li, L.; Cao, W.; Yao, J.; Liu, W.; Li, F.; Wang, C. Synergistic Piezo-Photocatalysis of BiOCl/NaNbO3 Heterojunction Piezoelectric Composite for High-Efficient Organic Pollutant Degradation. *Nanomaterials* 2022, *12* (3). https://doi.org/10.3390/nano12030353.
- Wang, Q.; Domen, K. Particulate Photocatalysts for Light-Driven Water Splitting: Mechanisms, Challenges, and Design Strategies. *Chem. Rev.* 2020, *120* (2), 919–985. https://doi.org/10.1021/acs.chemrev.9b00201.
- (58) Su, R.; Hsain, H. A.; Wu, M.; Zhang, D.; Hu, X.; Wang, Z.; Wang, X.; Li, F. tang;Chen, X.; Zhu, L.; Yang, Y.; Yang, Y.; Lou, X.; Pennycook, S. J. Nano-Ferroelectric

for High Efficiency Overall Water Splitting under Ultrasonic Vibration. *Angew. Chemie - Int. Ed.* **2019**, *58* (42), 15076–15081. https://doi.org/10.1002/anie.201907695.

- (59) Su, R.; Wang, Z.; Zhu, L.; Pan, Y.; Zhang, D.; Wen, H.; Luo, Z. D.; Li, L.; Li, F. tang;
 Wu, M.; He, L.; Sharma, P.; Seidel, J. Strain-Engineered Nano-Ferroelectrics for
 High-Efficiency Piezocatalytic Overall Water Splitting. *Angew. Chemie Int. Ed.*2021, 60 (29), 16019–16026. https://doi.org/10.1002/anie.202103112.
- (60) Ranjan, A.; Hsiao, K. Y.; Lin, C. Y.; Tseng, Y. H.; Lu, M. Y. Enhanced Piezocatalytic Activity in Bi1/2Na1/2TiO3for Water Splitting by Oxygen Vacancy Engineering. ACS Appl. Mater. Interfaces 2022, 14 (31), 35635–35644. https://doi.org/10.1021/acsami.2c07817.
- (61) Wang, C.; Hu, C.; Chen, F.; Li, H.; Zhang, Y.; Ma, T.; Huang, H. Polar Layered Bismuth-Rich Oxyhalide Piezoelectrics Bi₄O₅X₂ ((Formula Presented.), I): Efficient Piezocatalytic Pure Water Splitting and Interlayer Anion-Dependent Activity. *Adv. Funct. Mater.* 2023, 2, 1–12. https://doi.org/10.1002/adfm.202301144.
- (62) Hong, K. S.; Xu, H.; Konishi, H.; Li, X. Direct Water Splitting through Vibrating Piezoelectric Microfibers in Water. J. Phys. Chem. Lett. 2010, 1 (6), 997–1002. https://doi.org/10.1021/jz100027t.
- Mohanty, R.; Mansingh, S.; Parida, K.; Parida, K. Boosting Sluggish Photocatalytic Hydrogen Evolution through Piezo-Stimulated Polarization: A Critical Review. *Mater. Horizons* 2022, 9 (5), 1332–1355. https://doi.org/10.1039/d1mh01899j.
- (64) Guo, L.; Zhong, C.; Cao, J.; Hao, Y.; Lei, M.; Bi, K.; Sun, Q.; Wang, Z. L. Enhanced Photocatalytic H2 Evolution by Plasmonic and Piezotronic Effects Based on Periodic Al/BaTiO3 Heterostructures. *Nano Energy* 2019, 62 (May), 513–520. https://doi.org/10.1016/j.nanoen.2019.05.067.
- (65) Wang, F.; Zhang, J.; Jin, C. C.; Ke, X.; Wang, F.; Liu, D. Unveiling the Effect of Crystal Facets on Piezo-Photocatalytic Activity of BiVO₄. *Nano Energy* 2022, *101* (June), 107573. https://doi.org/10.1016/j.nanoen.2022.107573.
- (66) Tsukamoto, D.; Shiro, A.; Shiraishi, Y.; Sugano, Y.; Ichikawa, S.; Tanaka, S.; Hirai, T. Photocatalytic H₂O₂ Production from Ethanol/O 2 System Using TiO₂ Loaded with Au-Ag Bimetallic Alloy Nanoparticles. *ACS Catal.* 2012, *2* (4), 599–603. https://doi.org/10.1021/cs2006873.
- (67) Teranishi, M.; Naya, S. I.; Tada, H. In Situ Liquid Phase Synthesis of Hydrogen Peroxide from Molecular Oxygen Using Gold Nanoparticle-Loaded Titanium(IV)

Dioxide Photocatalyst. J. Am. Chem. Soc. **2010**, *132* (23), 7850–7851. https://doi.org/10.1021/ja102651g.

- Moon, G. H.; Kim, W.; Bokare, A. D.; Sung, N. E.; Choi, W. Solar Production of H₂O₂ on Reduced Graphene Oxide-TiO₂ Hybrid Photocatalysts Consisting of Earth-Abundant Elements Only. *Energy Environ. Sci.* 2014, 7 (12), 4023–4028. https://doi.org/10.1039/c4ee02757d.
- (69) Kaynan, N.; Berke, B. A.; Hazut, O.; Yerushalmi, R. Sustainable Photocatalytic Production of Hydrogen Peroxide from Water and Molecular Oxygen. *J. Mater. Chem. A* 2014, 2 (34), 13822–13826. https://doi.org/10.1039/c4ta03004d.
- (70) Wen, H.; Huang, S.; Meng, X.; Xian, X.; Zhao, J.; Roy, V. A. L. Recent Progress in the Design of Photocatalytic H₂O₂ Synthesis System. *Front. Chem.* 2022, *10* (December), 1–14. https://doi.org/10.3389/fchem.2022.1098209.
- (71) Guo, Y.; Tong, X.; Yang, N. Photocatalytic and Electrocatalytic Generation of Hydrogen Peroxide: Principles, Catalyst Design and Performance; Springer Nature Singapore, 2023; Vol. 15. https://doi.org/10.1007/s40820-023-01052-2.
- (72) Wang, L.; Li, B.; Dionysiou, D. D.; Chen, B.; Yang, J.; Li, J. Overlooked Formation of H2O2 during the Hydroxyl Radical-Scavenging Process When Using Alcohols as Scavengers. *Environ. Sci. Technol.* 2022, *56* (6), 3386–3396. https://doi.org/10.1021/acs.est.1c03796.
- (73) Bai, J.; Sun, Y.; Li, M.; Yang, L.; Li, J.; Hu, S. "Two Channel" Photocatalytic Hydrogen Peroxide Production Using g-C₃N₄ Coated CuO Nanorod Heterojunction Catalysts Prepared via a Novel Molten Salt-Assisted Microwave Process. *New J. Chem.* 2018, 42 (16), 13529–13535. https://doi.org/10.1039/c8nj02565g.
- (74) Tang, J.; Durrant, J. R.; Klug, D. R. Mechanism of Photocatalytic Water Splitting in TiO2. Reaction of Water with Photoholes, Importance of Charge Carrier Dynamics, and Evidence for Four-Hole Chemistry. J. Am. Chem. Soc. 2008, 130 (42), 13885– 13891. https://doi.org/10.1021/ja8034637.
- (75) Guo, Q.; Zhou, C.; Ma, Z.; Yang, X. Fundamentals of TiO2 Photocatalysis: Concepts, Mechanisms, and Challenges. *Adv. Mater.* 2019, *31* (50), 1–26. https://doi.org/10.1002/adma.201901997.
- (76) Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiuchi, Y.; Anpo, M.;
 Bahnemann, D. W. Schneider et Al. 2014 Understanding TiO 2 Photocatalysis
 Mechanisms and Materials(2).Pdf. *Chem. Rev.* 2014, *114* (9), 9919–9986.
- (77) Chatterjee, K.; Skrabalak, S. E. Durable Metal Heteroanionic Photocatalysts. ACS

Appl. Mater. Interfaces **2021**, *13* (31), 36670–36678. https://doi.org/10.1021/acsami.1c09774.

- Kageyama, H.; Hayashi, K.; Maeda, K.; Attfield, J. P.; Hiroi, Z.; Rondinelli, J. M.;
 Poeppelmeier, K. R. Expanding Frontiers in Materials Chemistry and Physics with Multiple Anions. *Nat. Commun.* 2018, 9 (1). https://doi.org/10.1038/s41467-018-02838-4.
- (79) Wang, G.; Chang, J.; Tang, W.; Xie, W.; Ang, Y. S. 2D Materials and Heterostructures for Photocatalytic Water-Splitting: A Theoretical Perspective. *J. Phys. D. Appl. Phys.* 2022, 55 (29). https://doi.org/10.1088/1361-6463/ac5771.
- (80) Li, H.; Hu, H.; Bao, C.; Guo, F.; Zhang, X.; Liu, X.; Hua, J.; Tan, J.; Wang, A.; Zhou, H.; Yang, B.; Qu, Y.; Liu, X. Forming Heterojunction: An Effective Strategy to Enhance the Photocatalytic Efficiency of a New Metal-Free Organic Photocatalyst for Water Splitting. *Sci. Rep.* 2016, *6* (June), 1–10. https://doi.org/10.1038/srep29327.
- (81) Afroz, K.; Moniruddin, M.; Bakranov, N.; Kudaibergenov, S.; Nuraje, N. A Heterojunction Strategy to Improve the Visible Light Sensitive Water Splitting Performance of Photocatalytic Materials. *J. Mater. Chem. A* 2018, 6 (44), 21696– 21718. https://doi.org/10.1039/c8ta04165b.
- (82) Wang, Z.; Luo, Y.; Hisatomi, T.; Vequizo, J. J. M.; Suzuki, S.; Chen, S.; Nakabayashi, M.; Lin, L.; Pan, Z.; Kariya, N.; Yamakata, A.; Shibata, N.; Takata, T.; Teshima, K.; Domen, K. Sequential Cocatalyst Decoration on BaTaO₂N towards Highly-Active Z-Scheme Water Splitting. *Nat. Commun.* 2021, *12* (1), 1–9. https://doi.org/10.1038/s41467-021-21284-3.
- (83) Raizada, P.; Soni, V.; Kumar, A.; Singh, P.; Parwaz Khan, A. A.; Asiri, A. M.; Thakur, V. K.; Nguyen, V. H. Surface Defect Engineering of Metal Oxides Photocatalyst for Energy Application and Water Treatment; Elsevier Ltd, 2021; Vol. 7. https://doi.org/10.1016/j.jmat.2020.10.009.
- (84) Xiong, J.; Di, J.; Xia, J.; Zhu, W.; Li, H. Surface Defect Engineering in 2D Nanomaterials for Photocatalysis. *Adv. Funct. Mater.* 2018, 28 (39), 1–19. https://doi.org/10.1002/adfm.201801983.
- (85) Takata, T.; Domen, K. Defect Engineering of Photocatalysts by Doping of Aliovalent Metal Cations for Efficient Water Splitting. J. Phys. Chem. C 2009, 113 (45), 19386– 19388. https://doi.org/10.1021/jp908621e.
- (86) Lamers, M.; Fiechter, S.; Friedrich, D.; Abdi, F. F.; Van De Krol, R. Formation and Suppression of Defects during Heat Treatment of BiVO₄ Photoanodes for Solar Water

Splitting. *J. Mater. Chem. A* **2018**, *6* (38), 18694–18700. https://doi.org/10.1039/c8ta06269b.

- (87) Zhang, X.; Liu, X.; Zeng, Y.; Tong, Y.; Lu, X. Oxygen Defects in Promoting the Electrochemical Performance of Metal Oxides for Supercapacitors: Recent Advances and Challenges. *Small Methods* **2020**, *4* (6), 1–18. https://doi.org/10.1002/smtd.201900823.
- (88) Bao, L.; Chang, L.; Yao, L.; Meng, W.; Yu, Q.; Zhang, X.; Liu, X.; Wang, X.; Chen, W.; Li, X. Acid Etching Induced Defective Co₃O₄ as an Efficient Catalyst for Methane Combustion Reaction. *New J. Chem.* 2021, *45* (7), 3546–3551. https://doi.org/10.1039/d0nj06110g.
- (89) Cao, D.; Xu, H.; Cheng, D. Construction of Defect-Rich RhCu Nanotubes with Highly Active Rh3Cu1 Alloy Phase for Overall Water Splitting in All PH Values. *Adv. Energy Mater.* 2020, *10* (9), 1–12. https://doi.org/10.1002/aenm.201903038.
- (90) Sezer, N.; Koç, M. A Comprehensive Review on the State-of-the-Art of Piezoelectric Energy Harvesting. *Nano Energy* 2021, *80* (August 2020), 105567. https://doi.org/10.1016/j.nanoen.2020.105567.
- (91) Li, S.; Zhao, Z.; Yu, D.; Zhao, J.; Su, Y.; Liu, Y. Nano Energy Water Splitting and Degradation of Organic Pollutants : Understanding the Piezocatalytic e Ff Ect. *Nano Energy* 2019, 66 (June), 104083.
- (92) Bettini, S.; Pagano, R.; Valli, D.; Ingrosso, C.; Roeffaers, M.; Hofkens, J.; Giancane, G.; Valli, L. ZnO Nanostructures Based Piezo-Photocatalytic Degradation Enhancement of Steroid Hormones. *Surfaces and Interfaces* 2023, *36* (December 2022), 102581. https://doi.org/10.1016/j.surfin.2022.102581.
- Li, Q.; Guan, Z.; Wu, D.; Zhao, X.; Bao, S.; Tian, B.; Zhang, J. Z-Scheme BiOCl-Au-CdS Heterostructure with Enhanced Sunlight-Driven Photocatalytic Activity in Degrading Water Dyes and Antibiotics. *ACS Sustain. Chem. Eng.* 2017, *5* (8), 6958–6968. https://doi.org/10.1021/acssuschemeng.7b01157.
- Moure, A. Review and Perspectives of Aurivillius Structures as a Lead-Free
 Piezoelectric System. *Appl. Sci.* 2018, 8 (1). https://doi.org/10.3390/app8010062.
- (95) Song, D.; Yang, J.; Yang, B.; Chen, L.; Wang, F.; Zhu, X. Evolution of Structure and Ferroelectricity in Aurivillius Bi4Bin-3Fe_{n-3}Ti₃O3_{n+3} Thin Films. *J. Mater. Chem. C* 2018, 6 (32), 8618–8627. https://doi.org/10.1039/c8tc02270d.
- (96) Tian, N.; Hu, C.; Wang, J.; Zhang, Y.; Ma, T.; Huang, H. Layered Bismuth-Based Photocatalysts. *Coord. Chem. Rev.* 2022, 463, 214515.

https://doi.org/10.1016/j.ccr.2022.214515.

- (97) Fujito, H.; Kunioku, H.; Kato, D.; Suzuki, H.; Higashi, M.; Kageyama, H.; Abe, R. Layered Perovskite Oxychloride Bi4NbO8Cl: A Stable Visible Light Responsive Photocatalyst for Water Splitting. *J. Am. Chem. Soc.* 2016, *138* (7), 2082–2085. https://doi.org/10.1021/jacs.5b11191.
- (98) Kusainova, A. M.; Stefanovich, S. Y.; Dolgikh, V. A.; Mosunov, A. V.; Hervoches, C. H.; Lightfoot, P. Dielectric Properties and Structure of Bi₄NbO₈Cl and Bi₄TaO₈Cl. J. *Mater. Chem.* 2001, *11* (4), 1141–1145. https://doi.org/10.1039/b0084921.
- (99) Bhat, S. S. M.; Swain, D.; Feygenson, M.; Neuefeind, J. C.; Mishra, A. K.; Hodala, J. L.; Narayana, C.; Shanbhag, G. V.; Sundaram, N. G. Bi₄TaO₈Cl Nano-Photocatalyst: Influence of Local, Average, and Band Structure. *Inorg. Chem.* 2017, *56* (10), 5525–5536. https://doi.org/10.1021/acs.inorgchem.6b01970.
- (100) Zhou, X.; Dong, H. Density Functional Studies on Layered Perovskite Oxyhalide Bi4MO8X Photocatalysts (M = Nb and Ta, X = Cl, Br, and I). J. Phys. Chem. C 2017, 121 (38), 20662–20672. https://doi.org/10.1021/acs.jpcc.7b06576.
- (101) Kato, D.; Hongo, K.; Maezono, R.; Higashi, M.; Kunioku, H.; Yabuuchi, M.; Suzuki, H.; Okajima, H.; Zhong, C.; Nakano, K.; Abe, R.; Kageyama, H. Valence Band Engineering of Layered Bismuth Oxyhalides toward Stable Visible-Light Water Splitting: Madelung Site Potential Analysis. *J. Am. Chem. Soc.* 2017, *139* (51), 18725–18731. https://doi.org/10.1021/jacs.7b11497.
- (102) Tao, X.; Shi, W.; Zeng, B.; Zhao, Y.; Ta, N.; Wang, S.; Adenle, A. A.; Li, R.; Li, C. Photoinduced Surface Activation of Semiconductor Photocatalysts under Reaction Conditions: A Commonly Overlooked Phenomenon in Photocatalysis. *ACS Catal.* 2020, *10* (10), 5941–5948. https://doi.org/10.1021/acscatal.0c00462.
- (103) Chatterjee, K.; Dos Reis, R.; Harada, J. K.; Mathiesen, J. K.; Bueno, S. L. A.; Jensen, K. M. Ø.; Rondinelli, J. M.; Dravid, V.; Skrabalak, S. E. Durable Multimetal Oxychloride Intergrowths for Visible Light-Driven Water Splitting. *Chem. Mater.* 2021, *33* (1), 347–358. https://doi.org/10.1021/acs.chemmater.0c04037.
- (104) Ogawa, K.; Nakada, A.; Suzuki, H.; Tomita, O.; Higashi, M.; Saeki, A.; Kageyama, H.; Abe, R. Flux Synthesis of Layered Oxyhalide Bi₄NbO₈Cl Photocatalyst for Efficient Z-Scheme Water Splitting under Visible Light. *ACS Appl. Mater. Interfaces* 2019, *11* (6), 5642–5650. https://doi.org/10.1021/acsami.8b06411.
- (105) Suzuki, H.; Kunioku, H.; Higashi, M.; Tomita, O.; Kato, D.; Kageyama, H.; Abe, R.
 Lead Bismuth Oxyhalides PbBiO₂X (X = Cl, Br) as Visible-Light-Responsive

Photocatalysts for Water Oxidation: Role of Lone-Pair Electrons in Valence Band Engineering. *Chem. Mater.* **2018**, *30* (17), 5862–5869. https://doi.org/10.1021/acs.chemmater.8b01385.

- (106) Nawaz, M.; Mou, F.; Xu, L.; Tu, H.; Guan, J. F-Bi₄TaO₈Cl Flower-like Hierarchical Structures: Controlled Preparation, Formation Mechanism and Visible Photocatalytic Hydrogen Production. *RSC Adv.* 2017, 7 (1), 121–127. https://doi.org/10.1039/c6ra25046g.
- (107) Tao, X.; Zhao, Y.; Mu, L.; Wang, S.; Li, R.; Li, C. Bismuth Tantalum Oxyhalogen: A Promising Candidate Photocatalyst for Solar Water Splitting. *Adv. Energy Mater.* **2018**, 8 (1), 1–7. https://doi.org/10.1002/aenm.201701392.
- (108) Nakada, A.; Saeki, A.; Higashi, M.; Kageyama, H.; Abe, R. Two-Step Synthesis of Sillén-Aurivillius Type Oxychlorides to Enhance Their Photocatalytic Activity for Visible-Light-Induced Water Splitting. J. Mater. Chem. A 2018, 6 (23), 10909–10917. https://doi.org/10.1039/c8ta03321h.

CHAPTER 1.2.

Materials and Characterization Techniques

1.2.1. Materials

Bismuth (III) nitrate pentahydrate (Bi(NO₃)₃.5H₂O, Sigma-Aldrich, \geq 98%), Potassium bromide (KBr, Himedia, 99.5%), Potassium chloride (KCl, Himedia, 99.5%), Potassium iodide (KI, Sigma Aldrich, 99.8%), Ethylene glycol (L.R, 99%), Bismuth (III) oxide (Bi₂O₃, Sigma-Aldrich, 99.99%), Tantalum (V) oxide (Ta₂O₅, Sigma-Aldrich, 99.9%), Strontium carbonate (SrCO₃ Sigma-Aldrich, 99.9%), Bismuth oxychloride (BiOCl, Himedia, Ltd., 99.5%) Titanium dioxide (P25 TiO2, Sigma-Aldrich, 99.9%), and Sodium Chloride (NaCl, Himedia, 99.5%), Magnesium chloride (MgCl₂, Sigma-Aldrich, 99.9%) Magnesium sulfate (MgSO₄, Sigma-Aldrich, 99.9%) Calcium sulfate (CaSO₄, Sigma-Aldrich, 99.9%) Potassium sulfate (K₂SO₄, Renkem, \geq 99%), Potassium carbonate (K₂CO₃, Loba Chemie, 99%) Magnesium bromide (MgBr₂, Sigma-Aldrich, 99.9%) Lactic acid (Himedia, 85-90%) and Silver nitrate (AgNO₃ Alfa Assar, 99%) Ammonium paramolybdate tetrahydrate (H₃₂Mo₇N₆O₂₈, Sigma Aldrich, 99%), and Terephthalic acid (TA, Sigma-Aldrich, \geq 98%) Rhodamine B (RhB, HPLC grade \geq 95%), Rhodamine 110 (Rh110, Sigma-Aldrich, \geq 99%), Methylene blue (MB, Sigma-Aldrich, \geq 98%), Methyl orange (MO, Sigma-Aldrich, \geq 85%), Ciprofloxin (Cipbid eye drops), Tetracycline (Resteclin, 500 tablet), Congo-red (Sigma-Aldrich, \geq 35%) and Ethanol (C₂H₅OH, ACS grade) Hydrogen peroxide (Rankem, 30%), Nitro blue tetrazolium (NBT, Sigma 90%), Sodium sulphate (Na₂SO₄, Rankem, 99%), Acetonitrile (CH₃CN, AR, 99.5%), (Benzoquinone (C₆H₄O₂, Alfa Aesar, 98%), Gold(III) chloride trihydrate (Sigma Aldrich, 99.9%), Isopropanol (C₃H₈O, Merck, 99%), Tertiary butanol (t-BuOH, spectrochem, 99.5%) ammonium oxalate ($C_2H_8N_2O_4$, Sigma Aldrich, >99%), Absolute ethanol (C₂H₅OH, Merck, 99.9%), Nafion solution (Sigma-Aldrich, 99%), Hydrochloric Acid (Conc. HCl, Himedia, 35% pure, Hi-AR), Palladium (II) Chloride (PdCl₂, 99.9% metals basis), Chloroform (CHCl₃, Himedia, AR), Hexachloro platinic acid (H₂PtCl₆, Sigma Aldrich, 99.99%), Acetonitrile (CH₃CN, AR, 99.5%), >97%), Sodium perchlorate (NaClO₄, Sigma-Aldrich, \geq 98%) Dihydrogen phosphate H₂PO₄ (Sigma-Aldrich, \geq 98%) Dimethyl sulfoxide (DMSO, Sisco research lab (SRL) 99.5%) (HPLC, Waters Mark milipore) methanol (CH₃OH, Rankem, 99%), were used without further purification. Distilled water was used for all the experiments.

1.2.2. Characterization techniques

Powder X-ray diffraction (XRD) patterns were recorded by using a Rigaku Ultima IV diffractometer equipped with Cu K α X-ray radiation with a wavelength of 1.5406 A° (40 kV and 40 mA) and a DTex Ultra detector using parallel beam geometry. Before recording the data, the samples were ground into a fine powder using a mortar and pestle. The data were collected from 5 to 80 degrees over 20 with a scanning speed of 1 degree/minute in 0.02 steps.

The morphology and size of the prepared samples were investigated by Field emission scanning electron microscopy (FESEM, JSM-7600F, accelerating voltage of 20-30 kV), Transmission Electron Microscopy (TEM, JEOL JEM-F200,), and Atomic force microscope (AFM, Park System XE7). For SEM and AFM analysis ethanolic dispersion of the samples was drop-casted on silicon wafers and allowed the solvent to evaporate slowly at room temperature in a vacuum desiccator. The samples for TEM were prepared by drop-casting on a holey carbon-coated Cu grid. The chemical composition of the synthesized samples was investigated by EDS (Energy Dispersive X-ray Spectroscopy, Oxford Instruments) operating at 15 kV.

The diffuse reflectance spectra (DRS) were recorded using a UV-Vis spectrophotometer (Cary 5000), and BaSO₄ powder was used as the reference to fix the baseline. The samples were ground into a fine powder before measurement.

Photoluminescence spectroscopy (PL) studies were carried out using a quartz cuvette and spectrofluorometer (Horiba Scientific). Time-correlated single photon counting (TCSPC, Fluorocube Horiba Jobin Yvon, NJ) measurements were carried out by using a laser diode head of 375 nm (NanoLED, Horiba Scientific) as an excitation source with a bandpass of 4 nm. The instrument response function (IRF) was collected using Ludox (colloidal silica, Sigma Aldrich). The width (FWHM) of IRF was ~250 ps. All data were collected by keeping the polarization at the magic angle (54.5⁰) and fixing the peak preset at 10,000 counts. DAS6 (Horiba Scientific) software was used to analyze the lifetime (maintaining best-fitting parameters).

X-ray photoelectron spectroscopy (XPS, Omicron Nanotechnology spectrometer with monochromatic Al K α X-radiation) was used to analyze the composition and electronic structure of the samples. The measurements were carried out by a Thermo K alpha+ spectrometer using micro-focused and monochromatic Al K α radiation (1486.6 eV).

Bruner Emmett Teller (BET) surface area was recorded at liquid nitrogen temperature (77 K) by using an autosorbiQ2 Quantachrome instrument (Autosorb Iq-c-XR-XR). Before

surface area measurement, the samples were degassed at 180 °C for 12 h. The apparent surface area was calculated by the Bruner Emmett Teller (BET) method.

Perkin Elmer (Lambda 365) UV-Vis. spectrophotometer was used to record UV-Vis. absorption spectra of all the samples at room temperature. The measurements were carried out with a step of 1nm from the 200-800 nm range.

High-performance liquid chromatography was performed by using (HPLC, Waters) equipped with 2998 array detector and Crest Pak C18 column in the mixed eluent (CH₃CN: $H_2O = 1:1$ by volume, ClO⁴⁻=150 mM, $H_2PO_4 = 50$ mM).

The 1H NMR spectra were recorded using a 400 MHz Bruker BioSpin Avance III FT-NMR spectrometer with TMS as the standard at room temperature and DMSO as solvent.

The High-resolution mass spectra (HRMS) studies were carried out with a Water Synapt G2-Si Q-TOF mass spectrometer using an electron spray ionization (ESI) positive mode of operation with a Q-TOF mass analyzer.

Gas chromatography (Shimadzu GC-2014, serial No. - C121656) equipped with a thermal conductive detector (TCD) and a 100 mesh porapack-N column, using He as a carrier gas to detect evolved H_2 gas.

Non-invasive Ocean Optics Neofox-Kit-Probe was used to measure the total oxygen (TO) content at room temperature $(25-27 \ ^{\circ} C)$.⁴ Typically, the experiment was done by attaching the sensing patch to the inner wall of the 50 ml round bottom flask in such a way that it is immersed in the aqueous solution and measures.

Electrochemical study: The electrochemical measurements were carried out in a three electrode configuration system on an electrochemical analyzer (CHI760E electrochemical workstation). Pt wire was used as a counter electrode, Ag/AgCl (saturated KCl) as the reference electrode, and ITO as the working electrode. A typical working electrode was prepared by taking 5 mg of the sample completely dispersed by sonication in 400 μ L of a mixed solution of isopropyl alcohol, Nafion, and water. Subsequently, the resulting suspension was dropped on an ITO glass (16 mm X 10 mm) and exposed to air overnight to dry. One edge of the ITO glass was connected with Cu-wire using conductive silver paste. The ITO glass was again kept for 4-6 h to get the silver paste dry. A certain quantity of epoxy glue (non-conductive) was used to cover the silver paste once the silver pastes dried completely, and air-dried for overnight. The (0.2 M) Na₂SO₄ aqueous solution was used as the electrolyte. The Mott–Schottky plot was obtained through the measurement of the capacitance as a function of potentials at two different

frequencies i.e., 1000 and 500 Hz in the different potential range. The conversion of potential *vs*. Ag/AgCl to potential *vs*. RHE was done by using the following equation:

 $E_{RHE} = E_{observed} + 0.0591 \times p^{H} + E^{0}_{Ag/AgCl}$

 $E_{observed} = experimentally observed potential using Ag/AgCl reference electrode$

 $E^{0}_{Ag/AgCl} = 0.2 V for 3M KCl filling$

pH = 6.5 for 0.5 M aqueous Na₂SO₄

Piezoelectric Study: The piezoelectric properties of the materials were examined by piezoelectric force microscopy (PFM) and Kelvin probe microscopy (KPFM) using an Asylum Research (MFP3D) atomic force microscope equipped with a Pt/Ir-coated Si cantilever 3 (Tips Nano, Nano World Arrow-EFM) with a resonance frequency of 50-130 kHz and a spring constant of 0.7-9 N/m. PFM was done in contact mode using the setup shown in (Figure 1.2.1.). The cantilever was oscillated by applying a sinusoidal AC voltage, Vac, to a piezo-chip attached to the cantilever. The cantilever was further tuned at the contact mode resonance frequency. To achieve maximum sensitivity, all the measurement was carried out at the resonance frequency. In the setup, a laser is directed on the cantilever and is reflected to a quadrupole photodiode. A moment of laser on the quadrupole photodiode tracks the defection of the cantilever while scanning over the surface. The cantilever gets deflected when the sample deforms in response to the applied voltage and this deflection is interpreted in terms of a piezoresponse signal. For PFM spectroscopy, DC voltage is also applied along with AC voltage in the form of V _{tip} = V _{dc} + V _{ac} sin (ω t) to the tip. A piezoelectric sample deforms below the tip in the presence of applied voltage. The response signal is interpreted in terms of phase, the first harmonic component of the tip deflection. The sample expands if the polarization direction below the tip is in the same direction as the applied DC voltage and vice versa. So, a sweeping DC voltage shows a switching behavior in phase. This can be observed as hysteric phase switching in the φ vs. V_{dc} curve. The amplitude of deformation can also be interpreted in the form $A = A0 + A \omega \cos (\omega t + \varphi)$. This is observed as a butterfly loop in the A ω vs V _{dc} curve. KPFM was used to determine the contact potential difference between a sharp AFM probe and the sample surface, as well as the sample's work function. To get the topography for KPFM investigations, the AFM probe scanned the sample surface in the tapping mode at first. The AFM scanner raised the probe 300 nanometers away from the sample surface and scanned it in parallel with a topographical profile. KPFM measurements are carried out in the noncontact mode, with the sample grounded and the AFM cantilever biased (AC and DC).



Figure 1.2.1. Schematic diagram of the Piezoresponse force microscopy (PFM) technique.

Positron annihilation Spectroscopy Study: Positron annihilation lifetime (PAL) has been measured with a pair of gamma-ray detectors (ultrafast 2.5 cm \times 2.5 cm BaF₂ scintillator optically coupled with XP2020Q photomultiplier tube) based γ - γ coincidence (fast-fast) assembly. The details of the positron annihilation lifetime setup are described elsewhere. The source of the positron is 8 µCi (micro Curie) NaCl deposited in a 6 µm thick Mylar foil covered by another 6µm thick Mylar foil. PATFIT-88 computer program has been used to deconvolute the recorded PAL spectrum with proper source corrections.

For the Coincidence Doppler broadening (CDB) studies, a pair of HPGe detectors of 12% efficiency (model number PGC 1216sp of DSG, Germany) has been used. The detectors are placed at 180 ° angles centering the source sample sandwich. The energy resolution of this HPGe detector is about 1.15 keV at 514 keV of 85 Sr. The Doppler broadening data have been recorded in a dual ADC-based multiparameter data acquisition system (Model # MPA-3 of FAST ComTec, Germany). The coincidence Doppler broadening spectra have been analyzed

by taking the area normalized point-by-point ratio with a CDB spectrum of 99.9999 % pure aluminum single crystal.

X-ray absorption study: X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) experiments at 300 K were performed at PETRA III, beamline P64, DESY, Germany. Measurements of Bi-L₃ and Ta-L₃ edges at ambient pressure were performed in fluorescence mode. Monochromatic X-rays were obtained using a Si (111) double-crystal monochromator. The acquired XAFS raw data was processed for background subtraction, normalization, and Fourier transformations using ATHENA software.

Part 2

Photocatalytic Investigation of Sillen Aurivillius

CHAPTER 2.1.

Synthesis of Bi₃TaO₇–Bi₄TaO₈Br composites in ambient air and their high photocatalytic activity upon metal loading



Summary

Sillen Aurivillius phases, a newly emerging material, known for its stability and structural flexibility. Herein, we show that composites of Bi_3TaO_7 – Bi_4TaO_8X (X = Cl, Br), two important Bi- and Ta-based light-responsive phases, can be prepared by high temperature, ambient air treatment of the precursors including easily oxidizable BiOX that retain the halide phases over 60% and exhibit high photocatalytic activity. Furthermore, when these phases were loaded with less than 1% noble metals (Pd, Pt, Ag), nearly complete separation of the photogenerated excitons was observed, leading to a significant enhancement in the photocatalytic activity.

A manuscript based on this work has appeared in Dalton Trans., 2019, 48, 7110-7116

2.1.1. Introduction

Bismuth and tantalum oxides and oxyhalides have emerged as attractive candidates for solar energy harvesting, renewable fuel production, and environmental pollutant removal because of their high stability under harsh working conditions such as strong acidic conditions as compared to many other efficient photocatalysts with simple elemental compositions.^{1–4} Such interesting properties stem from the interplay of unique atomic arrangements in their crystals and favorable electronic structures. Bi₃TaO₇ has a visible-light-active band gap of ~2.7–2.9 eV and an ordered pseudo-cubic fluorite-type crystal structure^{5–7} containing 25% intrinsic oxygen vacancies, where Ta occupies the Bi sites (**Figure 2.1.1. a**). Its hybridized VB is mainly composed of O 2p and Bi 6s and is relatively well-dispersed leading to the high mobility of photogenerated holes implying that these can travel longer distances as compared to other photocatalysts within the crystal to carry out photocatalysis before recombining. In addition, Bi₃TaO₇ exhibits high oxygen vacancies and disorder in its anionic lattice, resulting in high oxide ion mobility.



Figure 2.1.1. Crystal structures of (a) Bi₃TaO₇ and (b)Bi₄TaO₈Br.

Sillen Aurivillius phases viz. Bi_4MO_8X (M = Nb, Ta; X = Cl, Br), a family of rare mixedanion compounds, has been recently shown to exhibit very promising photocatalytic activity and more importantly, remarkable stability. Bi₄TaO₈X is the first member of Sillen Aurivilliustype perovskite Oxyhalide with the structural formula $(Bi_2O_2)_2X$ $(Bi_{n-1}Ta_nO_{3n+1})$, where n = 1, having alternately stacked $Bi_{n-1}Ta_nO_{3n+1}$ Aurivillius perovskite blocks and (Bi₂O₂)₂X Sillen blocks (Figure 2.1.1. b). Density functional theory calculations on these phases have shown that the VB maximum consists mainly of O 2p orbitals with little contribution from halide orbitals, and the same appears to be much more negative than those of other oxides or oxychlorides.^{4,8,9} This leads to a narrow band gap, allowing more absorption of visible light. The presence of O 2p orbitals around the VB maximum leads to the very high stability of these phases against photocorrosion. The band gap in the n = 1 member of the SA phases is smaller than Bi₃TaO₇, leading to a higher possibility of visible light absorption. Moreover, the strong internal electric fields between the layers in Sillen Aurivillius phases are expected to promote more spontaneous charge separation upon photoexcitation.^{10,11}

2.1.2. Scope of the present investigation

Recent investigations have led to the synthesis of phase-pure Sillen Aurivillius phases. Widely adopted techniques for their synthesis involve mixing of precursors in stoichiometric quantities, palatizing them, and inducing a diffusion-controlled reaction at 700–800 °C by placing the reactants inside an evacuated sealed tube, or by using an arc furnace in an inert atmosphere.^{4, 8,10,12,13} These have also been obtained using a large excess of flux.^{14, 15} Although these approaches are interesting for obtaining small quantities of the catalysts, their translation into applications may become difficult due to the expensive and complicated reaction set-up to create a non-oxidizing atmosphere, as in the case of other important functional materials.^{16–} ¹⁸ Another drawback that both Sillen Aurivillius phases and Bi₃TaO₇ suffer from is the poor separation efficiency of photogenerated electrons and holes, limiting their photocatalytic efficiency. Some progress has been made to overcome this challenge by combining these materials with another material, through the Z-scheme mechanism, to which one of the excitons can efficiently migrate from the photocatalyst, making both the hole and the electron available for a longer period to carry out redox reactions. The oxides of bismuth have been loaded with g-C₃N₄, Ag, and Bi.^{1,3,19–21} There are only two reports in the case of Sillen Aurivillius phases to the best of our knowledge, where Bi₄MO₈X has been combined with the hydrogen evolution

cocatalyst Ru/SrTiO₃ for efficient overall water splitting.^{1,40} Detailed investigations by loading these phases with more established cocatalysts such as noble metals are still lacking.

To simplify the synthesis procedure, here we have carried out the synthesis of Bi₄TaO₈X employing the reported conditions, but under ambient air, it resulted in a composite containing both the above-mentioned important photocatalysts, Bi₃TaO₇ and Bi₄TaO₈X, due to partial oxidation of the halide precursor, BiOX, even though the nucleation of the highly air-stable Sillen Aurivillius phases was quick enough to retain over 60% of the precursor halogen. The composite has exhibited significantly improved photocatalytic activity compared to pure Bi₃TaO₇ underscoring its importance. We have further shown that it is possible to separate the photogenerated electron–hole pairs in the composite almost completely by depositing a tiny weight fraction of noble metals such as Pt and Pd, which have not been attempted in either of these phases so far. Aided by this, our experiments reported here establish the metal-loaded conditions.

2.1.3. Methods

2.1.3.1. Synthesis of Bi₃TaO₇-Bi₄TaO₈X (X = Cl, Br) composite: Stoichiometric quantities of Bi₂O₃, BiOX, and Ta₂O₅ powders were weighed, and thoroughly mixed using Agate mortar and pestle. The resulting powder was transferred in a silica boat and heated in a muffle furnace at 1073 K for 24 hours with intermediate grindings after 12 hours. The heating rate was ~280 K per minute, while the cooling rate to room temperature was natural. Bi₃TaO₇ was prepared similarly by using Bi₂O₃ and Ta₂O₅ in a 3:1 molar ratio.

2.1.3.2. Loading of co-catalysts on to the composite: The metal nanoparticles loaded photocatalysts with less than 1wt% by photo-deposition method under sunlight. Appropriate amounts of PdCl₂, AgNO₃, and H₂PtCl₆.6H₂O were weighed and put into 10 vol% aqueous methanol solutions in three beakers, to each of them 0.4g of the composite was added. The solutions were irradiated with 400W Xe light (Newport, USA). The solution was purged with argon before starting the photodeposition, and the product was washed thoroughly with a DI water-ethanol mixture and dried in the air. The composite appeared darker in color after the deposition of metals.

2.1.3.3. Photocatalytic Experiments: A 400 W Xe lamp (Newport, USA) was used as the visible light source with an attached 1.5 AM and IR filter. The reactor used for the experiment is made of a Pyrex glass beaker of volume 50 ml. In the reactor, 25 ml of solution

was poured and continuously stirred to keep the suspension of the catalyst uniform throughout the solution. An aqueous 25 mL dye solution with a concentration of 10 mg/L of dye was used for photocatalytic studies unless otherwise mentioned. The amount of catalyst used was fixed as 40 mg for 25 ml of the dye solution unless otherwise mentioned. The suspension containing dye solution and catalyst was stirred for 30 minutes in the dark to attain adsorption-desorption equilibrium and the resulting aliquot was exposed to light. Photocatalytic experiments were carried out under visible light irradiation using the abovementioned light source. To carry out pH-dependent reactions, the solution pH was adjusted using perchloric acid and concentrated sodium hydroxide. During the illumination of the light, 1 ml of solution was continuously taken from the reaction cell for regular intervals of time. The collected samples were then centrifuged to remove any catalyst particles present in the solution for further analysis. Dye solutions were analyzed based on the Beer-Lambert law at their maximum absorption wavelength.

2.1.3.4. Characterization

All the characterization techniques are discussed in chapter 1.2.

2.1.4. Results and Discussion

The Bi₃TaO₇–Bi₄TaO₈X (X = Cl, Br) composites with a yellowish appearance were prepared at 1073 K by using Bi₂O₃, BiOX (X = Cl, Br), and Ta₂O₅ powders as precursors in stoichiometric amounts corresponding to the Sillen Aurivillius phases. (**Figure 2.1.2. a and b**) shows the powder X-ray diffraction (XRD) pattern of the bromide and chloride composites respectively. All peaks in the pattern can be indexed using the Bi₄TaO₈Br phase (ICSD #98-009-3561), Bi₄TaO₈Cl phase (ICSD #98-006-4664) and the Bi₃TaO₇ phase (ICSD #98-001-4207), indicating the completion of the reaction.

The morphology and size of the samples were characterized by field emission scanning electron microscopy (FE-SEM). As seen in **Figure 2.1.2. c and d**, both the bromide and chloride composite consist of agglomerated grains having corrugated surfaces, leading to a higher surface area. Each larger particle appears to have formed by the coalescence of smaller (500 nm to 2 micrometre) size particles. **Figure 2.1.2. e and f**, shows the typical Energy Dispersive X-ray Spectrum (EDS) from the bromide and chloride composites, where the Ta and Br peaks are visible. Quantitative estimation of these two components across the sample showed that the Sillen Aurivillius phases constitute nearly 60–75% of the sample. The relative ratios of the two phases could not be estimated in the case of chloride composite as the Cl peak overlaps with Bi. It is noteworthy that when the BiOX sample was heated alone under the same
conditions, it converted to Bi₂O₃ completely within two hours. Thus, the formation of the stable Sillen Aurivillius phases must have occurred within this period.



Figure 2.1.2. (a, b) Powder XRD pattern of the Bi₃TaO₇–Bi₄TaO₈Br and Bi₃TaO₇–Bi₄TaO₈Cl composite respectively. The panels on the top of the XRD pattern mark the expected peak positions. (c, d) FE-SEM image of the Bi₃TaO₇–Bi₄TaO₈Br (The inset shows a magnified image of its surface) and Bi₃TaO₇–Bi₄TaO₈Cl composite. (b) SEM-EDS spectrum recorded on the bromide and chloride composites.

The UV-visible (UV-vis) diffuse reflectance spectrum (DRS) of the Bi₃TaO₇ and Bi₃TaO₇–Bi₄TaO₈X (X = Cl, Br) composite was obtained using BaSO₄ as a reference and converted to absorbance by the Kubelka–Munk method.^{22,23} As shown in **Figure 2.1.3. a** (**inset**), a pronounced absorption onset for the Bi₃TaO₇–Bi₄TaO₈Br composite was observed at ~575 nm, which is red-shifted as compared to that reported for pure Bi₄TaO₈Br (~485 nm).⁴ The optical band gap was calculated using the Tauc equation:^{11,24}

$$\alpha hv = A (hv - E_g)^{n/2}$$

Where A = constant, hv = light energy, $E_g = \text{optical band gap energy}$, $\alpha = \text{measured absorption}$ coefficient, and *n* reflects the characteristics of the transition in a semiconductor, *i.e.* n = 1 or 4 for direct or indirect band-gap materials, respectively. Assuming that the lower energy absorption is primarily contributed by the Sillen Aurivillius phases (Bi₃TaO₇ has a higher band gap of 2.7–2.9 eV ^{1,25}) having an indirect band gap, the value of *n* was fixed as 4. The effective band gap of the Bi₃TaO₇–Bi₄TaO₈Br composite was estimated to be 2.59 eV. The Tauc plots and the DRS plots for Bi₃TaO₇–Bi₄TaO₈Cl and Bi₃TaO₇ are given in **Figure 2.1.3. b, c,** and their insets respectively.



Figure 2.1.3. DRS (insets) and Tauc Plot of (a) Bi₃TaO₇–Bi₄TaO₈Br, (b) Bi₃TaO₇–Bi₄TaO₈Cl composite and (c) Bi₃TaO₇ respectively.

2.1.4.1. Photocatalytic RhB Degradation

We have selected Rhodamine B (RhB) as a model dye to examine the photocatalytic activity of Bi_3TaO_7 – Bi_4TaO_8X (X = Cl, Br) composite and Bi_3TaO_7 . Waste generated by various industries contains different organic dye molecules which are difficult to degrade, and therefore photocatalytic degradation is a convenient way to get rid of such pollutants. Besides, degradation is easily monitored by UV-vis. spectroscopy. To understand the role of catalyst and light in RhB degradation, it was first attempted to degrade in the absence of catalyst, light, and both. The results show that the concentration of RhB remains the same in the absence of any one of these. The concentration of Rhodamine B decreased only in the presence of both catalyst and light. Figure 2.1.4. a, b, and c show the time-evolution of UV-vis. spectra of the RhB solution in the presence of catalyst and light. In this case, Rhodamine B gets converted into Rhodamine 110 (Rh110) at first, at least partially, as is evident from the shift in the absorption maxima from 553 nm towards 499 nm. Rhodamine 110 then further degrades. For the complete degradation of RhB, Bi₃TaO₇- Bi₄TaO₈Br, Bi₃TaO₇-Bi₄TaO₈Cl, and Bi₃TaO₇ took 210 min, 315 min, and 700 min respectively, indicating that the samples are all capable of responding to visible light. To understand the reaction kinetics of photocatalytic RhB disappearance, the following pseudo-first-order model was used to analyze our photocatalytic degradation data:

$$\ln A_t / A_o = k_1 t$$

Where, k_1 = pseudo-first-order rate constant; A_0 =initial absorbance and A_t = absorbance of the dye solution at reaction time t. It was found that degradation of RhB in the presence of Bi₃TaO₇-Bi₄TaO₈X (X =Cl, Br) composite and Bi₃TaO₇ follow pseudo-first-order reaction kinetics. The degradation rate of RhB is in the order of Bi₃TaO₇-Bi₄TaO₈Br > Bi₃TaO₇-Bi₄TaO₈Cl > Bi₃TaO₇. The degradation rate constant of RhB catalysed by Bi₃TaO₇-Bi₄TaO₈Br, Bi₃TaO₇-Bi₄TaO₈Cl, and Bi₃TaO₇ were estimated as 1.2546 h⁻¹, 0.906 h⁻¹, and 0.4692 h⁻¹ respectively (**Figure 2.1.4. d, e, and f**). Degradation efficiency (η) was calculated by using the following equation:

$$\eta = [1 - (A_t / A_o)] \times 100\%$$

where A_0 = initial absorbance and A_t = absorbance of the dye solution at reaction time t. The photocatalytic activities of the materials were found to decrease in the following order upon 210 min light irradiation: Bi₃TaO₇- Bi₄TaO₈Br > Bi₃TaO₇-Bi₄TaO₈Cl > Bi₃TaO₇ with efficiencies estimated as 95, 74, and 44% respectively.



Figure 2.1.4. (a, b, c) UV-vis. absorption spectra recorded during RhB degradation in aqueous Bi_3TaO_7 - Bi_4TaO_8Br , Bi_3TaO_7 - Bi_4TaO_8Cl and Bi_3TaO_7 dispersions as a function of light irradiation time respectively and their (d, e, f) corresponding rate constant plots.

The overall photocatalytic efficiency will rely on the (a) photon absorption cross-section of the catalyst, (b) dye adsorption ability, (d) desorption kinetics of the photo-degraded products and (c) charge-transfer ability from the catalyst to the dye (herein orientation of RhB on the catalyst surface is crucial). RhB adsorption studies on the different catalysts by placing together the same amount of dye solution (12μ M RhB) and the catalyst (20, 40, 60 mg) was carried out in the dark for 90 minutes. Bi₃TaO₇- Bi₄TaO₈Cl composite (Figure 2.1.5. a, b) absorbs ~63 micromoles/gram of RhB, whereas Bi₃TaO₇- Bi₄TaO₈Br composite (Figure 2.1.5. c, d) adsorb ~72 micromoles of RhB per gram which is about 12% higher than the Bi₃TaO₇- Bi₄TaO₈Cl composite. Adsorption on Bi₃TaO₇ was much lesser (Figure 2.1.5. e and f, 28 micromole/gram). The adsorption trend in the Bi compounds is similar to that of their photocatalytic efficiencies. Therefore, preferential adsorption of RhB on the surface of Bi₃TaO₇- Bi₄TaO₈Br composite may be a reason for exhibiting higher activity.



Figure 2.1.5. Adsorption of Rhodamine B on different phases: (a, b) Bi₃TaO₇- Bi₄TaO₈Cl, (c, d) Bi₃TaO₇- Bi₄TaO₈Br, (e, f) Bi₃TaO₇

2.1.4.2. Photodeposition of noble metal on Br Composite

We have further attempted to improve the efficiency of the bromide composite by decorating it with a tiny weight fraction (\geq 1%) of noble metal (Pd, Pt, and Ag) co-catalysts. The presence of co-catalysts on light-harvesting semiconductor surfaces can facilitate reactions by providing active sites for the reaction and enhance the quantum efficiency by lowering the activation energy.^{26, 27} These provide trapping sites for the photogenerated charges and suppress exciton recombination to an extent depending on their interaction with the semiconductor through junction formation. The co-catalysts were deposited photochemically which led to a slight darkening in the color of the composite. The presence of the co-catalysts on the thoroughly washed composite was confirmed by TEM, though powder XRD did not show any diffraction



Figure 2.1.6. (a) TEM image of Pd loaded Bi₃TaO₇-Bi₄TaO₈Br. The lower inset shows a scanning TEM image of another grain. (b) HRTEM of Pd nanostructures and (c) a typical SAED pattern of Pd-loaded bromide composite. (d) TEM image of Pt loaded bromide composite (Inset: HRTEM image displaying a single-crystalline Pt nanocrystal.) (e) HRTEM image of the Bi₃TaO₇-Bi₄TaO₈Br composite without metal loading.

peak corresponding to the metals due to low abundance. We observed nanocrystals of the metals measuring a few nanometres deposited on the surface. A typical TEM image of the Pdloaded bromide composite, which exhibited the highest improvement in photocatalytic activity as discussed vide infra, is shown in Figure 2.1.6. a, and its inset. One can see the deposited Pd nanocrystals measuring 5–15 nm decorating the catalyst surface, usually in higher densities across edges. Figure 2.1.6. b shows a high-resolution TEM (HRTEM) image of a Pd nanocrystal, where the lattice fringes separated by ~ 0.23 nm can be ascribed to the (111) planes in a face-centred cubic Pd structure. The selected area electron diffraction (SAED) pattern of the Pd-loaded Br composite is given in Figure 2.1.6. c, which consists of circular rings corresponding to Pd and clear spots belonging to a portion of the single-crystalline catalyst matrix. The indexed spots are close to the (200) plane of Bi₄TaO₈Br and the (220) plane of Bi₃TaO₇. Similarly, photodeposited Pt nanocrystals were also arranged on the catalyst surface in an identical fashion (Figure 2.1.6. d). The HRTEM images of the Pt particles confirm their single-crystalline nature while showing the lattice fringes of 0.22 nm corresponding to the dspacing of the (111) plane. It may be noted that the lattice spacing observed on the pristine sample is much larger than the same on Pd nanocrystals (Figure 2.1.6. e).



Figure 2.1.7. (a) Band gaps estimated from the Tauc plot of different co-catalyst loaded bromide composites. (b) Photoluminescence spectra of the various bromide composites.

The co-catalyst loading has led to significant changes in the optical absorption and emission properties in the composite. **Figure 2.1.7. a** shows Tauc plots corresponding to the different samples. While the Pt and Ag-loaded composites exhibited similar band gaps as that of the pristine composite, a considerable increase in the band gap of the Pd-loaded sample (2.62)

eV) was noticed. The origin of such a shift is not clear to us. However, we hypothesize that the Pd loading was induced by the defect-sites on the surface of the composite which led to annihilation of the corresponding mid-gap trap states resulting in a wider band-gap. The changes in the emission properties were found to be more pronounced, in two aspects, as seen in **Figure 2.1.7. b**. First is the distinct suppression of the emission peak indicating a facile separation of photogenerated electron and hole pairs. The Pd-loaded sample recorded the highest decrease (over 10 times) in the photoluminescence intensity. Besides, metal loading also led to a small but noticeable blue-shift of the emission peak in all the samples.

2.1.4.3. Enhanced activity by noble metal loading

The effects of depositing metal nanoparticles as a co-catalyst on the photocatalytic activity of bromide composite were evaluated again by measuring the degradation of RhB. We point out that the photocatalytic reactions were carried out at pH 2 to check not only their improved activity but also their stability under harsh working conditions. High H⁺ concentration in the reaction medium can significantly enhance the reaction rate in this case by favouring adsorption of RhB, provided the catalyst system is stable under these conditions.^{28,29} Figure 2.1.8. a, b, c, and d show the temporal evolution of the spectral changes during the photodegradation of RhB over the metal-loaded photocatalysts. These figures indicate that the co-catalyst loading leads to extremely high photocatalytic activity. Among the composites, the Pd-loaded sample exhibited the highest activity by completing the degradation within 15 min (rate constant, 0.35 min⁻¹). Under similar conditions, the Pt and Ag-loaded ones took nearly 30 minutes (rate constants = 0.13 min^{-1} and 0.12 min^{-1} respectively) while the unloaded composite required 50 minutes. We further compared our catalysts with that of commercial TiO₂ (P25) which we expect to have a much higher surface area (56 m^2/g originating from a small particle size of 26 nm³⁰) and better aqueous dispersibility as compared to our catalysts, showed that under the experimental conditions, its activity (rate constant = 0.11 min^{-1}) is comparable to the Pt and Ag loaded catalysts but poorer than the Pd loaded one. We have also compared our rate constant values with many other reports in the literature (Table 2.1.1). It shows that the ~ 4-fold enhancement in rate constant when we loaded the Sillen Aurivillius phases with Pd is better than those observed in other studies. Figure 2.1.8. e, points to another interesting fact that the post co-catalyst loading, the ability of the catalysts to adsorb the dye molecules has remarkably increased, which must have contributed to their higher efficiencies. The recyclability test for the degradation reaction was also carried out as shown in Figure 2.1.8. f, Pd loaded composite

demonstrated excellent reusability of the catalyst even after 10 cycles with a negligible loss of 2.15% in activity.



Figure 2.1.8. (a, b, c, d) UV-vis. spectra recorded at various time intervals (in minutes) during photocatalytic degradation of RhB by metal-loaded and unloaded Bi_3TaO_7 - Bi_4TaO_8Br composite. (e) Lowering of RhB concentration during its photocatalytic degradation by co-catalyst loaded and unloaded Bi_3TaO_7 - Bi_4TaO_8Br composite in comparison to P_{25} TiO₂. (f) Stability plot showing the RhB degradation efficiency by Pd loaded sample during 10 consecutive cycles.

Catalyst	Amount	Substrate	Rate Const.	Ref.
	(mg)	concentration	(h ⁻¹)	
BiaTaOa-BiaTaOaBr	40mg	10 mg/l (RhB)	5 7198	Our work
	Toms		01 0000	
Twt%Pd loading			21.2232	
$g - C_3 N_4 - Bi_2 WO_6$	50mg	10mg/l(RhB)	0.912	1
0.7wt% Pt loading			2.736	
TiO ₂ Nanotube Array	-	10mg/l (RhB)	0.2634	2
0.4wt%Au loading			0.3672	
TiO ₂	50mg	10 ⁻⁵ M (RhB)	6.12	3
1wt%Pt@TiO ₂			10.68	
BiOCl	100mg	20mg/l(RhB)	14.82	4
0.5wt%Ag loading			15.18	
ZnO Nanorods	25mg	0.03mM(Methyl orange)	0.828	5
10% Au loading			3.102	
Bi ₃ TaO ₇	50mg	22µM(Tetracycline)	0.4134	6
1w%Ag loading			0.972	
g-C ₃ N ₄	100mg	20mg/l(Tetracycline)	7.614	7
0.5wt%Pt loading			10.854	
2wt%Au loading			14.97	

Table 2.1.1: Activity comparison table of Bi_3TaO_7 - Bi_4TaO_8Br (1wt%Pd@ Bi_3TaO_7 - Bi_4TaO_8Br) with recent literature reports.

To understand whether the degradation of Rhodamine B is contributed by any self-sensitization process, we conducted a control experiment. 20 μ M RhB solution was irradiated under Xelamp without catalyst at pH=2. It revealed only a negligible decrease in absorbance even after 60 min of irradiation, as shown in **Figure 2.1.9. a**. Thus, we conclude that the degradation of RhB has taken place only in the presence of the catalyst. Further to examine whether the degradation is RhB specific, we have also carried out the oxidation of various other dyes using the Pd-loaded Br composite (**Figure 2.1.9. b and c**). The composite was found to be highly active in all cases. The corresponding rate constants were estimated to be 0.47 h^{-1} for Methyl orange and 1.29 h^{-1} for Congo-red.



Figure 2.1.9. (a) Temporal UV-vis. spectra of RhB solution under illumination; (b)-(c) Temporal UV-vis. spectra depicting Methyl-orange (12 μ M) and Congo-red (12 μ M) dye degradation by 20 mg Pd loaded Bi₃TaO₇-Bi₄TaO₈Br composite.

To explore the reaction pathway, we have analysed the different reactive species and fragmented species produced during the photodegradation of RhB by using controlled scavenging experiments and recording High-Resolution Mass Spectra (HRMS, **Figure 2.1.10.**) during the reaction. HRMS analysis showed that the degradation creates high molecular weight intermediates initially (325, 355, 179 m/z) before going on to produce small oxidized molecules such as 4-(methoxycarbonyl) benzoic acid (179 m/z), 2-(methoxycarbonyl) benzoic acid (179 m/z), benzoic acid (123 m/z), 2,6-dimethyl phenol (123 m/z), etc.³¹ Next, we performed the reaction in presence of various transient species scavengers. Ammonium oxalate (AO), tertiary butanol (t-BuOH), and benzoquinone (BQ) were used as holes (h⁺), hydroxyl radicals (OH•), and superoxide radical anions (O²⁺⁻) scavengers respectively.^{32,33} As seen in **Figure 2.1.11.**, the addition of hydroxyl radicals (OH•) scavenger did not have much effect on the RhB degradation.



Figure 2.1.10. High-resolution mass spectra of the species produced during photodegradation of RhB, showing intermediates and final products. RhB has its characteristic molecular ion peak at 443 m/z (a), which vanishes under visible light irradiation, and new peaks arise at 325, 355, and 197 m/z as seen in the spectrum recorded after 10 minutes of the reaction Finally, degradation leads to the formation of small oxidized molecules such as 4- (methoxycarbonyl) benzoic acid (179m/z), 2-(methoxycarbonyl) benzoic acid (179 m/z), benzoic acid (123 m/z), 2,6-dimethyl phenol (123 m/z) etc (c).

However, degradation was significantly inhibited upon the addition of hole and superoxide radical anions scavengers, indicating that these are dominant species in the RhB degradation. Based on these trapping experiments, the transfer of the exciton appears to be the rate-determining step. On the other hand, such transfer is known to finally yield 'OH radicals that

are responsible for dye degradation.^{34,35} Since •OH scavenger did not slow down the reaction, it may be related to higher adsorption of RhB on the catalyst surface (refer to **Figure 2.1.8. e**) ensuring high proximity to these radicals to annul any scavenger attack. We also reckon that the coexistence of two photoactive phases, Bi₃TaO₇ and Bi₄TaO₈Br may lead to electron transport pathways mimicking Z-scheme.^{36,37,38,39} Based on our control experiments and various literature data, we propose an electron transfer pathway involved in the photocatalytic reactions as shown in **Figure 2.1.12.** The conduction band (CB) of Bi₃TaO₇ lies in the range of 0.32-0.46 V *vs*. NHE whereas its VB is suggested to be in the 3.12-3.22 V range.^{40,3}



Figure 2.1.11. Percentage degradation of RhB in the presence of different scavengers using the Pd-loaded bromide composite.

Similarly for Bi₄TaO₈Br, the CB minima and the VB maxima were reported to be -0.79 V and 1.74 V *vs*. NHE respectively.⁴² The Fermi level of palladium is 0.45 V *vs*. NHE.⁴¹ The bandgaps derived from the positions of CB and VB in these materials correspond closely to our experimentally determined value. Besides, since the band positions are widely apart in these two materials, minor variations in their actual positions are not expected to alter the proposed scheme.



Figure 2.1.12. Schematic illustration of band-alignment and photo-induced electron transfer in the Bi₃TaO₇-Bi₄TaO₈Br composite.

2.1.5. Conclusion

In conclusion, a novel composite photocatalyst system was realized involving two important compounds, Bi_3TaO_7 and Bi_4TaO_8Br . By developing an easily scalable high-temperature approach. The composite exhibited high photocatalytic activity upon loading with $\geq 1\%$ of Pd in comparison to commercial P25 catalysts. In addition, it also exhibited very high stability working in harsh low pH conditions with a mere decrease of ~2% activity after 10 working cycles.

Bibliography

- B. Luo, M. Chen, Z. Zhang, J. Xu, D. Li, D. Xu and W. Shi, Facile synthesis of CdS/Bi4V2O11 photocatalysts with enhanced visible-light photocatalytic activity for degradation of organic pollutants in water.. Dalton Trans., 2017, 46, 8431– 8438. https://doi.org/10.1039/C7DT02151H
- G. Kakavelakis, I. Paradisanos, B. Paci, A. Generosi, M. Papachatzakis, T. Maksudov, L. Najafi, A. E. Del Rio Castillo, G. Kioseoglou, E. Stratakis, F. Bonaccorso and E. Kymakis, Extending the Continuous Operating Lifetime of Perovskite Solar Cells with a Molybdenum Disulfide Hole Extraction Interlayer. Adv. Energy Mater., 2018, 8, 1702287. https://doi.org/10.1002/aenm.201702287
- B. Luo, D. Xu, D. Li, G. Wu, M. Wu, W. Shi and M. Chen, Fabrication of a Ag/Bi3TaO7 Plasmonic Photocatalyst with Enhanced Photocatalytic Activity for Degradation of Tetracycline. ACS Appl. Mater. Interfaces, 2015, 7, 17061–17069.

https://doi.org/10.1021/acsami.5b03535

4. H. Fujito, H. Kunioku, D. Kato, H. Suzuki, M. Higashi, H. Kageyama and R. Abe, Layered Perovskite Oxychloride Bi4NbO8Cl: A Stable Visible Light Responsive Photocatalyst for Water Splitting. J. Am. Chem. Soc., 2016, 138, 2082–2085.

https://doi.org/10.1021/jacs.5b11191

5. I. Abrahams, F. Krok, M. Struzik and J. R. Dygas, Defect structure and electrical conductivity in Bi3TaO7. Solid State Ionics, 2008, 179, 1013–1017. https://doi.org/10.1016/j.ssi.2008.02.002

 M. Struzik, X. Liu, I. Abrahams, F. Krok, M. Malys and J. R. Dygas, Defect structure and electrical conductivity in the pseudo-binary system Bi3TaO7–Bi3NbO7. Solid State Ionics, 2012, 218, 25–30. https://doi.org/10.1016/j.ssi.2012.05.005

7. H. A. Harwig, Z. Anorg. On the Structure of Bismuthsesquioxide: The α , β , γ , and δ -phase . Allg. Chem., 1978, 444, 151–166. https://doi.org/10.1002/zaac.19784440118

H. Kunioku, M. Higashi, O. Tomita, M. Yabuuchi, D. Kato, H. Fujito, H. Kageyama and R. Abe, Strong hybridization between Bi-6s and O-2p orbitals in Sillén–Aurivillius perovskite Bi4MO8X (M = Nb, Ta; X = Cl, Br), visible light photocatalysts enabling stable water oxidation. J. Mater. Chem. A, 2018, 6, 3100–3107. https://doi.org/10.1039/C7TA08619A

 D. Kato, K. Hongo, R. Maezono, M. Higashi, H. Kunioku, M. Yabuuchi, H. Suzuki, H. Okajima, C. Zhong, K. Nakano, R. Abe and H. Kageyama, Valence Band Engineering of Layered Bismuth Oxyhalides toward Stable Visible-Light Water Splitting: Madelung Site Potential Analysis. J. Am. Chem. Soc., 2017, 139, 18725–18731. https://doi.org/10.1021/jacs.7b11497

10. X. Tao, Y. Zhao, L. Mu, S. Wang, R. Li and C. Li, Bismuth Tantalum Oxyhalogen: A Promising Candidate Photocatalyst for Solar Water Splitting. Adv. Energy Mater., 2018, 8, 1701392. https://doi.org/10.1002/aenm.201701392

 X. Lin, T. Huang, F. Huang, W. Wang and J. Shi, Ferroelectric Properties and Crystal Structure of the Layered Intergrowth Phase Bi3Pb2Nb2O11Cl. J. Phys. Chem. B, 2006, 110, 24629–24634. https://doi.org/10.1021/cm011145n

12. S. Liu, W. Miiller, Y. Liu, M. Avdeev and C. D. Ling, Sillen–Aurivillius Intergrowth Phases as Templates for Naturally Layered Multiferroics. Chem. Mater., 2012, 24, 3932–3942. https://doi.org/10.1021/cm302342v

- C. Zhong, D. Kato, F. Takeiri, K. Fujii, M. Yashima, E. Nishiwaki, Y. Fujii, A. Koreeda,
 C. Tassel, R. Abe and H. Kageyama, Inorganics, 2018, 6, 41.
- K. Ogawa, A. Nakada, H. Suzuki, O. Tomita, M. Higashi, A. Saeki, H. Kageyama and R. Abe, ACS Appl. Mater. Interfaces, 2019, 11, 5642.
- L. Li, Q. Han, L. Tang, Y. Zhang, P. Li, Y. Zhou and Z. Zou, Nanoscale, 2018, 10, 1905– 1911.
- D. H. Seo, S. Pineda, J. Fang, Y. Gozukara, S. Yick, A. Bendavid, S. K. H. Lam, A. T. Murdock, A. B. Murphy, Z. J. Han and K. (Ken) Ostrikov, Nat. Commun., 2017, 8, 14217.
- D. H. Seo, M. Batmunkh, J. Fang, A. T. Murdock, S. Yick, Z. Han, C. J. Shearer, T. J. Macdonald, M. Lawn, A. Bendavid, J. G. Shapter and K. (Ken) Ostrikov, FlatChem, 2018, 8, 1–8.
- 18. P. P. Prosini, M. Carewska and M. Pasquali, Solid State Ionics, 2016, 286, 66–71.
- 19. T. Zhang, W. Lei, P. Liu, J. A. Rodriguez, J. Yu, Y. Qi, G. Liu and M. Liu, J. Phys. Chem.C, 2016, 120, 2777–2786.

- H. Guo, C.-G. Niu, L. Zhang, X.-J. Wen, C. Liang, X.-G. Zhang, D.-L. Guan, N. Tang and G.-M. Zeng, ACS Sustainable Chem. Eng., 2018, 6, 8003–8018.
- 21. K. Wang, Y. Li, G. Zhang, J. Li and X. Wu, Appl. Catal., B,2019, 240, 39-49.
- 22. B. J. Brinkworth, Appl. Opt., 1972, 11, 1434–1435.
- 23. Y. Lee, S. Kim, J. K. Kang and S. M. Cohen, Chem. Commun., 2015, 51, 5735-5738.
- 24. A. B. Murphy, Sol. Energy Mater. Sol. Cells, 2007, 91, 1326–1337.
- B. Luo, M. Chen, Z. Zhang, Y. Hong, T. Lv and W. Shi, J. Solid State Chem., 2017, 256, 203–212.

26. J. Yang, D. Wang, H. Han and C. Li, Roles of Cocatalysts in Photocatalysis and Photoelectrocatalysis. Acc. Chem. Res., 2013, 46, 1900–1909. https://doi.org/10.1021/ar300227e

27. K. Zhang, J. Ran, B. Zhu, H. Ju, J. Yu, L. Song and S.-Z. Qiao, Nanoconfined Nickel@Carbon Core–Shell Cocatalyst Promoting Highly Efficient Visible-Light Photocatalytic H2 Production. Small, 2018, 14, 1801705. https://doi.org/10.1002/smll.201801705

28. T. S. Natarajan, M. Thomas, K. Natarajan, H. C. Bajaj and R. J. Tayade, Study on UV-LED/TiO2 process for degradation of Rhodamine B dye. Chem. Eng. J., 2011, 169, 126– 134. https://doi.org/10.1016/j.cej.2011.02.066

29. H. Fu, C. Pan, W. Yao and Y. Zhu, Visible-Light-Induced Degradation of Rhodamine B by Nanosized Bi2WO6. J. Phys. Chem. B, 2005, 109, 22432–22439. https://doi.org/10.1021/jp052995j

30. K. J. A. Raj and B. Viswanathan, Effect of surface area, pore volume and particle size of P25 titania on the phase transformation of anatase to rutile. Indian J. Chem., 2009, 48,1378–1382.

31. T. Liu, L. Wang, X. Lu, J. Fan, X. Cai, B. Gao, R. Miao, J. Wang and Y. Lv, Comparative study of the photocatalytic performance for the degradation of different dyes by ZnIn2S4: adsorption, active species, and pathways. RSC Adv., 2017, 7, 12292–12300. https://doi.org/10.1039/C7RA00199A 32. J. Zhang, H. Liu and Z. Ma, Flower-like Ag2O/Bi2MoO6 p-n heterojunction with enhanced photocatalytic activity under visible light irradiation. J. Mol. Catal. A: Chem., 2016, 424, 37–44. https://doi.org/10.1016/j.molcata.2016.08.009

33.B. Song, T. Wang, H. Sun, Q. Shao, J. Zhao, K. Song, L. Hao, L. Wang and Z. Guo, Twostep hydrothermally synthesized carbon nanodots/WO3 photocatalysts with enhanced photocatalytic performance. Dalton Trans., 2017, 46, 15769–15777. https://doi.org/10.1039/C7DT03003G

34. A. K. Adepu, V. Katta and V. Narayanan, Synthesis, characterization, and photocatalytic degradation of Rhodamine B dye under sunlight irradiation of porous titanosilicate (TS)/bismuth vanadate (BiVO4) nanocomposite hybrid catalyst. New J. Chem., 2017, 41, 2498–2504. https://doi.org/10.1039/C7NJ00071E

35.S. Fang, K. Lv, Q. Li, H. Ye, D. Du and M. Li, Photocatalytic degradation of Rhodamine B under UV irradiation over anatase TiO2:Ln3+ nanoparticles. Appl. Surf. Sci., 2015, 358, 336–342.

36. N. Tian, H. Huang, Y. He, Y. Guo, T. Zhang and Y. Zhang, Mediator-free direct Z-scheme photocatalytic system: BiVO4/g-C3N4 organic–inorganic hybrid photocatalyst with highly efficient visible-light-induced photocatalytic activity. Dalton Trans., 2015, 44, 4297–4307. https://doi.org/10.1039/C4DT03905J

37.Y. Miseki, S. Fujiyoshi, T. Gunji and K. Sayama, Photocatalytic Z-Scheme Water Splitting for Independent H2/O2 Production via a Stepwise Operation Employing a Vanadate Redox Mediator under Visible Light. J. Phys. Chem. C, 2017, 121, 9691–9697.

38.K. Maeda, Z-Scheme Water Splitting Using Two Different Semiconductor Photocatalysts. ACS Catal., 2013, 3, 1486–1503. https://doi.org/10.1021/cs4002089

- 39. T. B. Li, G. Chen, C. Zhou, Z. Y. Shen, R. C. Jin and J. X. Sun, New photocatalyst BiOCl/BiOI composites with highly enhanced visible light photocatalytic performances. Dalton Trans., 2011, 40, 6751–6758. https://doi.org/10.1039/C1DT10471C
- 40. K. Wang, G. Zhang, J. Li, Y. Li and X. Wu, Enhanced Visible-Light-Driven Photocatalytic Disinfection Performance and Organic Pollutant Degradation Activity of Porous g-C3N4 Nanosheets. ACS Appl. Mater. Interfaces, 2017, 9, 43704–43715. https://doi.org/10.1021/acsami.7b07657

41. R. Liang, R. Huang, S. Ying, X. Wang, G. Yan and L. Wu, Solvothermal synthesis of TiO2@MIL-101(Cr) for efficient photocatalytic fuel denitrification. Nano Res., 2018, 11, 1109–1123. https://doi.org/10.1016/S1872-5813(21)60170-6

Bibliography of Comparison:

- Y. Zhang, C. Chai, X. Zhang, J. Liu, D. Duan, C. Fan and Y. Wang Recent Advances of Silver-Based Coordination Polymers on Antibacterial Applications. Inorg. Chem. Commun.100, 81–91(2019). https://doi.org/10.3390%2Fmolecules27217166
- S. Sun, C. Chen, J. Sun, Q. Phen, k. Lu and K. Deng Procedia Environ. Sci.18, 620–624 (2013).
- E. Filippo, C. Carlucci, A. L. Capodilupo, P. Perulli, F. Conciauro, G. A. Corrente, G. Gigli and G. Ciccarella Enhanced Photocatalytic Activity of Pure Anatase Tio(2) and Pt-Tio(2) Nanoparticles Synthesized by Green Microwave Assisted Route .Materials Research 18, 473–481 (2015). http://dx.doi.org/10.1590/1516-1439.301914
- Kong, L., Jiang, Z., Lai, H. H.-C., Xiao, T. & Edwards, P. P. Does noble metal modification improve the photocatalytic activity of BiOCl? Prog. Nat. Sci. Mater. Int.23, 286–293 (2013). https://doi.org/10.1016/j.pnsc.2013.05.002
- Ong, W. L., Natarajan, S., Kloostra, B. & Ho, G. W.. Metal nanoparticle-loaded hierarchically assembled ZnO nanoflakes for enhanced photocatalytic performance. Nanoscale5, 5568–5575 (2013). https://doi.org/10.1039/c3nr00043e
- B.Luo, D.Xu, D.Li, G.Wu, W.Shi and M.Chen Fabrication of a Ag/Bi3TaO7 Plasmonic Photocatalyst with Enhanced Photocatalytic Activity for Degradation of Tetracycline. ACS Appl. Mater. Interfaces7, 17061–17069 (2015). https://doi.org/10.1021/acsami.5b03535
- Xue, J., Ma, S., Zhou, Y., Zhang, Z. & He, M. Facile Photochemical Synthesis of Au/Pt/g-C3N4 with Plasmon-Enhanced Photocatalytic Activity for Antibiotic Degradation. ACS Appl. Mater. Interfaces7, 9630–9637 (2015). https://doi.org/10.1021/acsami.5b01212

CHAPTER 2.2.

A 'self-activating' Bi₃TaO₇-Bi₄TaO₈Br photocatalyst and its use in the sustainable production of pro-fluorophoric Rhodamine-110



Summary

We counter two common notions that (i) photocatalysts are likely to degrade during use with barely any strategy to counter it and (ii) rhodamine-B (RhB) photo-degradation lacks any useful or commercial prospects even after 53 years of its discovery by developing a photocatalyst that continues to improve its activity for \sim 300 h due to a leaching induced 'self-activation' process. Rhodamine-110 (Rh110) is a widely used pro-fluorophore in biological studies. However, its commercial production is highly challenging due to the formation of various side-products originating from the presence of the two labile amino side-groups that induce the profluorophore activity, leading to purification difficulties, low yield, and unusually high costs. Herein, we demonstrate a facile strategy to produce pure Rh110 using extremely inexpensive RhB and Bi₃TaO₇–Bi₄TaO₈Br heterostructures as a catalyst in sunlight. The catalyst is not just stable over 30 catalytic cycles but also gets activated continuously in successive cycles to produce a reaction yield as high as 88%. The role of the heterostructure, the origin of surface activation, and the RhB \rightarrow Rh110 transformation mechanism have been established. Based on 150 days of sunlight experiments, large-scale production prospects (~4000 times scale-up) and isolation of Rh110 have also been realized, paving a novel way for its production by anyone, inexpensive biological essaying, and device fabrication. Continuously improving catalysts are unknown and compensatory leaching of metal atoms from the catalyst surface may pave the way to realize them.

A Manuscript based on this work has appeared in Green Chem., 2022, 24, 5514-5523

2.2.1. Introduction

Rhodamine 110 is a widely used xanthene-based pro-fluorophore containing two labile amino groups and invaluable in the clinical diagnosis of diseases such as SARS-Cov-2,¹⁻⁴ anti-cancer studies, drug development, fluorescence imaging, and enzymatic activity tests.⁵⁻¹²Rh110 is also used in optoelectronic devices such as solar cells, dye lasers, LEDs, etc.¹³⁻¹⁵ Substitution of its amino groups with bulkier substituents such as peptides or proteins enhances the nucleophilicity of the phenolic oxygen, leading to the formation of lactones. This disrupts the π -conjugation, quenching its fluorescence ability. Such an inherent diminution of the fluorescence is highly advantageous over conventional fluorophores since it can be used to establish bond formation or cleavage in biological processes *in-situ*, cementing Rh110 as one of the most popular pro-fluorophores.¹⁶⁻¹⁹ The reactivity of the same amine groups, on the other hand, creates enormous difficulty during its commercial production. The synthesis of Rh110 is realized commercially with very low yields by the condensation of phthalic anhydride and maminophenol.^{20,21} This process is energy-intensive as the condensation reaction requires high temperature due to which substrates are susceptible to oxidation and undesirable side reactions. The undesired side products have similar chemical properties with Rh110, which cause its purification difficult and result in poor yields (<10%), escalating the production cost enormously as compared to other stable xanthate dyes such as RhB. In the laboratory, the synthesis of Rh110 has been realized in small quantities by using Pd and Au, using laborious processes and without much information on the recyclability of catalysts.^{22,23} RhB has the same molecular structure as that of Rh110, except for the amine groups that are protected by ethyl substitution to render remarkably high stability. Therefore, RhB is not only highly inexpensive but usually becomes a stubborn pollutant in industrial waste.^{24,25} Attempts to remove RhB from water have led to over several thousand publications, highlighting humongous effort in such waste management, though its implementation has been impractical to date. From the cost perspective, RhB is 500-1000 times inexpensive than Rh110.¹⁰ Thus, the inexpensive and sustainable synthesis of Rh110 pro-fluorophore has remained an important research challenge and conversion of RhB to Rh110 can be beneficial way of waste utilization.

2.2.2. Scope of the present investigation

Several decades back, it was discovered that polluting RhB can be removed from water by its photocatalytic degradation to form CO_2 and H_2O . Subsequently in a key observation in 1977, Honda *et al.* showed that the degradation may commence with the removal of the ethyl groups attached to amine moieties of RhB.²⁶ Therein, Rh110 appears as an intermediate before it undergoes further mineralization. Several such catalysts were found later (e.g. CdS, TiO₂, NaBiO₃, C₃N₄ etc.) having the ability to de-ethylate RhB, though relatively rare as compared to a very large number of facile photocatalysts developed to date for RhB degradation, where Rh110 is not an intermediate.²⁷⁻³⁰ It has been speculated that the formation of Rh110 as an intermediate is dependent on the orientation of the RhB molecule on the photocatalyst surface.²⁷ It ought to be emphasized that Rh110 intermediate has been observed in over 5000 studies in the last five decades, though its isolation as a reaction product has not been envisioned, nor its purity, catalyst recyclability, scale-up production and isolation prospects have been investigated. Therefore, if a photocatalyst can be developed which stabilizes the appropriate '*on-surface*' orientation of RhB, relatively less-responsive towards Rh110 photodegradation, and also sustainable, it can be used to produce highly valued Rh110. Therein, the purification needs of Rh110 is negligible, making its production from a waste renewable energy-based and highly cost-effective.

Here, we put forth the concept of using photocatalytic deethylation of waste RhB to produce Rh110 with >99% purity employing Bi₃TaO₇- Bi₄TaO₈Br heterostructures as a photocatalyst under natural sunlight. The minimum yield of Rh110 is ~35% in the first cycle but steadily increases thereafter to ~88% at the end of the 30^{th} cycle due to a unique selfactivation of the catalyst. We establish (i) the origin of the catalyst 'self-activation' as a unique light-induced surface-reconstruction process due to preferential leaching of one of the metals with a weaker metal-oxygen bond, (ii) the prospects of scaling up of the reaction by ~4500 times as compared to usual RhB photocatalytic experiments. Thus, the findings demonstrate a sustainable strategy to convert a pollutant dye to an expensive pro-fluorophore that is convenient, usable by all, and scalable using renewable energy. Therein, the catalyst 'selfactivation' represents a rare phenomenon that is not known for any other heterogeneous photocatalyst so far.

Despite the existence of a large number of studies on deethylation of RhB, a careful look at them shows that the motivation has been to understand mineralization pathways of RhB as a pollutant, limiting the studies to just a few hours using milliliters of reagent solution. In that regard, with >500 h of photocatalytic study and establishing synthesis prospects using liter-scale reagent solutions, this study is expected to serve as a benchmark of Rh110 synthesis and catalyst stability from the novel approach of RhB photoconversion.

2.2.3. Methods

2.2.3.1. Catalyst Synthesis

Solvothermal Synthesis of BiOBr: In a typical procedure, Bi (NO₃)₃.5H₂O was added slowly into an ethylene glycol solution containing a stoichiometric amount of KBr with a Bi to Br molar ratio of 1. The mixture was stirred for 30 min at room temperature in air and then poured into a 25 ml Teflon-lined stainless autoclave until 80% of the volume was filled, which was then heated at 433 K for 12 hours and then air-cooled to room temperature. The resulting precipitate was collected by centrifugation and washed with ethanol and deionized water thoroughly and dried at 323 K in air.

Synthesis of Bi₃TaO₇-Bi₄TaO₈Br heterostructure: The heterostructures were prepared by taking a stoichiometric amount of Bi₂O₃, BiOBr, and Ta₂O₅. The precursors were first grounded using a motor and pestle then transferred onto a silica boat followed by heating for 24 h under ambient air in a muffle furnace at 1023 K (heating rate of 279 K min⁻¹) with intermediate grinding after 12 h. Bi₃TaO₇ was prepared by the same procedure as above without BiOBr. For comparison of catalytic activities, the Bi₃TaO₇-Bi₄TaO₈Br heterostructures were also prepared under Ar gas flow, keeping the other conditions the same.

Synthesis of Bi₄TaO₈ Br nanoplates: Bi₄TaO₈ Br was prepared by a flux method. In the process, the stoichiometric molar ratio of 3:2:1 Bi₂O₃, BiOBr and Ta₂O₅ were mixed thoroughly with NaCl and KCl flux in the molar ratio of 1:1 as molten salt and at the solute concentration (Bi₄TaO₈Br/(Bi₄TaO₈Br+flux)) of 3.2 mol%. Then, the mixture was placed in a muffle furnace and heated in air at 750 °C for 4 h with a heating rate of 3 °C min⁻¹. The products were thoroughly washed with deionized water five times to remove the flux after cooling at room temperature, collected by filtration, and dried at 60 °C for 10 h.

2.2.3.2. Photocatalytic Reactions:

Photocatalytic experiments: The photochemical reactor system consists of a 50 ml open beaker made of Pyrex glass. A solar simulator (1.00 kW/m^2 , Newport LSS-7120) was used to simulate natural sunlight in a top-down irradiation setup. The reactions were also carried out in direct sunlight at the institute campus (latitude 30.66° N longitude76.73° E) between 11 am to 4 pm when the sunlight was sufficiently bright.

25 ml RhB solution (10 mg/L) was used for all photocatalytic studies unless otherwise noted. The amount of catalyst used was fixed to 40 mg for 25 ml RhB solution. The suspension containing RhB solution and catalyst was magnetically stirred for 30 minutes in dark to attain adsorption-desorption equilibrium and the resulting aliquot was exposed to light for catalysis. 1 ml of the solution was taken out from the reaction cell every one hour during illumination and then poured back into the reaction cell after analysis. For analysis, the collected sample was first centrifuged to remove the catalyst particles and the remaining aliquot was used. The progress of reactions was analyzed by UV-visible absorption spectroscopy, high-resolution mass spectroscopy (HRMS), and high-performance liquid chromatography (HPLC). The reaction yields were estimated calorimetrically using an absorption coefficient of 106000 M⁻¹ cm⁻¹ for RhB and Rh110 respectively.⁵⁰

In the same reaction conditions, 2ml of benzoquinone (BQ) (10^{-2} g/mol) and isopropyl alcohol (IPA) were added respectively into the reaction system to assess the effect of O₂·⁻ and ·OH on Rh110 yield.

Superoxide Radical experiment was done by dispersing the 30 mg of Bi_3TaO_7 – Bi_4TaO_8Br heterostructure into a 100 mL of nitro blue tetrazolium (NBT) (0.025 × 10⁻³ m) solution and then the homogeneous suspension was exposed to light irradiation for 3h. The suspension was analyzed by UV-vis. Spectroscopy after the removal of the solid catalyst by centrifugation following literature procedure. Note that NBT is known to react with O_2^{\bullet} and display a maximum absorbance at 259 nm.

Scale-up production of Rh110 and catalyst recyclability test: 25 ml solution of RhB having different concentrations (e. g. 20, 40, 60, 80, and 100 μ M) and 40 mg Bi₃TaO₇- Bi₄TaO₈Br heterostructure were used for deethylation under photoirradiation. Each solution was suitably diluted to be analyzed by UV-Visible absorption spectroscopy.

In the second stage, to check recyclability under scale-up conditions, 1L of aqueous 20 μ M RhB solution was deethylated over 1.6 g of Bi₃TaO₇-Bi₄TaO₈Br under direct sunlight up to the 30 cycles. An adequate amount of a concentrated RhB solution was added to the beaker after each cycle. 40 mg catalyst (and a proportional amount of reaction aliquot) was taken out after every 10 cycles for characterization and washed with water and ethanol. The efficiency of this washed catalyst was analyzed using 25 ml of fresh 20 μ M RhB.

2.2.3.3. Characterization

All the characterization techniques are discussed in chapter 1.2.

2.2.4. Results and Discussion

2.2.4.1. Catalyst Characterization



Figure 2.2.1. (a) Powder XRD pattern of pure Bi_3TaO_7 , Bi_4TaO_8Br and the Bi_3TaO_7 - Bi_4TaO_8Br heterostructures synthesized in the air. (b) SEM-EDS spectra of the samples

confirming the presence of 35-40% of Bi₃TaO₇ phase in Bi₃TaO₇-Bi₄TaO₈Br heterostructures (c) FE-SEM image (inset is a high magnification image) of Bi₃TaO₇-Bi₄TaO₈Br heterostructures showing intergrowth particles having 100-500 nm feature sizes (d) TEM image of a heterostructure containing the Bi₄TaO₈Br (region-1) and Bi₃TaO₇ (region-2) phases. (e, f) EDS spectra recorded in the regions (1) & (2) respectively. (g, h, i) HRTEM image of the heterostructure. (j, k) indexed IFFT patterns corresponding to the HRTEM images in (h) and (i) respectively. (l) HRTEM image showing the intersection of the lattice planes of the two phases at the heterojunction. Inset is the corresponding IFFT pattern showing a crystalline orientation similar to that in (j) and (k). (m) HRTEM image of the heterostructure and IFFT images corresponding to the different areas of heterostructure marked as boxes showing the defects near the junction of the two phases.

The powder X-ray diffraction (XRD) patterns of the Bi₃TaO₇-Bi₄TaO₈Br heterostructures synthesized in the ambient air and pure Bi₄TaO₈Br and Bi₃TaO₇ (Figure 2.2.1. a) reveals the high crystallinity and phase purity of the samples. All peaks in the patterns can be indexed using the Sillen Aurivillius (SA) phases Bi₄TaO₈Br (ICSD #98-009-3561) and the Bi₃TaO₇ (ICSD #98-001-4207). Even though we use stoichiometric quantities of the reactants, the formation of heterostructure is enabled when the synthesis is carried out in the air due to a partial oxidation of BiOBr to Bi₂O₃,³¹ which, as described later, is beneficial not only for the ease of synthesis but also for improving the catalytic activity. Energy dispersive X-ray (EDS) analysis of the heterostructures by considering the Bi and the Br signals showed that the sample prepared in the air have 35-40% of the Bi₃TaO₇ phases respectively (Figure 2.2.1. b). The airsynthesized heterostructures contain intergrowth particles having 100-500 nm feature sizes (Figure 2.2.1. c) was analyzed by SEM. Figure 2.2.1. d is a low-magnification transmission electron microscopy (TEM) image of a heterostructure containing both the Bi₄TaO₈Br and Bi₃TaO₇ phases. The EDS spectra recorded on two spots from each side of the heterojunction are seen in Figure 2.2.1. e, f. The spectrum on the region (1) shows a Bi:Br ratio of 81:19, closely matching the SA phase, while the spectra from the region (2) corresponding to the Bi₃TaO₇ phase contains much lower Br (8%, the small Br signal is attributed to internal scattering of the electron beam to the SA phase). A careful analysis of the high-resolution TEM (HRTEM) images (Figure 2.2.1. g, h, i) and the corresponding inverse Fast Fourier Transform (IFFT) patterns (Figure 2.2.1. j, k) recorded across the interface contain lattice fringes with a separation of 0.30 nm and 0.32 nm that correspond to the (810) and (111) planes of Bi₄TaO₈Br and Bi₃TaO₇ respectively. The interface (Figure 2.2.1. i) appears relatively poorly crystalline

within a 2 nm region probably due to lattice mismatch from where the two planes emanate at an angle of 105°. Inset is the corresponding IFFT pattern showing a crystalline orientation similar to that in (j and k). A careful IFFT analysis of a larger area of the interface region shows



Figure 2.2.2. (**a**, **b**) HRTEM and FE-SEM images of Bi_4TaO_8Br obtained by flux method showing the formation of nanoplates with edges of several micrometers (**c**, **d**) AFM images and the corresponding height curves of Bi_4TaO_8Br with a thickness of ~100 nm.

the presence of a significant number of dislocations and stacking faults along the (810) planes of Bi₄TaO₈Br and (111) planes of Bi₃TaO₇, accompanied by lattice deformations that gradually diminishes away from the interface (**Figure 2.2.1. m**). The microscopic characterization of the pure Bi₄TaO₈Br phases is presented in **Figure 2.2.2.** TEM and FE-SEM images of Bi₄TaO₈Br obtained by flux method showing the formation of nanoplate with edges of several micrometers (**Figure 2.2.2. a, b**). AFM images and the corresponding height curves of Bi₄TaO₈Br with a thickness of ~100 nm (**Figure 2.2.2. c, d**).



Figure 2.2.3. (**a**, **b**) UV-vis. DRS spectrum and Tauc plot of the Bi₃TaO₇-Bi₄TaO₈Br heterostructures prepared in the air (inset is the photograph of as prepared sample). (**c**) The specific surface areas of pure Bi₃TaO₇, Bi₄TaO₈Br and Bi₃TaO₇-Bi₄TaO₈Br.

The optical properties of Bi_3TaO_7 - Bi_4TaO_8Br heterostructures were investigated by UV-vis. DRS spectrum (**Figure 2.2.3. a, b**). UV-vis. DRS spectrum of the Bi_3TaO_7 - Bi_4TaO_8Br heterostructures prepared in the air showing a steep absorption edge beginning from 510 nm and extending beyond 400 nm consistent with its intense yellow color (inset). The corresponding optical bandgap was estimated from Tauc analysis using the equation (1).

where A = constant, hv = light energy, Eg = optical bandgap energy, n = 2 considering an indirect bandgap and α = absorption coefficient. From the corresponding Tauc plot, a bandgap of the heterostructure was estimated to be 2.46 eV. The specific surface areas of Bi₃TaO₇-Bi₄TaO₈Br, Bi₄TaO₈Br and Bi₃TaO₇ powders were evaluated by the Brunauer–Emmett–Teller (BET) method as 0.77, 1.37 and 0.87 m²/g respectively (**Figure 2.2.3. c**).

2.2.4.2. RhB to Rh110 transformation by Bi₃TaO₇-Bi₄TaO₈Br heterostructures

The photocatalytic conversion of RhB to Rh110 over the heterostructures prepared in ambient air completes in nearly 480 min. The aqueous RhB solution shows a characteristic absorption maximum (λ_{max}) at 553 nm (**Figure 2.2.4. a**). Light irradiation of this solution in the presence of the heterostructures resulted in a hypsochromic shift gradually to a final $\lambda_{max} = 499$ nm



Figure 2.2.4. (a) UV-vis. absorption spectra recorded during the 1st photocatalytic cycle. (b) Photographs showing changes in color of the dye solution during solar irradiation under UV light. (c) Photoluminescence spectra showing the emission of RhB before irradiation (λ_{max} =583 nm) and after irradiation (λ_{max} =534 nm). (d) Fluorescence decay kinetics of the reaction solution before and after photoirradiation for 480 min. (e, f) UV-Vis. absorption spectra recorded during photocatalytic conversion of RhB to Rh110 over pure Bi₄TaO₈Br and Bi₃TaO₇. The yields of pure Rh110 are 13% for Bi₄TaO₈Br and negligible for Bi₃TaO₇.

corresponding to an aqueous solution of pure Rh110 over a period of ~480min, accompanied by a visual color-change of the solution (**Figure 2.2.4. b**). Furthermore, RhB has an emission maximum at 583 nm (**Figure 2.2.4. c**), which has undergone a blue-shift to 533 nm upon 480

min of photoirradiation representing Rh110. Similarly, the average fluorescence lifetime (τ_{avg}) of the aqueous dye solution before and after photoirradiation also changed from 1.75 ns to 3.85 ns corresponding to pure RhB and Rh110 respectively (**Figure 2.2.4. d**).^[34,35]The spectral shifts have been attributed to the de-ethylation of RhB, the nature of which has been confirmed in this study using high-resolution mass-spectroscopy (HRMS) and high-performance liquid chromatography (HPLC) measurements, as discussed *vide infra*, leading to the formation of pure Rh110 at the end of 480 min. The yield of Rh110 in the first cycle was estimated to be 35%, further confirmed by HPLC, corresponding to an apparent quantum efficiency (AQE) of 0.02% (**Note 2.2.1.**). We observed that persistent photoirradiation beyond 480 min leads to the loss of the conjugated structure of Rh110 as evident from the decrease in absorbance at 499 nm without any shifts in λ_{max} . Such observations led to the division of RhB along with its partial mineralization, in which the λ_{max} shifts gradually from 553 nm to 499 nm and the second stage is associated with the mineralization of Rh110.³⁵

The heterostructure between Bi_3TaO_7 and Bi_4TaO_8Br plays a crucial role in this catalytic transformation. When we used pure Bi_3TaO_7 , the reaction barely proceeded (**Figure 2.2.4. d, and e**). On the other hand, with pure Bi_4TaO_8Br the yield of pure Rh110 by photoirradiation was only 13%.

NOTE 2.2.1: Apparent Quantum Efficiency (**AQE**): The apparent quantum yield (AQE) for photocatalytic deethylation of RhB was calculated by carrying out the reaction under a solar simulator (Verasol Newport) with a conversion of 35% within 480 min. For calculation of AQE, we counted the number of incident photons from higher energies till 500 nm, where, based on the UV-Vis absorption spectrum of Bi₃TaO₇-Bi₄TaO₈Br, the absorption is >98%. The incident power (P_{incident} (λ)) on the sample can be represented as³

$$P_{\text{incident}}(\lambda) = \rho_{\text{incident}}(\lambda) \times A_{(\text{sample})} - \dots - \dots - \dots - \dots - \dots - \dots - (i)$$

A _(sample) is the area exposed to incident light (12.56 cm²), $\rho_{incident}$ (λ) is the incident power for a photon of wavelength λ , which is obtained from the solar simulator spectrum plotted (**Figure 2.2.5.**) as irradiance vs. wavelength.

The number of incident photons per second, as a function of wavelength can be expressed as:

$Nph(\lambda) = \rho incident Eph(\lambda)$	(ii)
Where $Eph(\lambda) = hc \lambda$	(iii)	

Eph(λ) is the photon energy for the corresponding λ . The total number of photons incident on the sample per second within the wavelength range of 400-500 nm can be calculated as:

Nph,*ident*(400 - 500) = $\int \rho incident(\lambda) \lambda hc 500 400 d(\lambda)$ ------ (iv)

(Considering the units for *pinciden* (λ) as W/m². nm and length units in nm)

 $= \int \rho \ incidencent \times (W \ m^2.nm) \times \lambda \ (nm) \ 6.63 \times 10^{-34} \ J.S \times 3 \times 108 \times 109 nm.s^{-1} \ 500 \ 400 \times d\lambda \ (nm)$

= $\int \rho incident \ 19.89 \times 10^{-17} m^2 .s \ 500 \ 400 \ \times \ (\lambda)$

In terms of moles:

= $\int \rho inciden(\lambda) \times \lambda 19.89 \times 10^{-17} \times 6.023 \times 1023 \ mol^{-1} m.s \ d\lambda 500 \ 400 \ 15$

= $\int \rho incident \times \lambda \ 0.12 \times 109 \ mol^{-1}.m2.s \ 500 \ 400 \ d\lambda$

i.e. $\int \rho incident \times \lambda \ 0.12 \times 109 \ mol^{-1}.m2.s \ 500 \ 400 \ d\lambda$ moles per second per square meter

= 0.006556 moles per second per square meter

The number of incident photons in the reaction mixture within the reaction time =*Nph*,*ident* (400 – 500) × A sample × *Reaction time* ------ (v)

 $= 0.175 \times 10-6$ moles in our reaction

The AQE can be derived from the following equation:

 $AQE = (No.of \ electron) \times No.of \ moles \ of \ RhB \times \%$ conversion Number of incident photons × 100(%) ------ (vi)

For RhB to Rh110 conversion, we considered n as 8 (Formation of a superoxide radical requires one electron while two superoxide radicals are needed for the removal of one ethyl group)⁵

No. of moles of RhB \times % conversion = 0.05×10^{-6} moles $\times (35\%) = 0.175 \times 10^{-6}$ moles Thus, for 400-500 nm:



Figure 2.2.5. Spectrum of the solar simulator.

Quite interestingly, the Rh110 yield increased significantly with continuous use of the Bi₃TaO₇-Bi₄TaO₈Br heterostructures to 61.5% in the 10th cycle, 71% in the 20th cycle, and 88% in the 30th cycle (**Figure 2.2.6. a, b, c, d and e**). This is unlike usual photocatalysis where the catalytic activity deteriorates with continuous use even for a few cycles, indicating an intriguing surface reconstruction of the heterostructures during solar irradiation (described later). XRD analysis of the heterostructures recorded up to 30 photocatalytic cycles (**Figure 2.2.6. f**) showed negligible change in the compound implying that the heterostructures are stable throughout the photocatalytic reactions, except for the unique surface reconstruction.

Furthermore, we examined the scale-up production prospects of Rh110 by using different amounts and concentrations of RhB solutions. The RhB solutions with 20, 40, 60, 80, and 100 μ M concentrations were photo-irradiated in the presence of the same amount of catalyst. The catalytic activity after the 1st cycle for the RhB to Rh110 conversion was nearly consistent for all the different concentrations of RhB solutions (**Figure 2.2.7.**) We then scaled up the reaction to 1 liter maintaining all other concentrations identical and observed a complete conversion after ~10 h of natural sunlight irradiation (**Figure 2.2.8. a**), Notably, adding a few drops of isopropyl alcohol (IPA) to scavenge the [•]OH radicals that are responsible for chromophore cleavage³⁶ further increases the Rh110 yield from 35% to 68% in the first cycle



Figure 2.2.6. (**a**, **b**, **c**, **d**) UV-vis. absorption spectra showing an increase in the yield of Rh110 over Bi₃TaO₇-Bi₄TaO₈Br heterostructures synthesized in the air atmosphere with continuous use of the catalyst up to the 30th cycle. (**e**) Plot showing % yield upto 30th catalytic cycle. (**f**) Powder XRD patterns of the heterostructures at different stages while continuously using up to the 30th cycle.

itself, without interfering with product purity due to its volatile nature (**Figure 2.2.8. b, c, d**) Considering the literature-based RhB photocatalytic reactions in 20–25 ml solution, our concentration scale up reactions, 30 cycles, and liter-scale reactions depict significant progress with ~4000 times scale up prospect (**Note 2.2.2.**), portraying a great promise for the largescale production of Rh110 from RhB using the novel heterostructures. The pure Rh110 powder could be collected by simple evaporation of the water content.



Figure 2.2.7.(a, b, c, d, e) UV-vis. absorption spectra recorded for different concentrations (20, 40, 60, 80, and 100 μ M) of RhB solution with the same amount of the catalyst (40 mg) and the volume of RhB solution (25 ml). Note that the solutions were appropriately diluted before recording the spectra. (**f**) Plot showing the % yield of Rh110 at different concentration.

Note 2.2.2. (On scale up): The large-scale production should be considered by comparing photocatalytic experiments of any colored samples where the concentration plays a barrier since at high concentration, light penetration is poor. We have shown the potential of up to ~20 mg of Rh110 per cycle (by considering 60% yield as average, 1 L RhB solution of 100 μ M). We have shown up to 5- time increase in RhB concentration without compromising efficiency and tested catalyst recyclability up to 30 cycles inferring we can convert 1437 mg of RhB to 658 mg of Rh110 (~2 mmol). This should be compared with 0.2 mg of RhB studies currently in practice. Therefore, from our control experiments, it is clear that we have made significant progress of ~4000 times scaleup.



Figure 2.2.8. (a) Image showing the synthesis of 1L solution of pure Rh110 in the presence of the heterostructures and sunlight. Evolution of UV-Vis spectra during photocatalytic conversion of RhB to Rh110 in the presence of (b) benzoquinone (BQ) and (c) isopropyl alcohol (IPA) as superoxide and hydroxide racial scavengers respectively. (d) Plot showing Rh110 yield under different scavengers.

2.2.4.3. Mechanism of RhB to Rh110 transformation

Earlier investigations have revealed that the transformation of RhB to Rh110 can proceed by forming several intermediate rhodamine compounds due to the removal of one ethyl group at a time and each of these intermediates has a different color with an absorption λ_{max} at 539 nm for N,N,N'-tri-ethylated rhodamine (TER), 522 nm for N,N'-di-ethylated rhodamine (DER) or N-ethyl-N'-ethyl-rhodamine110 (MMER), and 510 nm N-ethylated rhodamine (MER) to finally 499 nm which is characteristic of Rh110.^[37,38] The dynamics of the intermittent deethylation processes were examined by HPLC analysis of the reaction aliquot during photoirradiation (**Figure 2.2.9. a, b**).



Figure 2.2.9. (a) HPLC chromatogram depicting reaction intermediates during photoirradiation of RhB in the presence Bi_3TaO_7 – Bi_4TaO_8Br heterostructures. (b) Table showing retention time of RhB, intermediates, and Rh110 (c) The variation of concentrations of the intermediates with time.

The commercially available RhB sample exhibited a strong peak at the retention times of 13 min. Note that another low-intensity peak can be observed at 8.07 min due to contamination with TER (~16%).^[28,39] After light irradiation, new peaks with a lower retention time corresponding to various deethylated products began to rise and the ones at higher retention time diminished. Peaks with retention times of 5.5,5, 3.5, and 3 min corresponding to MMER, DER, MER, and Rh110 respectively appeared.^[28,40] When the irradiation time increased to 420min, the peak of RhB, TER, and MMER completely disappeared and the percentage of DER, MER, and Rh110 changed to 3, 29, and 67% respectively. Only a single peak corresponding to pure Rh110 remained after 480min of irradiation. Interestingly, the HPLC analyses of the intermediate samples (Figure 2.2.9. c) show a non-monotonous pattern of variation in the intermediate concentrations during the transformation $RhB \rightarrow TER \rightarrow (DER,$ MMER) \rightarrow MER \rightarrow Rh110. RhB de-ethylation occurs fast in the first 125 min and then slows down slightly in the next 100 min before becoming fast again to extinction at 300 min. TER concentration increases until 150 min and then starts decreasing. DER and MMER concentration peaks appeared at 250 min, and decreased thereafter at the same rate as it rises. Finally, at 250 min, quite late in the reaction, the generation of both MER and Rh110 takes place. However, beginning 300 min, the concentration of MER reduces and that of Rh110 becomes 100% at 480 min. HRMS spectra were recorded at different stages of photoirradiation as shown in (Figure 2.2.10.) to confirm the intermediates. RhB has its characteristic molecular ion peak at m/z = 443. The intermediates of photoirradiation, TER, MMER or DER, and MER have molecular ion peaks at m/z = 415, 387, and 359, respectively. It can be seen from the spectra that the relative intensities of these peaks change gradually and with increasing irradiation time, the peaks at lower m/z become more intense. The spectrum obtained for the sample at the end of 480 min of photoirradiation contained a single prominent molecular ion peak at 331 m/z, characteristic of pure Rh110. Both HPCL measurements and HRMS data corroborate that RhB undergoes de-ethylation in a stepwise manner with the loss of an ethyl moiety at each step, but the concentration profiles of the various intermediates are far from monotonous, indicating an extremely complicated reaction mechanism. On further photoirradiation beyond 480 min, multiple low-intensity peaks at m/z = 90, 97, 146, 162, and 129arise corresponding to 2-hyroxypropanoic acid, di-2-propenylamine, hexanedioic acid, 3,3'azanediyldipropionic acid and 4-chlorophenol, respectively, owing to the chromophore cleavage of Rh110. NMR spectroscopy was also performed to confirm the purity of Rh110 (Figure 2.2.11.).


Figure 2.2.10. ESI mass spectra in the positive mode collected at different time-intervals during photoirradiation of RhB over of Bi₃TaO₇–Bi₄TaO₈Br heterostructures.

Thus, the RhB \rightarrow Rh110 transformation can occur by the following two pathways, as described in **Figure 2.2.12.** In the dominant pathway, the TER converts to DER with the two ethyl groups positioned on one side of the molecule, and with continuous irradiation of light, Rh110 undergoes chromophore cleavage which further undergoes mineralization as confirmed by gas chromatography shown in **Figure 2.2.13**.



Figure 2.2.11. (a, b): H-NMR spectra for RhB and its de-ethylated product Rh110 in DMSO respectively. The NMR signals of the aromatic hydrogens Ha, Hb, Hc, Hd, and He are located at σ of 7.99-7.96, 7.80-7.76, 7.71-7.68, 7.27-7.25, and 6.46-6.39 ppm, respectively. Hf and Hg at σ of 3.65-3.64 and 1.22-1.19 ppm respectively representing the N-diethyl group of RhB which disappear after 480 min of light irradiation to confirm the formation of RH110.



Figure 2.2.12. Proposed transformation pathway of RhB to Rh110 by the Bi₃TaO₇–Bi₄TaO₈Br heterostructure under solar irradiation.



Figure 2.2.13. Gas chromatogram obtained from photocatalytic mineralization of RhB by Bi_3TaO_7 - Bi_4TaO_8Br heterostructures under an oxygen atmosphere in the sealed reaction vessel during continuous photoirradiation confirming mineralization of RhB and its de-ethylated products. The peaks correspond to CO_2 .

2.2.4.4. Spontaneous surface evolution during improved Rh110 yield

The tremendous improvement in the Rh110 yield with each passing cycle is rather intriguing considering that photocatalytic efficiency usually deteriorates, even in 5–10 cycles. The XRD analysis of the photocatalysts after different numbers of cycles did not show any appreciable change indicating that the changes originate on the catalyst surface (**Figure 2.2.6. f**). To examine the origin of the unusual improvement in efficiency, we characterized the surface of the used heterostructures using X-ray photoelectron spectroscopy (XPS) during continuous use which revealed a substantial surface-reconstruction from multiple events of leaching, creation of vacancies, etc. that led to excessive surface negative charge generation and enhanced reactant adsorption maintaining an appropriate on surface orientation. Excess Bi leaching compared to that of Ta was observed, attributable to a stronger Ta–O bond than the Bi–O bond as evident from the significantly lower melting point of bismuth oxide phases (Bi₂O₃–817 °C) than that of tantalum oxide phases (Ta₂O₅–1870 °C).

2.2.4.5. Surface vacancies

Figure 2.2.14. a, b, c, and d show the high resolution Bi 4f spectra of the catalyst used in the 1^{st} , 10^{th} , 20^{th} and 30^{th} cycles which can be fitted with four constituting peaks. The peaks at the binding energies of 159.4 eV and 164.6 eV are assigned to Bi $4f_{7/2}$ and Bi $4f_{5/2}$, respectively, characteristic of Bi³⁺ ions, and the remaining two peaks at binding energies of 158.58 eV and 164.01 eV are ascribed to the lower valence state of Bi²⁺. ^{41,42} The Bi²⁺ content in the used

catalyst increases with respect to Bi^{3+} , from 26: 74 in the first cycle to 30: 70, 36: 64, and 45: 56 in the 10th, 20th and 30th cycles, respectively **Figure 2.2.14. e.** The formation of Bi^{2+} during photocatalysis is a clear indication of the reduction of Bi^{3+} to Bi^{2+} which may have been assisted by the photo-excited electrons that would result in oxygen vacancy formation in close proximity to maintain charge-neutrality. This probability is stronger in the Bi_2O_2 layer due to weaker Bi-O bonds than the TaO_6 layers having stronger Ta-O bonds and Br groups. Its valence and conduction bands are contributed by the O-2p and Bi-6p orbitals, respectively.^{43,44}



Figure 2.2.14. (**a**, **b**, **c**, **d**) High-resolution Bi-4f XPS spectra of the used catalyst recorded after the 1st, 10th, 20th and 30th cycle. (**e**) Plot showing an increase in the Bi²⁺ content with respect to Bi³⁺ with increasing catalytic cycle. (**f**) Plot showing a decrease in the quantity of Bi with respect to Ta with the passing cycles. (**g**) Zeta potential of the catalyst used for different cycles. (**h**, **i**): UV-Vis absorption spectra of NBT solution over fresh and used catalyst under light irradiation.

Upon light irradiation, oxygen of the Bi₂O₂ layers is expected to transfer its 2p electrons to the conduction band contributed by the Bi-6p, increasing electron density around Bi³⁺, and in doing so, the oxide ions may become electron-deficient and leave the crystal relatively easily forming oxygen vacancies. Additionally, the quantity of Bi decreases with respect to Ta. The % abundance of Ta: Bi of 21: 79 in the first cycle changes to 22: 78, 23: 77, and 26: 74 in the 10th, 20th and 30th cycles, respectively, (Figure 2.2.14. f) indicating an increase in Ta surface concentration and leaching of Bi and complete Bi₂O₂ layer, and the formation of amorphous Ta₂O₅ surface layers in Bi₄TaO₈Br have been independently observed in different studies earlier.⁴⁵ Therefore, multiple events may take place in the present case such as (i) Bi₂O₂ layer leaching, (ii) Bi^{2+/}Bi³⁺ leaching or (iii) leaching of both Bi and O from neighboring sites leading to associated vacancies such as VBi'''VO••VBi''' (-4 charge) or VBi"VO••VBi''' (-3 charge) or VBi"VO••VBi" (-2 charge) or Bi'BiVO••Bi'Bi (neutral), etc., as in the case of BiOCl.^{46,47} Note that the presence of oxygen vacancies in the Ta containing layers too cannot be ruled out despite a lower possibility, though the same could not be ascertained from the XPS studies due to the overlap of the Ta 4f peak with the Bi-5d peak. We point out that considering the small surface area of the material, the leaching of Bi per cycle can be considered at the ppb level and relatively safe.

2.2.4.6. Reconstruction led surface-charge variation for increasing reactant adsorption with suitable on-surface orientation

To confirm the influence of the various surface vacancies on the surface charge of the heterostructures, we carried out Zetapotential measurements on the catalyst particles at various stages of recycling. As seen in (**Figure 2.2.14. g**) the heterostructures initially exhibited a zeta potential of -0.41 ± 0.1 mV. However, it changed significantly to -6 ± 1.4 mV after the first 10 cycles and continued to evolve further to attain a surface potential of -55 ± 3.6 mV after 30 cycles. Therefore, the catalyst is naturally expected to adsorb more dye molecules maintaining an 'on-surface' orientation suitable for de-ethylation, since the excess negative charge on the catalyst surface favors the adsorption of rhodamine dye with its N site placed on the catalyst surface to further enhance de-ethylation.^{29,30,48} Additionally, oxygen vacancies enhance molecular O₂ adsorption that under light turns into superoxide radicals,⁴⁹ primarily responsible

for deethylation to improve the Rh110 yield (**Figure 2.2.8. d**). Superoxide radicals thus generated were detected for the fresh and used catalyst powder in the 30^{th} cycle.



Figure 2.2.15. (a) Plot showing the amount of non-lattice oxygen compared to the lattice oxygen during continuous use of the catalyst. (b, c, d, e) High-resolution O-1s XPS spectra of the used catalyst recorded after the 1^{st} , 10^{th} , 20^{th} and 30^{th} cycle. catalyst.

As shown in the (Figure 2.2.14. h, i) superoxide radical concentration observed for the used catalyst is much higher as compared to the fresh catalyst, which establishes the presence of a higher abundance of oxygen vacancies on the surface of the used catalyst.⁴⁹ The increase in dye adsorption after successive catalytic cycles was confirmed from the XPS N 1s spectrum of the adsorbed dye molecules and the non-lattice O1s spectra. As shown in (Figure 2.2.15.) O 1s spectra were fitted with two peaks at 529.8 eV and 531.3 eV corresponding to lattice oxygen and non-lattice oxygen, respectively.⁴⁵ The amount of non-lattice oxygen compared to the lattice oxygen increased with increasing catalytic cycles indicating the presence of larger quantities of surface adsorbed species such as ⁻OH, dye and O₂ However, since the ratio may also be contributed by the O-vacancies, we further compared the ratio of the residual N content on the catalyst surface to its total metal content. As seen in Figure 2.2.16. a, the abundance of N in comparison to the total metal content increases with passing cycles confirming an increase in dye adsorption with catalytic cycles. The N 1s peaks show a noticeable shape change after adsorption as compared to the pure RhB and Rh110 (Figure 2.2.16. b, c, d, e) that could be fitted with a broad single peak centered at 400.4 eV, confirming a catalyst-N interaction and an 'on-surface' positioning of the molecules through N proximity to the surface. The extraction of the dyes adsorbed on the catalyst surface using sonication indeed showed the presence of various RhB de-ethylation intermediates at various time intervals (Figure 2.2.17.) In this context, we have also considered the fact that the core of the rhodamine molecule is relatively rigid due to the extended conjugation. Since there are only limited possibilities of vacancy formation on the catalyst surface, the RhB molecule must be positioning itself maintaining specific orientations with respect to the specific vacancies to enable the formation of higher quantities of the de-ethylation product in successive cycles. Thus, Figure 3.3.18. a show a schematic of the proposed adsorption model in which the catalyst surface becomes more negative with continuous use of the catalyst due to surface reconstruction which further increases the adsorption of Rh B through its positively charged diethylamino groups and thus enhancing de-ethylation of RhB on the surface of the Bi₃TaO₇-Bi₄TaO₈Br heterostructures. Based on experimental observations, analysis and various literature data, the electron transfer pathways involved in the photocatalytic reactions is shown in **Figure 3.3.18.** b



Figure 2.2.16. (a) Plot showing the abundance of N in comparison with the total metal content on the catalyst surface with the passing cycles. (b, c, d, e) High-resolution N-1s XPS spectra of the used catalyst recorded after the 1st, 10th, 20th and 30th cycle. catalyst. Insets show the N-1s XPS spectrum of pure Rh B and Rh 110.



Figure 2.2.17. UV-Vis. absorption spectra of the extracted dyes from the catalyst surface.

The heterostructure contains the coexistence of two photoactive phases, Bi₃TaO₇ and Bi₄TaO₈Br and it leads to electron transport routes that resemble the Z-scheme. CB of Bi₃TaO₇ is in the region of 0.32–0.46 V vs. NHE, while its valence band (VB) is in the range of 3.12– 3.22 V. Similarly, the CB minima and VB maxima for Bi₄TaO₈Br were found to be 0.79 V and 1.74 V, respectively, vs. NHE.⁴ The bandgaps calculated from the locations of CB and VB in these materials are quite similar to the value we determined experimentally. Furthermore, because the band locations in these two materials are so dissimilar, slight alterations in their actual placements are unlikely to affect the proposed scheme. When light shines on the sample, both the photoactive phases absorb photons with energy hv matching with the bandgap, and then electrons from the valance band are moved to the conduction band, leaving behind holes in the valance band. The photogenerated electrons on the CB of Bi₃TaO₇ could transfer to the VB of Bi₄TaO₈Br and quench the holes of Bi₄TaO₈Br, effectively inhibiting the recombination of the electron-hole pairs in both Bi₃TaO₇ and Bi₄TaO₈Br. Furthermore, it is observed from the XPS spectroscopy that there is a large density of surface oxygen vacancy sites on the catalyst surface and these vacancies play an important role as a carrier trapping center. The trapped electrons on the surface V₀ produce superoxide radicals through the reduction of oxygen molecules. Then, these radicals (the main active species responsible for deethylation) react with RhB and de-ethylate it into Rh110. Holes available in the VB of Bi₃TaO₇ could directly react with OH ion and form •OH which is responsible for chromophore cleavage of RhB.



Figure 3.3.18. (a) Schematic illustration showing increasing absorption of RhB due to spontaneous surface activation under solar irradiation, which results up to $\sim 88\%$ Rh110 production and (b) band-alignment and photoinduced electron transfer in the Bi₃TaO₇ – Bi₄TaO₈Br composite for RhB to Rh110 conversion.

2.2.5. Conclusion

In conclusion, we have developed a sustainable solar-energy driven strategy to produce pro-fluorophoric Rh110 employing a unique self-activating, highly stable Bi₃TaO₇-Bi₄TaO₈Br heterostructure as photocatalyst. The strategy is workable under larger-scale production

conditions and the yield of Rh110 is significantly higher than the current commercial processes, reaching over 80% of the precursor load. Therein, the Bi₃TaO₇-Bi₄TaO₈Br heterostructures demonstrated a unique phenomenon, not observed in any other heterogeneous photocatalyst, that its efficiency for Rh110 production never diminishes, but increases with every passing cycle as long as it is used. The self-activation has been attributed to a continual surface restructuring process under solar irradiation due to a controlled but unbalanced leaching of metal ions and lattice oxygen. The findings can truly rival an existing commercialized process after half a century of intense research on Rhodamine B photodegradation, arguably the most widely studied photocatalytic reaction.

Bibliography

- H. Tong, Y. Gao, J. Li, J. Li, D. Huang, J. Shi, H. A. Santos, B. Xia, Mitochondria-Targeted Bovine Serum Albumin@Copper Sulfide Nanocomposites Conjugated with Rhodamine-110 Dye for an Enhanced Efficacy of Cancer Photothermal Therapy*Part*. *Part. Syst. Charact.* 2021, *38*, 2100013. DOI: 10.1002/ppsc.202100013
- Y. Wu, W. Guo, W. Peng, Q. Zhao, J. Piao, B. Zhang, X. Wu, H. Wang, X. Gong, J. Chang, ACS Appl. Mater. Interfaces 2017, 9, 9369–9377.
- [3] H. Shan, J. Liu, J. Shen, J. Dai, G. Xu, K. Lu, C. Han, Y. Wang, X. Xu, Y. Tong, et al., Development of potent and selective inhibitors targeting the papain-like protease of SARS-CoV-2*Cell Chem. Biol.* 2021, 28, 855-865.e9. https://doi.org/10.1016/j.chembiol.2021.04.020
- C. J. Kuo, P. H. Liang, Characterization and Inhibition of the Main Protease of Severe Acute Respiratory Syndrome Coronavirus. *ChemBioEng Rev.* 2015, *2*, 118–132. https://doi.org/10.1002/cben.201400031
- S. S. Chandran, K. A. Dickson, R. T. Raines, Latent fluorophore based on the trimethyl lock. *J. Am. Chem. Soc.* 2005, *127*, 1652–1653. https://doi.org/10.1021/ja043736v
- [6] D. A. Costello, J. K. Millet, C. Y. Hsia, G. R. Whittaker, S. Daniel, Single particle assay of coronavirus membrane fusion with proteinaceous receptor-embedded supported bilayers. *Biomaterials* 2013, *34*, 7895–7904. https://doi.org/10.1016/j.biomaterials.2013.06.034
- M. Beija, C. A. M. Afonso, J. M. G. Martinho, Synthesis and applications of Rhodamine derivatives as fluorescent probes. *Chem. Soc. Rev.* 2009, *38*, 2410–2433. https://doi.org/10.1039/B901612K
- [8] B. L. Zerfas, D. J. Trader, Monitoring the Immunoproteasome in Live Cells Using an Activity-Based Peptide–Peptoid Hybrid Probe. J. Am. Chem. Soc. 2019, 141, 5252– 5260. https://doi.org/10.1021/jacs.8b12873
- M. M. Pires, J. Chmielewski, Fluorescence imaging of cellular glutathione using a latent rhodamine. *Org. Lett.* 2008, *10*, 837–840. https://doi.org/10.1021/ol702769n
- [10] V. Graziano, W. J. McGrath, A. M. DeGruccio, J. J. Dunn, W. F. Mangel, First

generation inhibitors of the adenovirus proteinase. *FEBS Lett.* **2006**, *580*, 2577–2583. https://doi.org/10.1016%2Fj.febslet.2013.05.033

- J. Fan, Y. Ye, G. Chu, Z. Zhang, Y. Fu, Y. M. Li, J. Shi, Semisynthesis of Ubiquitin and SUMO-Rhodamine 110-Glycine through Aminolysis of Boc-Protected Thioester Counterparts. J. Org. Chem. 2019, 84, 14861–14867. https://doi.org/10.1021/acs.joc.9b01529
- [12] R. Kooij, S. Liu, A. Sapmaz, B. T. Xin, G. M. C. Janssen, P. A. van Veelen, H. Ovaa,
 P. ten Dijke, P. P. Geurink, Small-Molecule Activity-Based Probe for Monitoring
 Ubiquitin C-Terminal Hydrolase L1 (UCHL1) Activity in Live Cells and Zebrafish
 Embryos. J. Am. Chem. Soc. 2020, 142, 16825–16841.
 https://doi.org/10.1021/jacs.0c07726
- K. Sharma, V. Sharma, S. S. Sharma, Dye-Sensitized Solar Cells: Fundamentals and Current Status. *Nanoscale Res. Lett.* 2018, *13*, 381. https://doi.org/10.1186/s11671-018-2760-6
- P. M. W. French, J. R. Taylor, Passively mode-locked continuous-wave Rhodamine 110 dye laser. *Optics Letters* 1986, 11, 297–299. https://doi.org/10.1364/OL.11.000297
- [15] J. W. Woodcock, R. Beams, C. S. Davis, N. Chen, S. J. Stranick, D. U. Shah, F. Vollrath, J. W. Gilman, *Adv. Mate. Interfaces* 2017, 1–5.
- [16] H. Singh, K. Tiwari, R. Tiwari, S. K. Pramanik, A. Das, Small Molecule as Fluorescent Probes for Monitoring Intracellular Enzymatic Transformations. *Chem. Rev.* 2019, *119*, 11718–11760. https://doi.org/10.1021/acs.chemrev.9b00379
- [17] J. Gooch, V. Abbate, B. Daniel, N. Frascione, Solid-phase synthesis of Rhodamine-110 fluorogenic substrates and their application in forensic analysis. *Analyst* 2016, 141, 2392–2395. https://doi.org/10.1039/C6AN00686H
- [18] R. B. Kargbo, Ubiquitin-Specific Inhibitors for the Treatment of Cancers, Autoimmune, and Infectious Diseases. *Acs.Med.Chem.Lett.* 2017, 1211–1212. https://doi.org/10.1021/acsmedchemlett.7b00449
- [19] H. Hug, M. Los, W. Hirt, K. M. Debatin, Rhodamine 110-linked amino acids and peptides as substrates to measure caspase activity upon apoptosis induction in intact

cells. Biochemistry 1999, 38, 13906–13911. https://doi.org/10.1021/bi9913395

- [20] S. J. Dwight, S. Levin, Scalable Regioselective Synthesis of Rhodamine Dyes. Org. Lett. 2016, 18, 5316–5319. https://doi.org/10.1021/acs.orglett.6b02635
- [21] D. D. Nolting, J. C. Gore, W. Pham, NEAR-INFRARED DYES: Probe Development and Applications in Optical Molecular Imaging. *Curr. Org. Synth.* 2011, *8*, 521–534. https://doi.org/10.2174%2F157017911796117223
- [22] K. Bera, T. Ghosh, S. Basak, Synthesis of Chiral, Crystalline Au-Nanoflower Catalyst Assisting Conversion of Rhodamine-B to Rhodamine-110 and a Single-Step, One-Pot, Eco-Friendly Reduction of Nitroarenes. J. Phys. Chem. C 2015, 119, 1800–1808. https://doi.org/10.1021/jp5086125
- J. B. Grimm, L. D. Lavis, Synthesis of Rhodamines from Fluoresceins Using Pd-Catalyzed C–N Cross-Coupling. *Org. Lett.* 2011, *13*, 6354–6357. https://doi.org/10.1021/ol202618t
- [24] S. Mondal, C. P. Vinod, U. K. Gautam, 'Autophagy'and unique aerial oxygen harvesting properties exhibited by highly photocatalytic carbon quantum dots. *Carbon N. Y.* 2021, *181*, 16–27. https://doi.org/10.1016/j.carbon.2021.04.054
- [25] S. Mondal, P. E. Karthik, L. Sahoo, K. Chatterjee, M. Sathish, U. K. Gautam, *Nanoscale* **2020**, *12*, 10480–10490.
- [26] T. Watanabe, T. Takizawa, K. Honda, High and reversible oxygen uptake in carbon dot solutions generated from polyethylene facilitating reactant-enhanced solar light harvesting. *J. Phys. Chem.* 1977, *81*, 1845–1851. https://doi.org/10.1039/D0NR00266F
- [27] H. Liang, S. Liu, H. Zhang, X. Wang, J. Wang, New insight into the selective photocatalytic oxidation of RhB through a strategy of modulating radical generation. *RSC Adv.* 2018, 8, 13625–13634. https://doi.org/10.1039/C8RA01810C
- F. Chen, J. Zhao, H. Hidaka, Highly selective deethylation of rhodamine B: Adsorption and photooxidation pathways of the dye on the TiO2/SiO2 composite photocatalyst. *Int. J. Photoenergy* 2003, *5*, 209–217. https://doi.org/10.1155/S1110662X03000345
- [29] B. Xu, X. Wang, C. Zhu, X. Ran, T. Li, L. Guo, Probing the inhomogeneity and

intermediates in the photosensitized degradation of rhodamine B by Ag3PO4 nanoparticles from an ensemble to a single molecule approach*RSC Adv.* **2017**, *7*, 40896–40904. https://doi.org/10.1039/C7RA07163A

- [30] J. Huang, G. Nie, Y. Ding, Metal-Free Enhanced Photocatalytic Activation of Dioxygen by g-C3N4 Doped with Abundant Oxygen-Containing Functional Groups for Selective N-Deethylation of Rhodamine B. *Catalysts* 2020, 10, 6. https://doi.org/10.3390/catal10010006
- [31] J. Zhao, Photooxidation Pathway of Sulforhodamine-B. Dependence on the Adsorption Mode on TiO2 Exposed to Visible Light Radiation. *Environ. Sci. Technol.* 2000, 34, 3982–3990. https://doi.org/10.1021/es001064c
- K. Chatterjee, M. Banoo, S. Mondal, L. Sahoo, U. K. Gautam, A 'self-activating' Bi3TaO7–Bi4TaO8Br photocatalyst and its use in the sustainable production of profluorophoric rhodamine-110. *Dalt. Trans.* 2019, 48, 7110–7116. https://doi.org/10.1039/D2GC01574A
- [33] L. Li, Q. Han, L. Tang, Y. Zhang, P. Li, Y. Zhou, Z. Zou, Flux synthesis of regular Bi4TaO8Cl square nanoplates exhibiting dominant exposure surfaces of {001} crystal facets for photocatalytic reduction of CO2 to methane. *Nanoscale* 2018, *10*, 1905– 1911. https://doi.org/10.1039/C7NR06279F
- [34] A. S. Kristoffersen, S. R. Erga, B. Hamre, Ø. Frette, Testing Fluorescence Lifetime Standards using Two-Photon Excitation and Time-Domain Instrumentation: Rhodamine B, Coumarin 6 and Lucifer Yellow. J. Fluoresc. 2014, 24, 1015–1024. DOI 10.1007/s10895-014-1368-1
- [35] X. F. Zhang, Y. Zhang, L. Liu, Fluorescence lifetimes and quantum yields of ten rhodamine derivatives: Structural effect on emission mechanism in different solvents. *J. Lumin.* 2014, 145, 448–453. https://doi.org/10.1016/j.jlumin.2013.07.066
- [36] T. K. M. Prashantha Kumar, S. K. Ashok Kumar, Visible-light-induced degradation of rhodamine B by nanosized Ag2S–ZnS loaded on cellulose. *Photochem. Photobiol. Sci.* 2019, *18*, 148–154. https://doi.org/10.1039/C8PP00330K
- [37] S. Liu, K. Yin, W. Ren, B. Cheng, J. Yu, Tandem photocatalytic oxidation of Rhodamine B over surface fluorinated bismuth vanadate crystals. *J. Mater. Chem.*

2012, 22, 17759–17767. https://doi.org/10.1039/C2JM33337F

- [38] K. Yu, S. Yang, H. He, C. Sun, C. Gu, Y. Ju, Visible Light-Driven Photocatalytic Degradation of Rhodamine B over NaBiO3: Pathways and Mechanism. *J. Phys. Chem.* A 2009, *113*, 10024–10032. https://doi.org/10.1021/jp905173e
- [39] X. Chang, M. A. Gondal, A. A. Al-Saadi, M. A. Ali, H. Shen, Q. Zhou, J. Zhang, M. Du, Y. Liu, G. Ji, Photodegradation of Rhodamine B over unexcited semiconductor compounds of BiOCl and BiOBr. *J. Colloid Interface Sci.* 2012, 377, 291–298. https://doi.org/10.1016/j.jcis.2012.03.021
- [40] Y. Zhang, J. Zhou, Z. Li, Q. Feng, Photodegradation pathway of rhodamine B with novel Au nanorods @ ZnO microspheres driven by visible light irradiation. *J. Mater. Sci.* 2018, 53, 3149–3162. https://doi.org/10.1007/s10853-017-1779-x
- [41] G. Zhang, L. Cai, Y. Zhang, Y. Wei, Bi5+, Bi(3-x)+, and Oxygen Vacancy Induced BiOClxI1-x Solid Solution toward Promoting Visible-Light Driven Photocatalytic Activity. *Chem. - A Eur. J.* 2018, 24, 7434–7444. https://doi.org/10.1002/chem.201706164
- [42] L. Ye, Y. Deng, L. Wang, H. Xie, F. Su, Bismuth-Based Photocatalysts for Solar Photocatalytic Carbon Dioxide Conversion. *ChemSusChem* 2019, *12*, 3671–3701. https://doi.org/10.1002/cssc.201901196
- [43] C. Long, H. Fan, High oxide ion conductivity in layer-structured Bi4Ti3O12-based ferroelectric ceramics. J. Mater. Chem. C. 2019, 7, DOI 10.1039/c9tc02507c.
- M. Guan, C. Xiao, J. Zhang, S. Fan, R. An, Q. Cheng, J. Xie, M. Zhou, B. Ye, Y. Xie, Vacancy Associates Promoting Solar-Driven Photocatalytic Activity of Ultrathin Bismuth Oxychloride Nanosheets. *J. Am. Chem. Soc.* 2013, *135*, 10411–10417. https://doi.org/10.1021/ja402956f
- [45] J. Di, C. Chen, C. Zhu, P. Song, J. Xiong, M. Ji, J. Zhou, Q. Fu, M. Xu, W. Hao, et al., ACS Appl. Mater. Interfaces 2019, 11, 30786–30792.
- [46] Q. Wang, C. Chen, D. Zhao, M. Wanhong, J. Zhao, Change of Adsorption Modes of Dyes on Fluorinated TiO2 and Its Effect on Photocatalytic Degradation of Dyes under Visible Irradiation. *Langmuir* 2008, 24, 7338–7345. https://doi.org/10.1021/la800313s
- [47] G. Liu, X. Li, J. Zhao, H. Hidaka, N. Serpone, Photooxidation Pathway of

Sulforhodamine-B. Dependence on the Adsorption Mode on TiO2 Exposed to Visible Light Radiation. *Environ. Sci. Technol.* **2000**, *34*, 3982–3990. https://doi.org/10.1021/es001064c

- [48] X. Tao, W. Shi, B. Zeng, Y. Zhao, N. Ta, S. Wang, A. A. Adenle, R. Li, C. Li, ACS Catal. 2020, 10, 5941–5948.
- [49] L. Wang, W. Du, Z. Hu, K. Uvdal, L. Li, W. Huang, Hybrid Rhodamine Fluorophores in the Visible/NIR Region for Biological Imaging. *Angew. Chemie - Int. Ed.* 2019, 58, 14026–14043. https://doi.org/10.1002/anie.201901061

CHAPTER 2.3

Surface reconstruction route for increasingly improved photocatalytic H₂O₂ production using Sr₂Bi₃Ta₂O₁₁Cl



Summary

Photocatalytic hydrogen peroxide (H₂O₂) generation is attractive for the chemical industry and energy production. However, photocatalysts generally deteriorate significantly during use to limit their application. Here we present the highly active, $Sr_2Bi_3Ta_2O_{11}Cl$ single-crystal nanoplates for conversion of O₂ to H₂O₂ using ambient air with a production rate of ~3 mmol/h/g (maximum 17.5% photon conversion). Importantly, $Sr_2Bi_3Ta_2O_{11}Cl$ is not only stable during 15 days of H₂O₂ production but also gets consistently activated to increase the H₂O₂ yield by >200% to 6.5 mmol/h/g, unlike any other catalyst for H₂O₂ production. Multipronged characterization confirms that the synergistic increase in activity originates from *insitu* surface reconstruction by oxygen-deficient vacancy associate formation that improves (i) surface oxygen adsorption, (ii) sunlight harvesting, and (iii) charge-transfer from the lowvalent metal atoms surrounding oxygen vacancies to reactants. The study establishes the prospects of rational defect engineering for realizing non-degrading photocatalysts for realistic H₂O₂ production.

2.3.1. Introduction

Improved production of H_2O_2 is highly desirable due to its extensive utilization as a clean, low-cost, environment-friendly oxidant, and high-energy density fuel.^{1–3} However, conventional industrial approaches such as the anthraquinone oxidation route are not environmentally benign because of the utilization of high-energy multistep reactions and safety concerns while handling high-pressure hydrogen.⁴ In this context, photocatalytic H_2O_2 production using light-harvesting semiconductors is highly promising and has gathered widespread research attention recently, leading to the development of several facile catalytic materials, including metal oxides, sulfides, nitrides, metal-free materials, etc.^{5–7} Even though progress in developing highly active materials is rapid, a serious drawback with photocatalysts, in general, is the degradation of their catalytic activities with continued use, while industries spent billions per year just for the replacement.

Photocatalyst deactivation usually originates from chemical deactivation such as leaching or mechanical deactivation.^{8,9} Upon careful investigation, it is now becoming possible to develop activity restoration strategies for a handful of photocatalysts by using thermal or ultrasonic annealing, or by co-catalyst reloading.^{10–12} However, long-term stability studies and restoration of catalytic activity in photocatalysts used for H_2O_2 production is yet to be undertaken. In this scenario, the realization of a semiconductor photocatalyst with high catalytic efficiency and further self-activating properties instead of deactivation will be a meaningful contribution to a sustainable goal.

A careful analysis of the recent literature reveals that anion defect introduction is a preferred means to improve H₂O₂ production because molecular oxygen activation and dissociation are highly favourable at oxygen vacancies.^{13–15} Besides, defects can alter the catalyst's electronic structure also for harnessing more visible light and suppressing the recombination of excitons.¹⁵ However, the atomic-level healing of anion vacancies during the oxygen reduction would macroscopically reoxidize the oxide surface and thus block the molecular oxygen activation.¹⁴ Therefore, self-healing kinetics in the material should ideally be overcompensated by ion leaching dynamics at the surface.

The Sillen-Aurivillius (SA) oxide phases of layered perovskites are interesting due to several advantages over conventional photocatalysts. SA phase consists of a layer sequence of fluorite [Bi₂O₂], perovskite [A_{n-1}B_nO_{3n+1}], fluorite [Bi₂O₂], and halide [X] layers (where A: Ca²⁺, Sr²⁺, Bi³⁺, etc.; B: Nb⁵⁺, Ta⁵⁺, Ti⁴⁺, etc.; X: halide; n = 1,2,3, etc., the number of perovskite layers)^{16,17} Their advantages include high photostability and a narrow band gap (2.1-2.7 eV)

unlike other mixed anion metal oxides. This is attributed to the unusual occupation of highly dispersive O-2p orbital near valance band maxima (VBM) originating from a small Madelung potential at the oxygen sites in the fluorite-based [Bi₂O₂] layer and sizable interaction between O-2p and Bi-6s orbitals^{18,19} The immense structural flexibility originating from the selection possibility of different stacking sequences of the Sillen and Aurivillius layers makes SA phases promising for many photocatalytic applications. Besides, the compositional versatility of the cations with different valences and the presence or absence of lone-pair electrons becomes more advantageous when *n* is of a higher order than its basic and well-explored *n*=1 system. In contrast to Bi₄MO₈X (*n*=1), which has almost similar E_{CBM} and E_{VBM} for different X and M, *n* = 2,3... etc. compounds have highly tailorable E_{CBM} and E_{VBM}.²⁰ Such a compound with *n*=2, Sr₂Bi₃Ta₂O₁₁Cl has an electron mobility of 1.76×10⁻⁷ m² V⁻¹ s⁻¹ and a more negative CBM (-0.55 eV) than molecular oxygen reduction potential to make it promising for photocatalytic H₂O₂ production.²¹

2.3.2. Scope of the present investigation

Sr₂Bi₃Ta₂O₁₁Cl has a non-centrosymmetric (pseudo-tetragonal) crystal structure with a space group of P4/mmm (Figure 2.3.1. a, b, and c). It consists of four different lattice oxygen sites. O1 and O2 are part of the 12-coordinated Bi-alone site, distorting the polyhedron due to the presence of stereochemically active Bi 6s² lone pair and the octahedral off-centering of the adjacent Ta octahedra from second-order Jahn-Teller effect. The O3 is distorted to a rather high extent at the interface between the [BiSrO₂]⁺ layer and the perovskite block, while O4 is present toward the halide layer. This distortion-led Sr₂Bi₃Ta₂O₁₁Cl possesses an inherent ferroelectric polarization and contributes to efficient electron and hole separation along the (001) and (100) directions respectively.^{21–23} Because hole scavenging is rate-determining for H₂O₂ production (from O₂) that can be greatly accelerated by using alcohols as holescavengers, enhancing those facets that the holes migrate can lead to enhanced H₂O₂ production. Recent studies have established that the holes preferentially migrate to the (001) facets of a SA nanoplate while the electrons migrate to the edges, therefore, an improved ratio of the (001)/(100) surface area can be deemed to improve H₂O₂ production²⁴ The traditional solid-state method of synthesizing SA phases has the limitation of uncontrolled facet-less growth and significantly low surface area $(1-2 \text{ m}^2/\text{g})$ observed at high-temperature sintering, while lower temperature leads to impurity phases. The flux method, on the other hand, can reduce their synthesis temperature and increases crystallinity due to an increase in the rate of ion diffusion to make the process sustainable and also can control the growth of specific facets..²⁵ This possibility has not been explored for the n=2 Sr₂Bi₃Ta₂O₁₁Cl phase yet. The other factor that can result in high H₂O₂ production is the abundance of adsorbed molecular O₂ on the catalyst surface, which is usually less due to poor oxygen solubility in water. O₂ molecules absorb on an oxide surface preferably at the oxygen vacancies due to an excess electron density that transfers to oxygen having a low reduction potential to stabilize it. We recently observed the facile formation of oxygen vacancies in the SA phases during photocatalysis originating from the Bi₂O₂ layers while the Aurivillius layers with strong M-O bonds maintain structural stability. ¹⁷ Therefore, SA phases can potentially exhibit a high H₂O₂ photo-production rate that does not deteriorate or remain stable but rather increases further with time. Examples of such self-activating photocatalyst are rare.



Figure 2.3.1. Crystal structure of $Sr_2Bi_3Ta_2O_{11}Cl$ viewed from the (a) *bc* plane and (b) *ab* plane. Blue, light green, red, and dark green balls represent Bi, Ta, O, and Cl atoms, respectively. (c) The different types of lattice oxygen in $Sr_2Bi_3Ta_2O_{11}Cl$.

Herein, we report on the highly active facet-controlled $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates enclosed with the [100], [010], and [001] facets for efficient exciton separation by using a Flux method for the first time. The single-crystal nanoplates have significantly high surface area and facet area ratios of [001]/[100] or [001]/[010] along which the excitons separate than that achievable by the traditional approaches and photocatalytically produce H_2O_2 with remarkable efficiency even without an oxygen atmosphere. The amount of H_2O_2 produced is 2.9 mmol/h/g, at par with the state-of-the-art catalysts, and further improves by oxygen purging. More importantly, we established that due to surface reconstruction from the formation of oxygen vacancies and Bi leaching during continuous use, the catalyst exhibits self-activation behavior and can increase the H_2O_2 production by ~240% after 15 days of sunlight exposure that we have checked, and probably improve even more, unlike the common photocatalysts that exhibit deactivation. The oxygen vacancies formed during the reuse play a decisive role in molecular oxygen activation along with boosting carrier separation and transfer.

2.3.3. Methods

2.3.3.1. Catalyst Synthesis

Flux Synthesis of Sr₂Bi₃Ta₂O₁₁Cl: Sr₂Bi₃Ta₂O₁₁Cl nanoplates were prepared by taking the stoichiometric molar ratio of SrCO₃, Bi₂O₃, Ta₂O₅, and BiOCl (2:1:1:1) as precursors. A molten salt i.e., eutectic mixture of KCl and NaCl (1:1) with a solute concentration (Sr₂Bi₃Ta₂O₁₁Cl / (Sr₂Bi₃Ta₂O₁₁Cl + flux)) of 3.2 mol % was used as a flux. The mixture was first ground thoroughly by using a mortar and pestle and placed in an aluminum crucible followed by heating at 1023K for 4 h in a muffle furnace. After natural cooling, the product was thoroughly washed with deionized water and finally collected by filtration. The off-white powder product was dried at room temperature. For comparison Sr₂Bi₃Ta₂O₁₁Cl is also prepared by traditional solid-state method.

Solid state synthesis of Sr₂Bi₃Ta₂O₁₁Cl: Sr₂Bi₃Ta₂O₁₁Cl agglomerated grains were synthesized by a two-step procedure. SrBi₂Ta₂O₉ and SrBiO₂Cl were first prepared separately. SrBi₂Ta₂O₉ was prepared by using a stoichiometric mixture of Bi₂O₃, Ta₂O₅, and SrCO₃ and heated at 1073 K for 5 h in air. SrBiO₂Cl was also synthesized by calcination of a mixture of BiOCl (10 mmol) and SrCO₃ (10 mmol) at 1073 K for 10 h in air. Finally, the main target compound was synthesized by heating the SrBi₂Ta₂O₉ and SrBiO₂Cl precursors. SrBi₂Ta₂O₉

(1.0 mmol) was thoroughly mixed with SrBiO₂Cl (1.05 mmol) and heated in a muffle furnace at 1123 K for 15 h in air. Both procedures are summarized in Scheme-2.3.1.



Scheme 2.3.1. Synthesis procedure of Sr₂Bi₃Ta₂O₁₁Cl by flux method and Two-step solid states synthesis method.

2.3.3.2. Photocatalytic reactions

Photocatalytic experiments: The photocatalytic reactions were performed in a 50 ml open beaker made of Pyrex glass. A 400 W Xe lamp was used as a light source in a top-down irradiation setup. 10 mg of the as-synthesized photocatalyst was dispersed in 30 mL ethanol aqueous solution (10 vol%) and then exposed to light. 500 μ l of an aliquot from the reaction solution was taken out after 20 min, and treating it with 2 ml 0.1 M KI solution and 50 μ l 0.01 M H₃₂Mo₇N₆O₂₈ solution. The concentration of H₂O₂ was obtained by evaluating the absorbance of the KI/ H₃₂Mo₇N₆O₂₈ combination at 352 nm by UV-Vis. spectroscopy.

For recyclability, the reactions were conducted in two ways. Firstly, 10 mg of the assynthesized photocatalyst was dispersed in 30 mL of pure water and examined the continuous activity under the same light source, i.e. natural sunlight at the institute campus when the sunlight was sufficiently bright (maximum power density: 100 mW/cm² and ~23% variation within the day), for a duration of 15 days. During this period, both the photocatalytic and activation processes were undergone simultaneously and were evaluated under identical conditions. To determine the H₂O₂ yield, a 500 µl sample was collected from the reaction solution and was treated with 2 ml of 0.1 M KI solution and 50 μ l of 0.01 M H₃₂Mo₇N₆O₂₈ solution. The concentration of H₂O₂ was quantified by measuring the absorbance of the KI/ H₃₂Mo₇N₆O₂₈ combination at 352 nm using UV-Vis. spectroscopy every initial two hours of each day.

However, data from sunlight may not be reproducible by other laboratories. Therefore, we also performed an initial activity measurement under a xenon lamp (400 W). 100 mg of catalyst was dispersed in 100 ml of a water-ethanol mixture (10 volume% ethanol) and kept under natural sunlight. After exposure, the activity was tested by taking just 10 mg of the activated catalyst and following the above-mentioned Subsequently, after testing, the catalyst was put back into the 100 ml beaker. the reaction system was exposed to sunlight for 10 days, after which the activity was measured again under the Xe lamp. Following this, the solution was again exposed to sunlight for an additional 5 days, and the activity was once again measured under the lamp, The concentration of H_2O_2 was determined the same as the above method. (Note that due to variations in sunlight intensity, the quantum of activation may somewhat vary from place to place).

Detection of superoxide radicals: The experiment was performed by dispersing 40 mg of $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates into 25 mL of nitro blue tetrazolium (NBT) (0.025×10^{-3} m) solution and then the reaction mixture was exposed to light irradiation for 3 h using a 400 W Xe lamp. The suspension was analyzed by UV-Vis absorption spectroscopy after the removal of the solid catalyst by centrifugation.

Measurement of total oxygen content in the aqueous dispersion of a catalyst: Non-invasive Ocean Optics Neofox-Kit-Probe was used to measure the total oxygen (TO) content in pure water and an aqueous dispersion of fresh and activated $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates at room temperature (25-27 ° C).4 Typically, the experiment was done by attaching the sensing patch to the inner wall of the 50 ml round bottom flask in such a way that it is immersed in the aqueous solution and measures the amount of oxygen dissolved in it. first, the amount of oxygen dissolved in pure water was measured, which was 322 µmol/L. Then to check the effect of the catalyst on oxygen content, 10 mg of $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates (fresh/activated) was dispersed in 100 ml of water.

2.3.3.3 Characterization

All the characterization techniques are discussed in chapter1.2.

2.3.4. Results and Discussion

2.3.4.1. Catalyst Characterization



Figure 2.3.2. (a) PXRD patterns and (b) surface area of SBTOC-F and SBTOC-S. (c,d) Scanning and Transmission electron microscopy images of the nanoplates. (e,f) Atomic force microscopy image and the corresponding height profile respectively. (g,h) Scanning and Transmission electron microscopy images of solid state synthesized SBTOC-S. (i) HRTEM image and (j) single crystalline SAED pattern acquired on 001 facets of a Sr₂Bi₃Ta₂O₁₁Cl nanoplates. (k,l) HRTEM image and SAED pattern acquired solid state synthesized Sr₂Bi₃Ta₂O₁₁Cl.

The double layer perovskite Sillen Aurivillus phase of Sr₂Bi₃Ta₂O₁₁Cl, where *n*=2, was realized by using a eutectic mixture of NaCl and KCl (SBTOC-F, Scheme 2.3.1.) and also by the traditional solid-state method (SBTOC-S) for comparison. Powder X-ray diffraction (PXRD, Figure 2.3.2. a) analysis confirms the purity of the samples.²³ The sharp peaks of SBTOC-F and altered peak intensity patterns indicate the high crystallinity of the fluxsynthesized sample and an interesting preferred grown orientation absent in the solid-state sample. N₂ adsorption-desorption isotherm analysis shows that the surface area of SBTOC-F $(3.74 \text{ m}^2/\text{g})$ exhibits a threefold enhancement over SBTOC-S (1.38 m²/g, Figure 2.3.2. b). This was further affirmed by scanning electron microscopy (SEM, Figure 2.3.2. c), transmission electron microscopy (TEM, Figure 2.3.2. d), and atomic force microscopy (AFM, Figure 2.3.2. e and f) analysis which revealed that SBTOC-F consists of well-defined rectangularshaped nanoplates having an average edge length of ~1 µm and 60-100 nm of heights, whereas SBTOC-S consists of large irregularly shaped particles (Figure 2.3.2. (g, SEM) and (h,TEM)). The high-resolution TEM (HRTEM) images acquired on the nanoplate (Figure **2.3.2.** i) confirmed the high crystallinity of the nanoplates having lattice fringes (0.38 and 0.28 nm) corresponding to the (110) and (010) planes respectively and therefore, consideration of the uniform plate thickness indicated the dominantly exposed facet as {001}. The selected area electron diffraction (SAED, Figure 2.3.2. j) recorded on a single nanoplate along the [001] zone axis contained sharp diffraction spots indexable on its crystal structure, depicting the single crystalline nature of SBTOC-F. An HRTEM image and SAED pattern of SBTOC-S are shown in Figure 2.3.2. k and l to show the polycrystalline nature of the shapeless individual particles. The average band gaps for SBTOC-F and SBTOC-S were estimated at 2.66 eV and 2.7 eV (Figure 2.3.3. a) with the valance and conduction band positioned at 2.16 and -0.50 eV vs. RHE respectively for SBTOC-F (Figure 2.3.3. b), indicating visible light sensitivity of the samples (**Figure 2.3.3. c**).²¹



Figure 2.3.3. (a) UV-Vis diffuse reflectance spectra of SBTOC-S and SBTOC-F (inset is the corresponding Tauc Plot). (b) Mott–Schottky plots of SBTOC-F measured at 200 and 800 Hz. (c) Schematic diagram of the experimentally determined energy levels for SBTOC-F.

2.3.4.2. Photocatalytic hydrogen peroxide generation: The H_2O_2 production efficiencies were investigated in the air by using water mixed with 10 vol% ethanol as a hole scavenger. As seen in Figure 2.3.4. a, SBTOC-S exhibited only a little H_2O_2 production. SBTOC-F nanoplates exhibited substantially enhanced activity, with an H_2O_2 evolution rate of 2.96 mmol/h/g (or 0.8 mmol/h/m²), nearly 3.3 times (or ~1.45 times surface normalized) higher than SBTOC-S to confirm the rate-enhancing role of facet control and defect density control (since lower defect centers improve exciton harvesting) beyond surface area improvement. The reactions were further performed employing different atmospheres to examine the active species responsible for H_2O_2 production. The production rate increases when the solution is saturated with oxygen (3.5 mmol/h/g, Figure 2.3.4. b). Under nitrogen saturation, on the other hand, the production rate sharply decreases to 0.45 mmol/h/g, suggesting that the formation of H_2O_2 occurs primarily via the 2e⁻ oxygen reduction reaction (ORR) pathway.²⁶ In the process, photoirradiation of SBTOC-F produces the excited hole (h^+) and electron (e^-) pairs. h^+ oxidizes

ethanol (C₂H₅OH + 2*h*⁺ \rightarrow CH₃CHO + 2H⁺), while *e*⁻ promotes the two-electron reduction of O₂ to H₂O₂.²⁷ In the process, the O₂ reduction could occur following two distinct routes: a twostep single-electron O₂ reduction (O₂ + e⁻ \rightarrow O₂⁺⁻ (-0.33 eV), O₂⁺⁻ + e⁻ + 2H⁺ \rightarrow H₂O₂ (1.44 eV)), or a direct two-electron O₂ reduction (O₂ + 2e⁻ + 2H⁺ \rightarrow H₂O₂, 1.76 eV) route, both of which are feasible in SBTOC-F for its high CB position.²⁸ Therefore, superoxide radical (O₂⁺⁻) formation was further quantified for both SBTOC-S and SBTOC-F using Nitro blue tetrazolium in the air. As seen in **Figure 2.3.4. c**, the O₂⁺⁻ production over SBTOC-F (297 µmol/h/g or 82 µmol/h/m²) is significantly higher than SBTOC-S (66 µmol/h/g or 47 µmol/h/m²), closely matching H₂O₂ production rate in pure water in the air atmosphere (±11% deviation) and confirming the involvement of two-step single-electron transfer route. Importantly, the recyclability tests using SBTOC-S and SBTOC-F unfurled a rare selfactivation phenomenon, unknown for any H₂O₂-producing photocatalyst so far. Both of them were used for 5 consecutive days, and unexpectedly, the H₂O₂ production was found to increase consistently and significantly for both samples (**Figure 2.3.4. d**). This stands in contrast to typical photocatalyst where catalytic activity progressively degrades within a few cycles.

Additionally, the activity increment in SBTOC-F is ~17 times more than that in SBTOC-S to establish the importance of facet control in (001) facet-exposed nanoplates. These facets often possess higher surface energy and increased surface reactivity, making them prone to rapid surface reconstruction during catalysis. To further evaluate, the recyclability of SBTOC-F nanoplates was extended up to 15 days (**Figure 2.3.4. e**), and the activity kept on rising from 590 μ M on 1st day to 1320 μ M on the 15th day, a massive 2-fold increase in yield. We further found that the catalyst activation process is unaffected by the presence of alcohol and therefore easily achievable before catalysis also. We suspended SBTOC-F in pure water and kept it under sunlight, and extracted it intermittently to check H₂O₂ production efficiency. As seen in **Figure 2.3.4. f**, the rate enhancement is similar to that observed in the presence of ethanol.

To comprehend the remarkable boost in activity, the capability of fresh and self-activated SBTOC-F nanoplates to photo-reduce molecular O_2 to superoxide radicals was evaluated using electron spin resonance (ESR) technique and spin-trapping with 5,5-dimethyl-pyrroline N-oxide (DMPO). Four characteristic DMPO- O_2^{\bullet} peaks were observed in both instances (**Figure 2.3.4. g I**), confirming the generation of O_2^{\bullet} and indicating a two-step single electron reduction process.^{13,29} In addition, the strong signal intensity in the activated SBTOC-F than in the fresh nanoplates validates its enhanced O_2^{\bullet} generation activity. Spectral quantification



Figure 2.3.4. Catalytic performance and self-activation. (a, b) H_2O_2 production comparison among SBTOC-S and SBTOC-F (b) H_2O_2 production by SBTOC-F photocatalyst under different atmospheres. (c) Comparison of superoxide radical production efficiency by SBTOC-S and SBTOC-F. (d) Plot showing 17 times more self-activation in SBTOC-F during H_2O_2 production as compared to SBTOC-S. (e, f) Performance of SBTOC-F during continuous use for 15 days with or without ethanol respectively. (g-i) Electron paramagnetic resonance (EPR) spectra of DMPO-O₂⁻⁻ over fresh and activated SBTOC-F. (g-ii) oxygen content and photocatalytic superoxide radical production over fresh and activated SBTOC-F. (h) Absorption spectrum of SBTOC-F nanoplate correlated to wavelength-dependent AQY.

showed that superoxide radical production also doubles in the activated sample to match the enhanced H_2O_2 production rate, indicating that the activated catalysts may adsorb more molecular O_2 due to surface restructuring (discussed *vide-infra*). We, therefore, estimated the

total oxygen content in the catalyst solution and found it to be significantly high in the case of the activated sample (**Figure 2.3.4.g II**). The wavelength-dependent apparent quantum yield (AQY) for the H_2O_2 production by SBTOC-F is seen in (**Figure 2.3.4. h**, **Note 2.3.1**) agreeing well with its absorption spectrum and exhibiting an AQY of 17.1% at 360 nm. Notwithstanding surface reconstruction, the catalyst in bulk is highly stable as revealed by negligible changes in the powder XRD pattern of the used sample (**Figure 2.3.5.**).

Catalyst	Light Sources	Scavenger	H_2O_2 (mmol/h/g)	Atmosphere	References
SBTOC-S	400 W Xe Lamp	Ethanol (10 vol%)	0.8	Air	This Work
SBTOC-F	400 W Xe	Ethanol (10 vol%)	2.9	Air	
Activated	Lamp		6.5		
SBTOC-F					
BiOCl	500 W Xe- Lamp	НСООН	0.68	Air	5
Au/Bi ₂ O ₃ -TiO ₂	300 W Xe Lamp	Ethanol (4 wt%)	0.9	Air	6
Au0.1Ag _{0.4} /TiO ₂	450 W high pressure Hg lamp	Ethanol (4 wt%)	0.3	O ₂	7
CFT	300 W Xe Lamp	-	1.67	O ₂	8
ZrS ₃ nanobelts	300 W Xe	Benzyl alcohol	1.5	O ₂	9
	Lamp	(1mmol)			
NH ₂ -MIL-	300 W Xe	benzyl alcohol	0.4	O ₂	10
125@ZnS	Lamp	(1.0 mL) and			
		acetonitrile (4ml)			

SN-GQD/TiO ₂	500 W Xe	2-propanol	1.7	O 2	11
	Lamp				
Bi ₄ O ₅ Br ₂ /g-C ₃ N ₄	300 W Xe	-	0.124	O ₂	12
	Lamp				
MMO@C ₃ N ₄	300 W Xe) W Xe - 0.		O ₂	13
	Lamp				
rGO/TiO ₂	300 W Xe	propanol	0.533	O ₂	14
	Lamp				
PM-CDs-30	>400 nm	-	1.770	Air	15
SN-GQD/TiO ₂	500W Xenon	2-propanol	0.902	O ₂	16
	Lamp				
CNP	300 W Xe	-	3.2	O ₂	17
	Lamp				

Table 2.3.1. Comparison table showing photocatalytic H_2O_2 evolution activity of $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplate as compared to other reported catalyst.

The photocatalytic H_2O_2 peroxide production rate (>6 mmol/h/g) by the SBTOC-F nanoplates is highly encouraging by considering that no noble metal or external oxygen was used, and no catalyst deactivation was observed (**Table 2.3.1.**).



Figure 2.3.5. Powder XRD patterns of Bi₄TaO₈Cl nanoplates before and after catalysis.

2.3.4.3. Origin of self-Activation of SBTOC-F: The fundamental processes of surface reconstruction and molecular O₂ activation, photon absorption, the exciton separation efficiency of the catalyst, etc. were systematically examined to clarify the origin of the unusual increase in H₂O₂ production efficiency with increasing cycles. Noteworthy that there were no discernable differences in the PXRD analysis of the samples before and after use. However, Xray photoelectron spectroscopy (XPS) indicated a significant surface reconstruction from vacancy generation processes. Figure 2.3.6. a compares the high-resolution XPS Bi-4f spectra of the fresh sample with the different degree of activated samples showing an evident shift of 0.82 eV and 1.1 eV to a smaller binding energy after 10 and 15 days of activation, respectively, characterizing a change in the chemical environment of Bi atoms with a reduced number of coordinating oxygen atoms by oxygen vacancy (O_V) formation.³⁰ Alongside, (Figure 2.3.6. b) the percentage abundance of Bi also decreases with respect to the total Sr and Ta content from 40.2% in fresh catalyst to 39.3% and 37.8% after 10 and 15 days of activation, respectively, indicating increasing Bi leaching during reuse. The oxygen peaks were then analyzed to support its vacancy formation. As seen in Figure 2.3.6. c, the O-1s XPS spectra are characterized by three peaks of lattice oxygen (O_L, 529.3 eV), dissociative oxygen around Bi vacancies (Ov, 531.0 eV), and surface-adsorbed molecular oxygen or hydroxyl species (Oads, 532.5 eV).³¹The abundance of vacancy oxygen and adsorbed oxygen with respect to lattice oxygen increases in the activated sample (Figure 2.3.6. d) to confirm the leaching of lattice oxygen from the sample to facilitate molecular O₂ adsorption.^{36,37} Notably, recent theoretical studies also revealed that oxygen-surface interaction in Bi-O surface can tremendously improve upon vacancy creation. The Sr-3d (Figure 2.3.6. e) and Ta-4f spectra (Figure 2.3.6. f), on the other hand, exhibited much lesser shifts indicating that Ov formation in perovskite layers is less likely to take place during the activation of the catalyst, understandably due to a stronger (Sr/Ta)-O bond than Bi-O. Similarly, we estimated the catalyst's Cl/Sr atomic ratio before and after activation which remains the same, implying the dissolution of Cl under light irradiation is negligible. This we expected because the VBM of the Sillen Aurivillius phases is composed of the dispersive O-2p band, while the Cl-3p orbital energetically lies far too below. For confirmation, the concentration of leached metal ions into the solution during the activation process was evaluated using inductively coupled plasma mass spectrometry (ICP-MS, Figure **2.3.7.a**), which revealed that ~11 parts per billion (ppb) of Bi per gram of catalyst leached from the nanoplates into the solution after a 10-day activation period, which increased to ~16 ppb after 15 days. Leached Sr and Ta amounts were negligible though ICP-MS. Subsequently, the

existence of O_V (g = 2.003) was confirmed by EPR spectroscopy (**Figure 2.3.7 b**).^{13,32} A threefold increase in EPR peak intensity in the activated catalyst asserts a high level of oxygen vacancy.



Figure 2.3.6. Surface characterization of the catalyst. (a) Bi-4f XPS spectra of fresh and activated SBTOC-F. (b) Plot showing a decrease in the surface Bi content as compared to (Ta + Sr) in activated SBTOC-F. (c) High-resolution O-1s XPS spectra showing (d) an increase in oxygen vacancy and adsorbed oxygen in comparison to lattice oxygen in activated SBTOC-F. (e, f) High-resolution Sr 3d and Ta 4f XPS spectra showing no shifting.

Positron annihilation lifetime (PAL) and coincidence Doppler broadening spectroscopy (CDB) were employed to characterize the chemical nature of the defects. PAL spectra were fitted with three-lifetime components (**Table 2.3.2**.), the longer component (τ_3) ~ 2300 ps with small intensity (~2%) corresponds to the pick-off annihilation of the positronium atoms. τ_1 and τ_2 are attributed to isolated vacancies and Bi-O vacancy associates (such as V_{Bi} , V_{O} , V_{Bi} , etc.) respectively,. $^{33-35}$ The relatively high contribution of τ_2 in both the fresh and activated samples suggests that Bi–O vacancy associates are the predominant forms of defects in the Sr₂Bi₃Ta₂O₁₁Cl nanoplates. Additionally, the relative intensity of τ_2 further increases with activation whereas τ_1 decreases to depict that the isolated vacancies are progressively converted into vacancy associates during reuse. CDB spectra were analyzed by taking a point-by-point

intensity ratio with a 99.9999% pure aluminum single crystal. The ratio curve of CDB of the fresh and activated samples (**Figure 2.3.7 c**) shows a characteristic peak at $p_L = 11 \times 10^{-3} \times m_0 c$, attributed to the annihilation of positrons with the 2p electrons of oxygen anions, (m₀: electron rest mass, c:speed of light).³⁶ The decreased peak intensity with the activation confirms an increase in the number of vacancy clusters by decreasing the oxygen anions.

Sample	t1 (ps)	I ₁ (%)	t2 (ps)	I ₂ (%)	t3 (ps)	I3 (%)
Fresh	105 ± 3	31 ± 2	295 ± 2	67 ± 2	2218 ± 51	2 ± 0.1
Activated	107 ± 3	25 ± 2	299 ± 5	73 ± 2	2306 ± 83	2 ± 0.1

Table 2.3.2. Positron lifetime parameters of the fresh and activated SBTOC-F nanoplates.



Figure 2.3.7. (a) ICP-MS data showing increase in Bi leaching from the nanoplates to the reaction solution with increasing activation day. (b) EPR spectra of fresh and activated SBTOC-F. (c) Ratio curves generated from the coincidence Doppler broadening spectra of fresh and activated SBTOC-F. (d) Zeta potential of the catalyst used for different cycles.

Such vacancy clusters are expected to affect the surface charge of the catalyst drastically.¹⁷ Therefore, zeta potential of the samples during activation was recorded. **Figure 2.3.7. d** depicts the initial zeta potential of the catalyst to be ~11.6 mV, which significantly changed to -3, -15, and -27 mV after the first 5th, 10th and 15th day respectively.



Figure 2.3.8. XAS study on surface reconstruction. (a) $Bi-L_3$ edge XANES and (b) EXAFS spectra of fresh and activated SBTOC-F. (c) Ta-L₃ edge XANES and (d) EXAFS spectra of fresh and activated SBTOC-F.

X-ray absorption spectroscopy studies were conducted on the fresh and the used catalysts to visualize the electronic and geometric structural distortions arising from increased defect concentrations. The X-ray absorption near edge spectra (XANES) of the Bi-L₃ edge for the activated catalyst moves to a lower binding energy (0.15 eV, **Figure 2.3.8. a**), indicating an average reduced oxidation state of bismuth arising from the surrounding oxygen vacancies,
corroborating the *d*-orbital shifts in the XPS analysis. In addition, the smaller energy shift while using the high-energy synchrotron beam infers the nanoplate surface as the primary region for O_V creation. From the extended X-ray absorption fine structure spectroscopy (EXAFS, Figure **2.3.8.** b), we observed a major peak at the k^2 -weighted oscillations in the R-space centering ~1.7 Å corresponding to the Bi-O bond.^{37,38} The reduction in its intensity by ~6% as well as its shift towards lower R confirms the decrease in the oxygen coordination number around the Bi atoms and a distorted local geometry in the Bi₂O₂ layer.^{35,39,40}. Conversely, negligible changes were observed for the Ta-L₃ edge in XANES and EXAFS data (Figure 2.3.8. c, d) suggesting the higher stability of the Ta-O perovskite layer originating from the higher Ta-O bond strength. Earlier studies on oxide phases undergoing surface reconstruction induced by ion leaching revealed the formation of a surface amorphous layers. Therefore, we further examined the fresh and activated samples using TEM. As shown in Figure 2.3.9., crystalline particle edges in the fresh catalyst transforms into an amorphous layer after activation, reaching a depth of 1-2 nm, accompanied by the emergence of a heightened number of defects at the interface between the crystalline and amorphous phases in the activated catalyst. Overall, the detailed XRD, EPR, XPS, PAS, EXAFS, ICP-MS, Zeta-potential and TEM analysis of the fresh and the activated samples confirmed that the surfaces of the nanoplates reconstruct under the experimental conditions from preferential leaching of Bi and O atoms to form negatively charged vacancy clusters and an amorphous surface layer. The stronger Lewis acidity of Bi as compare to Ta and Sr leads to easy formation of Bi-OH bonds, which precedes the leaching step.

Metal-rich surfaces usually create swallow trap states that can improve light harvesting and also, charge transfer to reactants. The UV-Vis DRS plots (**Figure 2.3.10. a and b**) of the activated samples showed a shift of the optical absorption edge to longer wavelengths leading to a narrower band gap of 2.4 eV to enhance absorption of light with recycling of the catalyst. To investigate its effect on their ability to separate and transport the photogenerated charge carriers, we further carried out photocurrent and electrochemical impedance spectroscopic measurements. As shown in **Figure 2.3.10. c**, both the fresh and the activated catalysts were quick to produce photocurrent in response to the visible light. However, the activated nanoplates displayed a higher photocurrent response than the fresh one, indicating more effective charge separation in it, attributed to the trapping of excited electrons at the swallow vacancy states.¹³ In addition, electrochemical impedance spectroscopy (Nyquist plot, **Figure 2.3.10. d**) revealed that the electron-transfer resistance (R_{ct}) of activated nanoplates is ~ 20% smaller than fresh nanoplates implying a low charge transfer resistance originating from the low valent metal moieties.



Figure 2.3.9. (a and b) TEM and (c and d) HR-TEM image of Sr2Bi3Ta2O11Cl nanoplates before and after activation respectively. (e) Crystal structure of Sr2Bi3Ta2O11Cl nanoplate along the ab plane as seen in HRTEM images.

In brief, the diverse experiments confirmed that, besides excess molecular oxygen harvesting by the surface of SBTOC-F, superior charge separation efficiency, improved light absorption and electron transfer properties contribute to the enhanced catalytic activity.



Figure 2.3.10. Light harvesting and synergy. (a) DRS and (b) the corresponding Tauc plots, (c) transient photocurrent response, and (d) Nyquist plots for fresh and activated SBTOC-F.

2.3.5. Conclusion

In conclusion, we show that during facile photocatalytic H_2O_2 production, the competitive leaching of metal ions and anions within a complex inorganic lattice framework can overcompensate catalyst degradation observed in the usual photoactive materials, and this can continuously improve the efficiency of an already facile photocatalyst. Our single-crystalline $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates enclosed by the [100], [010], and [001] facets have double the surface area that is achievable by traditional methods and a facile H_2O_2 production rate of 2.9 mmol/h/g in the air. Further, the progressive leaching of surface Bi and oxide anions generates more surface vacancies that transform into vacancy clusters and aid in excess O_2

adsorption. The swallow energy levels of the vacancies lead to excess light absorption and facile exciton separation to further improve catalytic efficiency synergistically, leading to doubled H_2O_2 production in 15 days. The findings establish the potential of rational defect engineering in developing sustainable photocatalysts for realistic applications by avoiding catalyst deactivation.

Note 2.3.1 Calculation of Apparent Quantum Yield: The apparent quantum yield (AQE) for photocatalytic H₂O₂ production over flux synthesized Sr₂Bi₃Ta₂O₁₁Cl nanoplate was calculated by carrying out the reaction under a 400 W Xe lamp as a function of wavelength with the help of different bandpass filters. (Newport, Model No.- 843-R) attached with a thermopile sensor (Newport, Model No.- 919P-010-16) was used to measure the power of the incident beam (P_{incident}) coming through a particular bandpass filter. Incident power density on the sample corresponding to a photon of wavelength λ (p_{incident}) was calculated as;

$$P_{\text{incident}} = \rho_{\text{incident}(\lambda)} \times A_{\text{sample}}$$

where A_{sample} is the area exposed to the incident light (20 cm²).

The number of moles of incident photons per second $N_{ph(\lambda)}$, as a function of wavelength can be expressed as:

$$N_{ph(\lambda)} = \frac{\rho_{incident(\lambda)}}{N_A E_{ph(\lambda)}}$$

where $\rho_{\text{incident}(\lambda)}$ is the incident power density on the sample and N_A is the Avogadro number and $E_{\text{ph}(\lambda)} (= \text{hc}/\lambda)$ is the energy of one photon for the corresponding wavelength.

To correlate with the number of moles of hydrogen peroxide produced per hour, the total number of moles of the incident photon was calculated using the equation given below:

number of moles of incident photons per hour = $N_{ph(\lambda)} \times 3600 \times area$ of an incident beam.

Finally, the AQE can be derived from the following equation:

 $AQE = \frac{n \text{ (No.of electron transferred)} \times \text{Number of moles of hydrogen peroxide produced per hour}}{\text{Total no.of moles of incident photons per hour}} * 100\%$

Where, n=2 for hydrogen peroxide production

Bibliography

- 1. Wu, Q. *et al.* A metal-free photocatalyst for highly efficient hydrogen peroxide photoproduction in real seawater. *Nat. Commun.* **12**, (2021).
- Tian, Z. *et al.* Efficient photocatalytic hydrogen peroxide generation coupled with selective benzylamine oxidation over defective ZrS₃ nanobelts. *Nat. Commun.* 12, 1–10 (2021).
- 3. Sun, J. *et al.* Dye-sensitized photocathodes for oxygen reduction: Efficient H₂O₂ production and aprotic redox reactions. *Chem. Sci.* **10**, 5519–5527 (2019).
- Tsukamoto, D. *et al.* Photocatalytic H₂O₂ production from ethanol/O₂ system using TiO₂ loaded with Au-Ag bimetallic alloy nanoparticles. *ACS Catal.* 2, 599–603 (2012).
- Chai, S. *et al.* Rational design of covalent organic frameworks for efficient photocatalytic hydrogen peroxide production. *Environ. Sci. Nano* 9, 2464–2469 (2022).
- Liu, C. *et al.* Semiconducting MOF@ZnS Heterostructures for Photocatalytic Hydrogen Peroxide Production: Heterojunction Coverage Matters. *Adv. Funct. Mater.* 32, (2022).
- Kim, H.K. *et al.* Triphasic Metal Oxide Photocatalyst for Reaction Site-Specific Production of hydrogen peroxide from oxygen reduction and water oxidation. *Advanced Energy Materials*. 12, 2104052, (2022)
- Argyle, M. D. *et al.* Heterogeneous catalyst deactivation and regeneration: A review. *Catalysts* 5, 145–269 (2015).
- Molnár, Á. *et al.* Catalyst recycling—A survey of recent progress and current status. *Coord. Chem. Rev.* 349, 1–65 (2017).
- Ohno, T. *et al.* Photocatalytic water splitting using modified GaN:ZnO solid solution under visible light: Long-time operation and regeneration of activity. *J. Am. Chem. Soc.* 134, 8254–8259 (2012).
- Sun, S. *et al.* Photocatalytic degradation of gaseous toluene on Fe-TiO₂ under visible light irradiation: A study on the structure, activity and deactivation mechanism. *Appl. Surf. Sci.* 258, 5031–5037 (2012).
- Wang, H. *et al.* High quantum efficiency of hydrogen production from methanol aqueous solution with PtCu–TiO₂ photocatalysts. *Nat. Mater.* (2023). doi:10.1038/s41563-023-01519-y
- 13. Li, H. et al. Oxygen Vacancy-Mediated Photocatalysis of BiOC1 Reactivity

Selectivity and Perspectives. Angew Chem Int Ed. 57,122-138 (2017)

- Zhao, K. *et al.* Surface structure-dependent molecular oxygen activation of BiOCl single-crystalline nanosheets. *J. Am. Chem. Soc.* 135, 15750–15753 (2013).
- Wang, L. *et al.* Inorganic Metal-Oxide Photocatalyst for H₂O₂ Production. *Small*, 18, 2104561, (2021)
- Chatterjee, K. *et al.* Synthesis of Bi₃TaO₇-Bi₄TaO₈Br composites in ambient air and their high photocatalytic activity upon metal loading. *Dalt. Trans.* 48, 7110–7116 (2019).
- Banoo, M., *et al.* A 'self-activating' Bi₃TaO₇-Bi₄TaO₈Br photocatalyst and its use in the sustainable production of pro-fluorophoric rhodamine-110. *Green Chem.* 24, 5514– 5523 (2022).
- Zhong, C. *et al.* Lone-Pair-Induced Intra- and Interlayer Polarizations in Sillen-Aurivillius layered pervoskite Bi₄NbO₈Br. *Inorg. Chem.* 61, 25, 9816–9822,(2022).
- Kato, D. *et al.* Valence Band Engineering of Layered Bismuth Oxyhalides toward Stable Visible-Light Water Splitting: Madelung Site Potential Analysis. *J. Am. Chem. Soc.* 139, 18725–18731 (2017).
- Banoo, M. *et al.* Bi₄TaO₈Cl as a New Class of Layered Perovskite Oxyhalide Materials for Piezopotential Driven Efficient Seawater Splitting. *Nano Lett.* 22, 8867–8874 (2022).
- Nakada, A. *et al.* Band Engineering of Double-Layered Silleń –Aurivillius Perovskite oxychlorides for visible light driven water splitting. *Chem. Mater.* 31, 3419–3429, (2019)
- Liu, S. *et al.* Designing new n = 2 Sillen-Aurivillius phases by lattice-matched substitutions in the halide and [Bi₂O₂]²⁺ layers. *J. Solid State Chem.* 205, 165–170 (2013).
- Nakada, A. *et al.* Two-step synthesis of Sillén-Aurivillius type oxychlorides to enhance their photocatalytic activity for visible-light-induced water splitting. *J. Mater. Chem. A* 6, 10909–10917 (2018).
- Hu, C. *et al.* Coupling Piezocatalysis and Photocatalysis in Bi₄NbO₈X (X = Cl, Br)
 Polar Single Crystals. *Adv. Funct. Mater.* **30**, (2020).
- Li, L. *et al.* Flux synthesis of regular Bi₄TaO₈Cl square nanoplates exhibiting dominant exposure surfaces of {001} crystal facets for photocatalytic reduction of CO₂ to methane. *Nanoscale* 10, 1905–1911 (2018).
- 26. Guo, Y. et al. Photocatalytic and Electrocatalytic Generation of Hydrogen Peroxide:

Principles, Catalyst Design and Performance. Nano-Micro Letters **15**, (Springer Nature Singapore, 2023).

- Shiraishi, Y. *et al.* Highly selective production of hydrogen peroxide on graphitic carbon nitride (g-C₃N₄) photocatalyst activated by visible light. *ACS Catal.* 4, 774–780 (2014).
- Zhao, X. *et al.* Z-scheme photocatalytic production of hydrogen peroxide over Bi₄O₅Br₂/g-C₃N₄ heterostructure under visible light. *Appl. Catal. B Environ.* 278, 119251 (2020).
- Ma, X. *et al.* Oxygen vacancies assist a facet effect to modulate the microstructure of TiO₂ for efficient photocatalytic O₂ activation. *Nanoscale* 15, 768–778 (2022).
- Tao, X. *et al.* Photoinduced Surface Activation of Semiconductor Photocatalysts under Reaction Conditions: A Commonly Overlooked Phenomenon in Photocatalysis. *ACS Catal.* 10, 5941–5948 (2020).
- 31. Wang, Z. *et al.* Formation, Detection, and Function of Oxygen Vacancy in Metal Oxides for Solar Energy Conversion. *Adv. Funct. Mater.* **32**, (2022).
- 32. Cui, D. *et al.* Controlled hydrogenation into defective interlayer bismuth oxychloride via vacancy engineering. *Commun. Chem.* **3**, 1–8 (2020).
- Guo, S. Q. *et al.* Improving Photocatalytic Water Treatment through Nanocrystal Engineering: Mesoporous Nanosheet-Assembled 3D BiOCl Hierarchical Nanostructures That Induce Unprecedented Large Vacancies. *Environ. Sci. Technol.* 52, 6872–6880 (2018).
- Guan, M. *et al.* Vacancy associates promoting solar-driven photocatalytic activity of ultrathin bismuth oxychloride nanosheets. *J. Am. Chem. Soc.* 135, 10411–10417 (2013).
- 35. Shi, Y. *et al.* Van Der Waals gap-rich BiOCl atomic layers realizing efficient, purewater CO₂-to-CO photocatalysis. *Nat. Commun.* **12**, 1–10 (2021).
- Asgarian, S. M. *et al.* Investigation of Cation and Cation Vacancy Distributions in the Zinc Substituted Maghemite, Prepared by One Pot Room Temperature Coprecipitation Method. *J. Supercond. Nov. Magn.* 34, 2933–2944 (2021).
- Wang, L. *et al.* Bismuth Vacancy-Induced Efficient CO₂ Photoreduction in BiOCl Directly from Natural Air: A Progressive Step toward Photosynthesis in Nature. *Nano Lett.* 21, 10260–10266 (2021).
- Shi, Y. *et al.* Simultaneous Manipulation of Bulk Excitons and Surface Defects for Ultrastable and Highly Selective CO₂ Photoreduction. *Adv. Mater.* 33, 1–10 (2021).

- 39. Liu, L. *et al.* Bottom-up growth of homogeneous Moiré superlattices in bismuth oxychloride spiral nanosheets. *Nat. Commun.* **10**, (2019).
- Li, M. *et al.* Unprecedented Eighteen-Faceted BiOCl with a Ternary Facet Junction Boosting Cascade Charge. *Angew Chem Int Ed*, 58,9517 –9521 (2019).

Bibliography of comparison Table

- Luitel, H. *et al.* Positron annihilation lifetime characterization of oxygen ion irradiated rutile TiO₂. *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* 379, 215–218 (2016).
- Luitel, H. *et al.* Defect generation and recovery in polycrystalline ZnO during annealing below 300 °C as studied by in situ positron annihilation spectroscopy. *J. Mater. Sci.* 52, 7615–7623 (2017).
- Sampathkumaran, P. *et al.* Surface and Bulk Defects in Cr-Mn Iron Alloy Cast in Metal and Sand Moulds: Characterization by Positron Annihilation Techniques. *J. Surf. Eng. Mater. Adv. Technol.* 01, 136–143 (2011).
- Mondal, S. *et al.* Light-Induced Hypoxia in Carbon Quantum Dots and Ultrahigh Photocatalytic Efficiency. *J. Am. Chem. Soc.* 144, 2580–2589 (2022).
- 5. Su, Y. *et al.* Internal Electric Field Assisted Photocatalytic Generation of Hydrogen Peroxide over BiOCl with HCOOH. *ACS Sustain. Chem. Eng.* **6**, 8704–8710 (2018).
- Feng, L. *et al.* Au modified Bi₂O₃-TiO₂ hybrid for photocatalytic synthesis of hydrogen peroxide. *Catal. Commun.* 155, 106315 (2021).
- Tsukamoto, D. *et al.* Photocatalytic H ₂O₂ production from ethanol/O₂ system using TiO₂ loaded with Au-Ag bimetallic alloy nanoparticles. *ACS Catal.* 2, 599–603 (2012).
- Kim, K. H. *et al.* Triphasic Metal Oxide Photocatalyst for Reaction Site-Specific Production of hydrogen peroxide from oxygen reduction and water oxidation. *Advanced Energy Materials* 12, 2104052 (2022).
- Tian, Z. *et al.* Efficient photocatalytic hydrogen peroxide generation coupled with selective benzylamine oxidation over defective ZrS₃ nanobelts. *Nat. Commun.* 12, 1–10 (2021).
- Liu, C. *et al.* Semiconducting MOF@ZnS Heterostructures for Photocatalytic Hydrogen Peroxide Production: Heterojunction Coverage Matters. *Adv. Funct. Mater.* 32, (2022).
- 11. Zheng, L. et al. Highly selective photocatalytic production of H₂O₂ on sulfur and

nitrogen co-doped graphene quantum dots tuned TiO₂. Applied Catalysis B: Environmental **239**, (Elsevier B.V., 2018).

- Zhao, X. *et al.* Z-scheme photocatalytic production of hydrogen peroxide over Bi₄O₅Br₂/g-C₃N₄ heterostructure under visible light. *Appl. Catal. B Environ.* 278, 119251 (2020).
- Wang, R. *et al.* Solar-Driven H₂O₂ Generation From H₂O and O₂ Using Earth-Abundant Mixed-Metal Oxide@Carbon Nitride Photocatalysts. *ChemSusChem* 9, 2470–2479 (2016).
- Moon, G. H. *et al.* Solar production of H₂O₂ on reduced graphene oxide-TiO₂ hybrid photocatalysts consisting of earth-abundant elements only. *Energy Environ. Sci.* 7, 4023–4028 (2014).
- 15. Wu, Q. *et al.* A metal-free photocatalyst for highly efficient hydrogen peroxide photoproduction in real seawater. *Nat. Commun.* **12**, (2021).
- 16. Kim, H. il *et al*.Photocatalytic hydrogen peroxide production by anthraquinoneaugmented polymeric carbon nitride. *Appl. Catal. B Environ.* **229**, 121–129 (2018).
- Yang, H. *et al.* Packing-induced selectivity switching in molecular nanoparticle photocatalysts for hydrogen and hydrogen peroxide production. *Nat. Nanotechnol.* 18, (2023).

CHAPTER 2.4

Massive self-activation in n=2 Sillen Aurivillus phase by vacancy associate formation for promoted photocatalytic pro-fluorophore Rh110 formation



Summary

Rhodamine-110 (Rh110), a pivotal xanthene-based pro-fluorophore, holds immense significance in biological research, particularly in the context of severe-acute-respiratorysyndrome coronavirus (SARS CoV-2) studies. However, the industrial production of Rh110 poses challenges due to the inherent presence of two labile amino side groups, which are essential for its pro-fluorophore activity but also trigger the formation of numerous unwanted side products. These complications lead to complex purification intricacies, low yields (5%), and exorbitant production costs. Herein, we have successfully synthesized an active highordered Sillen Aurivillius phase (Sr₂Bi₃Ta₂O₁₁Cl nanoplates), a feat not easily accomplished. We have harnessed its potential to efficiently produce pure pro-fluorophore Rh110 using the remarkably inexpensive Rhodamine-B (RhB) and natural sunlight as the energy source. Notably, our method yields an impressive 54% yield of Rh110, a substantial improvement compared to the present commercial method, where the yield is only 5%. And our previous report on photocatalytic RhB deethylation over Bi₃TaO₇-Bi₄TaO₈Br heterostructures. Equally remarkable is the discovery of a rare self-activation property inherent to Sr₂Bi₃Ta₂O₁₁Cl nanoplates, achieving an extraordinary 100% efficiency by the 11th cycle. Thus, highlighting the potential of Sr₂Bi₃Ta₂O₁₁Cl nanoplates for significant Rh110 production and surpassing the performance of Bi₃TaO₇-Bi₄TaO₈Br heterostructures.

2.4.1. Introduction

Rhodamine 110 (Rh110) a widely recognized pro-fluorophore, presents numerous advantages over traditional fluorescent molecules, finding extensive utility in biological studies, clinical diagnostics, drug development, and recent research related to SARS-CoV-2.1-7 The profluorophoric activity of Rh110 stems from the presence of two highly reactive free amino (-NH₂) groups attached to the xanthate framework, which readily form chemical bonds, including amide bonds, with other reagents, effectively acting as fluorescence ON-OFF switches in biological systems.^{8,9} However, the commercial production of Rh110 faces considerable challenges due to this high reactivity. The current commercial method involves the condensation of phthalic anhydride and m-aminophenol, necessitating high reaction temperatures and yielding numerous difficult-to-separate side products, resulting in low purity and elevated purification costs.^{10,11} Another xanthene base dye Rhodamine B (RhB) shares nearly identical structures with Rh110 but features protected amino groups through alkylation making it quite stable, and rendering them unsuitable as pro-fluorophores. Additionally, their remarkable stability prevents their decomposition and acts as a toxic pollutant.^{12,13} Notably, RhB is approximately 1000 times more inexpensive than Rh110.¹⁴ In our previous research, we introduced an innovative concept: the utilization of a photocatalytic RhB deethylation method, employing efficient and self-activating Bi-based heterostructures (Bi₃TaO₇-Bi₄TaO₈Br) as a promising solution for the cost-effective large-scale synthesis of Rh110. We successfully achieved the conversion of RhB to Rh110 using the Bi3TaO7-Bi4TaO8Br heterostructures within 8 hours. What's particularly intriguing is that the initial yield of Rh110, which was a minimum of 35% in the first cycle, consistently increased to an impressive 88% by the end of the 30th cycle during continuous use. This remarkable improvement can be attributed to the unique self-activating property of the Bi₃TaO₇-Bi₄TaO₈Br heterostructures.¹⁴

2.4.2. Scope of the present investigation

In this study, our primary objective is to enhance the yield and rate of Rh110 production by utilizing highly active double-layered perovskite Sillen Aurivillius (SA) $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates. $Sr_2Bi_3Ta_2O_{11}Cl$ is non-centrosymmetric and has a pseudo-tetragonal crystal structure (**Figure 2.4.1. a, b**). Sillen Aurivillius phases are characterized by the general formula $[A_{n-1}B_nO_{3n+1}]$ [Bi₂O₂] [X], where A: Ca²⁺, Sr²⁺, Bi³⁺, etc.; B: Nb⁵⁺, Ta⁵⁺, Ti⁴⁺, etc. and 'n' signifies the number of perovskite layers, n = 1,2,3, etc. and in this case, 'n' equals 2. Sillen Aurivillius Phases are renowned for their inherent stability and ability to absorb visible light. This is attributed to their unique electronic band structure, in which the Valence Band Maximum (VBM) is primarily influenced by O 2p orbitals rather than X np orbitals, contributing to its stability from oxidation by photogenerated holes. Furthermore, synthesizing high-ordered Sillen Aurivillus phases poses challenges due to the requirement of elevated reaction temperatures and extended reaction times. The conventional solid-state method for generating SA phases leads to uncontrolled facet-less growth and a consequent reduction in surface area. In certain instances, these phases are not even formed when employing traditional solid-state techniques.

Herein, we have employed the Flux method to synthesize highly active, facetcontrolled double-layered Sillen Aurivillius $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates. This approach significantly reduces both the reaction time and the required reaction temperature when compared to the solid-state method. These $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates are characterized by their high surface area and demonstrate an impressive Rh110 yield of 54% right from the initial stages of the process, achieved within 3 hours, as opposed to the 8 hours required by the previous work using Bi_3TaO_7 - Bi_4TaO_8Br heterostructure. Furthermore, it is worth noting the rare and highly relevant self-activation property observed in this high-ordered Sillen Aurivillius phase as well. This self-activation phenomenon can be attributed to surface reconstruction resulting from the formation of oxygen vacancies and the leaching of Bi during continuous use. Remarkably, this self-activation phenomenon ultimately led to a remarkable 100% yield for Rh110 by the 11th cycle, outperforming Bi_3TaO_7 - Bi_4TaO_8Br heterostructures. This highlights the potential for Rh110 production using $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates as a photocatalyst.

2.4.3. Methods

2.4.3.1. Flux Synthesis of Sr_2Bi_3Ta_2O_{11}Cl: The sample was prepared using a stoichiometric molar ratio of 2:1:1:1, combining strontium carbonate (SrCO₃), bismuth (III) oxide Bi₂O₃, tantalum pentoxide (Ta₂O₅), and bismuth oxychloride BiOCl as starting materials. A molten salt, specifically a eutectic mixture of KCl and NaCl in a 1:1 ratio, was employed as a flux. The flux was blended with the finely ground starting materials, achieving a solute concentration of 3.2 mol% for Sr₂Bi₃Ta₂O₁₁Cl relative to the total (Sr₂Bi₃Ta₂O₁₁Cl + flux). The resulting mixture was thoroughly mixed with a mortar and pestle, and then placed in an alumina crucible. Subsequently, it was heated in a muffle furnace at a temperature of 1023 K for a

duration of 4 hours, with a temperature ramping rate of 30°C per minute. After natural cooling, the product was meticulously washed with deionized water and subsequently collected by filtration. The resulting off-white powder product was dried at room temperature.

2.4.3.2. Photocatalytic Reaction: The photocatalytic reactions were conducted in a 50 ml open beaker made of Pyrex glass. A solar simulator (Newport LSS-7120) emitting light at an intensity of 1.00 kW m⁻² was employed as the light source in a top-down irradiation setup. To initiate the reaction, 40 mg of photocatalytic powder was dispersed in a 25 ml aqueous solution of Rhodamine B (with a concentration of 20 μ M). To establish an adsorption-desorption equilibrium of RhB on the catalyst surface, the reaction mixture was stirred in the dark for 30 minutes. Subsequently, the reaction solution was exposed to visible light. After each hour of light irradiation, a 1 ml aliquot was extracted from the reaction mixture. Following centrifugation, the supernatants were subjected to analysis using various characterization methods.

Trapping experiments were carried out under the same reaction conditions to assess the influence of O_2^{\cdot} and 'OH species on Rh110 yield. This was achieved by introducing benzoquinone (BQ) (at a concentration of 10^{-2} g mol⁻¹) and 2 ml of isopropyl alcohol (IPA) as scavengers for O_2^{\cdot} and 'OH, respectively.

For studies related to recyclability, the reactions were conducted using natural sunlight on the institute campus when sunlight was sufficiently intense. It's worth noting that the laboratory light sources were not capable of irradiating large quantities of samples. In this regard, 1 liter of aqueous 20 μ M RhB solution was subjected to de-ethylation using 1.6 g of Sr₂Bi₃Ta₂O₁₁Cl nanoplates as the photocatalyst. After the 1st, 5th, 8th, and 11th cycles, 40 mg of the catalyst was removed and its efficiency was assessed by employing 25 ml of fresh 20 μ M RhB solution.

2.4.3.3. Characterization

All the characterization techniques are discussed in Chapter 1.2.

2.4.4. Result and discussion

2.4.4.1. Catalyst Characterization



Figure 2.4.1. Crystal structure of $Sr_2Bi_3Ta_2O_{11}Cl$ viewed from the (a)*bc* plane and (b) *ab* plane. Gray, Blue, red, and dark green balls represent Bi or Sr, Ta, O, and Cl atoms, respectively. (c) PXRD patterns and (d, e) Scanning and Transmission electron microscopy images of the nanoplates (f) HRTEM image and (g) single-crystalline SAED pattern acquired on 001 facets of a $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplate.

The X-ray diffraction (XRD) patterns displayed in **Figure 2.4.1. c** demonstrate the crystallinity and purity of Sr₂Bi₃Ta₂O₁₁Cl samples synthesized by the Flux method employing a eutectic mixture of NaCl and KCl.¹⁵ Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analyses were conducted to assess the morphology, which revealed that Sr₂Bi₃Ta₂O₁₁Cl consists of well-defined rectangular nanoplates. Each nanoplate has an average edge length of approximately 1 µm (Figure 2.4.1. d and e). High-resolution TEM (HR-TEM) images in Figure 2.4.1.f further confirmed the remarkable crystallinity of these nanoplates. They displayed distinct lattice fringes spaced at 0.56 nm and 0.38 nm, corresponding to the (110) and (010) planes, respectively. Furthermore, the Selected Area Electron Diffraction (SAED) pattern, as depicted in Figure 2.4.1. g, was obtained from a single nanoplate oriented along the [001] zone axis. This pattern exhibited sharp and easily indexable diffraction spots that are consistent with the crystal structure, indicating the single crystalline nature of Sr₂Bi₃Ta₂O₁₁Cl which is difficult to synthesize with the traditional solid-state method. The surface area analyzed by N₂ adsorption-desorption isotherm shows that the surface area of $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates $(3.74\pm0.32m^2/g)$ exhibits a threefold enhancement over solid-state synthesized Sr₂Bi₃Ta₂OCl samples (Figure 2.4.2. a). The optical properties of S Sr₂Bi₃Ta₂O₁₁Cl nanoplates were examined using UV-Vis Diffuse Reflectance Spectroscopy (DRS, Figure 2.4.2. b and c)). The analysis revealed that the material exhibits an optical absorption edge at 467 nm with a bandgap of 2.63 eV.



Figure 2.4.2. (a) BET Specific surface area measurements of the $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates. (b, c) UV-Vis DRS spectra of $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates showing a sharp absorption edge around 450 nm. The corresponding optical bandgap was estimated from the Tauc plot at 2.63 eV.

2.4.4.2. Photocatalytic RhB to Rh110 transformation by Sr₂Bi₃Ta₂OCl nanoplates

In the investigation of $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates as photocatalysts for the transformation of Rhodamine B (RhB) into Rhodamine 110 (Rh110), remarkable efficiency was observed. The aqueous solution of RhB exhibited a distinctive absorption peak (λ_{max}) at 553 nm, as shown in **Figure 2.4.3. a**. When subjected to light in the presence of $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates, the solution experienced a shift towards shorter wavelengths, known as a hypsochromic shift. After approximately 3 hours of irradiation, the absorption peak reached 499 nm, indicating the formation of a pure Rh110 solution. This represents a significant advancement in conversion



Figure 2.4.3. (a) UV-Vis. absorption spectra recorded during the 1st photocatalytic cycle. (b) Plot showing the enhanced yield and reaction kinetics of $Sr_2Bi_3Ta_2OC1$ nanoplates (c) Photoluminescence spectra showing the emission of RhB before irradiation ($\lambda max = 583$ nm) and after irradiation ($\lambda max = 533$ nm). (d) Fluorescence decay kinetics of the reaction solution before and after photoirradiation for 480 min. (e) Recyclability of the $Sr_2Bi_3Ta_2OC1$ nanoplates photocatalysts up to the 11th cycle. (f) Powder XRD patterns of the heterostructures at different stages while continuously using up to the 11th cycle.

Kinetics when compared to the previously reported Bi_3TaO_7 - Bi_4TaO_8Br heterostructures, which necessitated a longer 8-hour timeframe for full conversion (**Figure 2.4.3. b**). This accelerated rate of RhB to Rh110 conversion can be attributed to the substantial increase in surface area and enhanced exposure of the active facets provided by the $Sr_2Bi_3Ta_2OCl$ nanoplates. Furthermore, the formation of Rh110 was further confirmed by detailed analyses of emission properties (**Figure 2.4.3. c**) and the average fluorescence lifetime (τavg , **Figure 2.4.3. d**) of the aqueous dye solution before and after photoirradiation. Initially, the emission maximum centered at 533 nm, with a τavg of 1.75 ns corresponding to RhB. After 3 hours of photoirradiation, a notable shift in fluorescence properties was observed, the emission maximum shifted to 533 nm and τavg increased to 3.75 ns, consistent with Rh110.^{16,17} This shift provides compelling evidence of the conversion from pure RhB to Rh110, thereby firmly confirming the success of the transformation process.

The observed hypsochromic shift in the UV-Vis spectra is attributed to the process of de-ethylation of Rhodamine B (RhB), ultimately culminating in the formation of Rhodamine 110 (Rh110). The precise nature of this transformation has been elucidated through comprehensive analyses utilizing high-resolution mass spectrometry (HRMS) and highperformance liquid chromatography (HPLC), discussed vide infra. Importantly, the yield of Rh110 resulting from this process was quantified, and this determination was further corroborated through HPLC analysis, revealing an impressive yield of 54%. This yield surpasses the performance of Bi₃TaO₇-Bi₄TaO₈Br heterostructures, underscoring the superior efficiency of Sr₂Bi₃Ta₂O₁₁Cl nanoplates for RhB to Rh110 transformation. Additionally, in contrast to the typical behavior observed in photocatalysis, where catalytic activity tends to degrade even after a few cycles, quite surprisingly, the yield of Rh110 over Sr₂Bi₃Ta₂O₁₁Cl nanoplates exhibited a substantial increase with continued utilization, reaching 64% in 5th, 77% in 8th, and a remarkable100% in 11th cycles (as illustrated in Figure 2.4.3.e). Furthermore, X-ray diffraction (XRD) analysis conducted on the Sr₂Bi₃Ta₂OCl nanoplates throughout 11th photocatalytic cycles, as depicted in Figure 2.4.3. f indicated minimal changes in the compound. This finding reinforces the notion that the Sr₂Bi₃Ta₂O₁₁Cl nanoplates remain stable at the bulk level.

2.4.4.3. Mechanism of RhB De-ethylation

The photocatalytic transformation of Rhodamine B (RhB) into Rhodamine 110 (Rh110) has been extensively studied, revealing a multi-step process that involves the gradual removal of ethyl groups. This process leads to the formation of distinct intermediate rhodamine compounds, each characterized by its unique color and absorption spectrum. Specifically, these intermediates include N,N,N'-triethylated rhodamine (TER) with an absorption maximum at 539 nm, N-ethyl-N'-ethyl-rhodamine 110 (MMER) at 527 nm, N,N'-diethylated rhodamine (DER) at 523 nm, and N-ethylated rhodamine (MER) at 510 nm. This process ultimately results in the distinctive absorption peak at 499 nm for Rh110.¹⁸ The progression of the de-ethylation process was monitored through High-Performance Liquid Chromatography (HPLC) analysis, as shown in Figure 2.4.4. a. Initially, pure RhB exhibited a prominent peak at 12 min. However, with increasing light irradiation, new peaks representing de-ethylated products emerged at shorter retention times. These peaks corresponded to TER, MMER, DER, MER, and Rh110 at 9, 6.2, 5.9, 4, and 2.9 min, respectively. These peaks also started to disappear with increasing irradiation time. After 180 min of irradiation, only the Rh110 peak remained, confirming the purity of Rh110.^{19,20} Furthermore, High-Resolution Mass Spectrometry (HRMS) spectra, presented in Figure 2.4.4. b were acquired at different stages of photoirradiation to validate the presence of intermediates. Rhodamine B (RhB) exhibited a distinctive molecular ion peak at m/z = 443. During photoirradiation, intermediates like TER, MMER, DER, and MER displayed molecular ion peaks at m/z values of 415, 387, 359, and so forth, respectively. The relative intensities of these peaks gradually changed, with lower m/z peaks becoming more pronounced as irradiation time increased. At the end of 180 minutes of photoirradiation, a single prominent molecular ion peak at 331 m/z, characteristic of pure Rh110, confirmed the purity of Rh110. Both High-Performance Liquid Chromatography (HPLC) measurements and High-Resolution Mass Spectrometry (HRMS) data confirm that RhB undergoes a stepwise de-ethylation process, with the removal of an ethyl group at each step, and also confirm that the synthesized Rh110 is 100% pure.²¹ The proposed mechanism for RhB to Rh110 is given in **Figure 2.4.4.** c.



Figure 2.4.4. (a) HPLC chromatogram illustrating the reaction intermediates formed during photoirradiation of RhB in the presence of $Sr_2Bi_3Ta_2OCl$ nanoplates. (b) ESI mass spectra in the positive mode were collected at different time intervals during photoirradiation of RhB over of $Sr_2Bi_3Ta_2OCl$ nanoplates. (c) A proposed transformation pathway outlining how RhB is converted into Rh110 over $Sr_2Bi_3Ta_2OCl$ nanoplates under solar irradiation.

2.4.4.4. Origin of enhanced catalytic activity

Unlike the usual photocatalytic reactions, the unusual enhancement in Rh 110 production with each successive cycle in the photocatalytic process, where catalytic activity decreases within a few catalytic cycles, has prompted further investigation. Powder X-ray Diffraction (XRD) analysis of the catalyst after multiple cycles did not reveal any discernible alterations, indicating that the modifications are occurring at the cataloyst's surface. To probe the source of this remarkable efficiency improvement, we initially explored the active species responsible for the de-ethylation of Rhodamine B (RhB) (**Figure 2.4.5.**). Benzoquinone (BQ) and isopropyl alcohol (IPA) were used as superoxide and OH radical scavengers, respectively. In the presence of BQ, there was an absolute absence of de-ethylation process. Furthermore, when IPA was introduced, the Rh110 yield increased from 54% to 71% in the first cycle itself. This increase was attributed to a reduction in the overoxidation of the RhB.



Figure 2.4.5. (a, b) UV-Vis. spectra showing photocatalytic conversion of RhB to Rh110 in the presence of isopropyl alcohol (IPA), and benzoquinone (BQ) as hydroxide, and superoxide racial scavengers respectively.



Figure 2.4.6. (a) High-resolution Bi 4f spectra of the fresh and used $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates (b) Plot showing a decrease in the quantity of Bi with respect to Ta+Sr with the passing cycles. (c) High-resolution O-1s spectra of the fresh and used $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates (f) Plot showing the decreases in the amount of lattice oxygen as compared to the non-lattice oxygen during continuous use of the catalyst. (d) Zeta potential of the catalyst used for different cycles. (g) Plot showing the abundance of N in comparison with the Bi content on the catalyst surface with the passing cycles.

Furthermore, X-ray Photoelectron Spectroscopy (XPS) was utilized to investigate surface changes in the catalyst during continuous use, revealing a significant surface reconstruction attributed to vacancy formation. In Figure 2.4.6. a, high-resolution XPS spectra of Bi-4f for both the fresh and used catalyst (11th cycle) displayed two distinct peaks at binding energies of 159.4 eV and 164.6 eV, corresponding to Bi $4f_{7/2}$ and Bi $4f_{5/2}$, indicative of Bi³⁺ ions.^{22,23} Notably, the used sample exhibited a clear shift towards lower binding energy, signifying a change in the Bi environment. Figure 2.4.6. b illustrated a decreasing trend in the percentage of Bismuth (Bi) relative to the total content of Strontium (Sr) and Tantalum (Ta) over time, from an initial 45.1% in the fresh catalyst to 44.8% after 5 days, 43.4% after 8 days, and 42% after 15 days of continuous use, suggesting increasing Bi leaching during catalyst reuse. Additionally, the analysis of oxygen peaks (Figure 2.4.6. c) provided supporting evidence for oxygen vacancy formation. The O-1s XPS spectra revealed three distinct peaks: lattice oxygen (O_L) at 529.3 eV, dissociative oxygen surrounding Bismuth vacancies (O_V) at 531.0 eV, and surface-adsorbed molecular oxygen or hydroxyl species (O_{ads}) at 532.5 eV.²⁴ As the number of catalytic cycles increased (Figure 2.4.6. d), the relative abundance of vacancy oxygen and adsorbed oxygen compared to lattice oxygen grew, confirming the leaching of lattice oxygen and promoting the superoxide radical production by activation of adsorbed molecular O₂, the active species responsible for RhB deethylation. On the other hand, Ta-4f and Sr-3d spectra, show minimal shifts, suggesting that the creation of oxygen vacancies (OV) within the perovskite layers is difficult because of the strong (Sr/Ta)-O bond than Bi-O bond.

Surface vacancies can affect the surface charge of the catalyst. So, to confirm the impact of the various surface vacancies on the surface charge of the heterostructures, we conducted Zeta-potential measurements at various stages of recycling. **Figure 2.4.6. e** illustrates that the initial zeta potential of the catalyst is approximately 11.6 mV, which significantly changes to -8.6, -26.63, and -33.6 mV after the first 1st, 8th, and 11th catalytic cycles, respectively. The excess negative charge on the catalyst surface promotes the adsorption of rhodamine dye with its positive charges N site, suitable for its de-ethylation, further enhancing Rh110 yield. The increase in dye adsorption with the catalytic cycle is confirmed by quantification of N1s spectra of adsorbed dyes with respect to bismuth (Bi). As illustrated in Figure 4f, the decrease in the percentage abundance of nitrogen compared to bismuth after each catalytic cycle confirms the enhanced adsorption of dye with continuous use of the catalyst.



Figure 2.4.7. A Schematic illustrating the progressive enhancement in RhB absorption attributed to the natural surface activation occurring under solar irradiation, leading to the achievement of approximately 100% Rh110 production.

Based on the explanations above, **Figure 2.4.7.** provides a schematic representation of the photocatalytic deethylation of RhB on the catalyst surface. The adsorption of RhB, primarily through its positively charged N sites, intensifies with each successive use of the catalyst because the catalyst surface becomes progressively more negatively charged as vacancy associates form. Additionally, increased vacancy formation, in turn, augments the production of superoxide radicals, which play a pivotal role in deethylation by enhancing the adsorption of molecular oxygen onto these vacancies.

2.4.5. Conclusion

In conclusion, we successfully synthesized double-layered Sillen Aurivillius phase nanoplates, specifically Sr₂Bi₃Ta₂O₁₁Cl. We further explored their capacity for the efficient production of the pro-fluorophore Rh110. The significance of our findings lies in achieving an impressive 54% Rh110 yield in just 180 minutes during the first catalytic cycle, outperforming the 480 minutes required by Bi₃TaO₇-Bi₄TaO₈Br heterostructures in their first cycle. Notably, our

research unveiled an unprecedented self-activation rate, resulting in a remarkable 100% efficiency by the 11th cycle, surpassing the performance of Bi_3TaO_7 - Bi_4TaO_8Br heterostructures. These results emphasize the substantial potential of $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates for enhanced Rh110 production.

Bibliography:

- (1) Shan, H.; Liu, J.; Shen, J.; Dai, J.; Xu, G.; Lu, K.; Han, C.; Wang, Y.; Xu, X.; Tong, Y.; Xiang, H.; Ai, Z.; Zhuang, G.; Hu, J.; Zhang, Z.; Li, Y.; Pan, L.; Tan, L. Development of Potent and Selective Inhibitors Targeting the Papain-like Protease of SARS-CoV-2. *Cell Chem. Biol.* 2021, 28 (6), 855-865.e9. https://doi.org/10.1016/j.chembiol.2021.04.020.
- Kuo, C. J.; Liang, P. H. Characterization and Inhibition of the Main Protease of Severe Acute Respiratory Syndrome Coronavirus. *ChemBioEng Rev.* 2015, 2 (2), 118–132. https://doi.org/10.1002/cben.201400031.
- (3) Tong, H.; Gao, Y.; Li, J.; Li, J.; Huang, D.; Shi, J.; Santos, H. A.; Xia, B.
 Mitochondria-Targeted Bovine Serum Albumin@Copper Sulfide Nanocomposites Conjugated with Rhodamine-110 Dye for an Enhanced Efficacy of Cancer Photothermal Therapy. *Part. Part. Syst. Charact.* 2021, *38* (4). https://doi.org/10.1002/ppsc.202100013.
- Wu, Y.; Guo, W.; Peng, W.; Zhao, Q.; Piao, J.; Zhang, B.; Wu, X.; Wang, H.; Gong, X.; Chang, J. Enhanced Fluorescence ELISA Based on HAT Triggering Fluorescence "Turn-on" with Enzyme-Antibody Dual Labeled AuNP Probes for Ultrasensitive Detection of AFP and HBsAg. *ACS Appl. Mater. Interfaces* 2017, *9* (11), 9369–9377. https://doi.org/10.1021/acsami.6b16236.
- Kooij, R.; Liu, S.; Sapmaz, A.; Xin, B. T.; Janssen, G. M. C.; van Veelen, P. A.; Ovaa, H.; ten Dijke, P.; Geurink, P. P. Small-Molecule Activity-Based Probe for Monitoring Ubiquitin C-terminal Hydrolase L1 (UchL1) Activity in Live Cells and Zebrafish Embryos. J. Am. Chem. Soc. 2020, 142 (39), 16825–16841. https://doi.org/10.1021/jacs.0c07726.
- Pires, M. M.; Chmielewski, J. Fluorescence Imaging of Cellular Glutathione Using a Latent Rhodamine. *Org. Lett.* 2008, *10* (5), 837–840. https://doi.org/10.1021/ol702769n.
- Zerfas, B. L.; Trader, D. J. Monitoring the Immunoproteasome in Live Cells Using an Activity-Based Peptide-Peptoid Hybrid Probe. *J. Am. Chem. Soc.* 2019, *141* (13), 5252–5260. https://doi.org/10.1021/jacs.8b12873.

- Beija, M.; Afonso, C. A. M.; Martinho, J. M. G. Synthesis and Applications of Rhodamine Derivatives as Fluorescent Probes. *Chem. Soc. Rev.* 2009, *38* (8), 2410– 2433. https://doi.org/10.1039/b901612k.
- (9) Singh, H.; Tiwari, K.; Tiwari, R.; Pramanik, S. K.; Das, A. Small Molecule as Fluorescent Probes for Monitoring Intracellular Enzymatic Transformations. *Chem. Rev.* 2019, *119* (22), 11718–11760. https://doi.org/10.1021/acs.chemrev.9b00379.
- (10) Dwight, S. J.; Levin, S. Scalable Regioselective Synthesis of Rhodamine Dyes. *Org. Lett.* 2016, *18* (20), 5316–5319. https://doi.org/10.1021/acs.orglett.6b02635.
- (11) D. Nolting, D.; C. Gore, J.; Pham, W. Near-Infrared Dyes: Probe Development and Applications in Optical Molecular Imaging. *Curr. Org. Synth.* 2011, 8 (4), 521–534. https://doi.org/10.2174/157017911796117223.
- (12) Chatterjee, K.; Banoo, M.; Mondal, S.; Sahoo, L.; Gautam, U. K. Synthesis of Bi3TaO7-Bi4TaO8Br Composites in Ambient Air and Their High Photocatalytic Activity upon Metal Loading. *Dalt. Trans.* 2019, 48 (21), 7110–7116. https://doi.org/10.1039/c9dt00068b.
- Banoo, M.; Kaur, J.; Sah, A. K.; Roy, R. S.; Bhakar, M.; Kommula, B.; Sheet, G.; Gautam, U. K. Universal Piezo-Photocatalytic Wastewater Treatment on Realistic Pollutant Feedstocks by Bi4TaO8Cl: Origin of High Efficiency and Adjustable Synergy. *ACS Appl. Mater. Interfaces* 2023, *15* (27), 32425–32435. https://doi.org/10.1021/acsami.3c04959.
- Banoo, M.; Chatterjee, K.; Mondal, S.; Vinod, C. P.; Gautam, U. K. A 'Self-Activating' Bi3TaO7-Bi4TaO8Br Photocatalyst and Its Use in the Sustainable Production of pro-Fluorophoric Rhodamine-110. *Green Chem.* 2022, 24 (14), 5514–5523. https://doi.org/10.1039/d2gc01574a.
- (15) Nakada, A.; Saeki, A.; Higashi, M.; Kageyama, H.; Abe, R. Two-Step Synthesis of Sillén-Aurivillius Type Oxychlorides to Enhance Their Photocatalytic Activity for Visible-Light-Induced Water Splitting. *J. Mater. Chem. A* 2018, 6 (23), 10909–10917. https://doi.org/10.1039/c8ta03321h.
- (16) Zhang, X. F.; Zhang, Y.; Liu, L. Fluorescence Lifetimes and Quantum Yields of Ten Rhodamine Derivatives: Structural Effect on Emission Mechanism in Different

Solvents. J. Lumin. 2014, 145, 448–453. https://doi.org/10.1016/j.jlumin.2013.07.066.

- Kristoffersen, A. S.; Erga, S. R.; Hamre, B.; Frette, Ø. Testing Fluorescence Lifetime Standards Using Two-Photon Excitation and Time-Domain Instrumentation: Rhodamine B, Coumarin 6 and Lucifer Yellow. *J. Fluoresc.* 2014, 24 (4), 1015–1024. https://doi.org/10.1007/s10895-014-1368-1.
- (18) Liu, S.; Yin, K.; Ren, W.; Cheng, B.; Yu, J. Tandem Photocatalytic Oxidation of Rhodamine B over Surface Fluorinated Bismuth Vanadate Crystals. *J. Mater. Chem.* 2012, 22 (34), 17759–17767. https://doi.org/10.1039/c2jm33337f.
- (19) Chen, F.; Zhao, J.; Hidaka, H. Highly Selective Deethylation of Rhodamine B: Adsorption and Photooxidation Pathways of the Dye on the TiO2/SiO2 Composite Photocatalyst. *Int. J. Photoenergy* 2003, *5* (4), 209–217. https://doi.org/10.1155/S1110662X03000345.
- (20) Chang, X.; Gondal, M. A.; Al-Saadi, A. A.; Ali, M. A.; Shen, H.; Zhou, Q.; Zhang, J.; Du, M.; Liu, Y.; Ji, G. Photodegradation of Rhodamine B over Unexcited Semiconductor Compounds of BiOCl and BiOBr. *J. Colloid Interface Sci.* 2012, *377* (1), 291–298. https://doi.org/10.1016/j.jcis.2012.03.021.
- (21) Zhang, Y.; Zhou, J.; Li, Z.; Feng, Q. Photodegradation Pathway of Rhodamine B with Novel Au Nanorods @ ZnO Microspheres Driven by Visible Light Irradiation. J. Mater. Sci. 2018, 53 (5), 3149–3162. https://doi.org/10.1007/s10853-017-1779-x.
- (22) Zhang, G.; Cai, L.; Zhang, Y.; Wei, Y. Bi5+, Bi(3-x)+, and Oxygen Vacancy Induced BiOClxI1-x Solid Solution toward Promoting Visible-Light Driven Photocatalytic Activity. *Chem. A Eur. J.* 2018, 24 (29), 7434–7444. https://doi.org/10.1002/chem.201706164.
- (23) Long, C.; Ren, W.; Li, Y.; Liu, L.; Xia, Y.; Fan, H. High Oxide Ion Conductivity in Layer-Structured Bi4Ti3O12-Based Ferroelectric Ceramics. *J. Mater. Chem. C* 2019, 7 (29), 8825–8835. https://doi.org/10.1039/c9tc02507c.
- (24) Tao, X.; Shi, W.; Zeng, B.; Zhao, Y.; Ta, N.; Wang, S.; Adenle, A. A.; Li, R.; Li, C. Photoinduced Surface Activation of Semiconductor Photocatalysts under Reaction Conditions: A Commonly Overlooked Phenomenon in Photocatalysis. *ACS Catal.* 2020, *10* (10), 5941–5948. https://doi.org/10.1021/acscatal.0c00462.

CHAPTER 2.5 Conclusion & future outlook of part 2

Conclusions

In summary, the global energy crises, clean water shortages, and our heavy reliance on finite fossil fuels present monumental challenges with profound implications for the sustainability and well-being of our planet. To address these critical issues, Part 2 of this thesis is dedicated to tackling urgent global challenges through the harnessing of solar energy's vast potential via photocatalysis using Sillen Aurivillius phases as potential photocatalysts, offering innovative solutions to the persistent issues of inefficiency and instability commonly encountered with photocatalysts. The key findings of part 2 are summarized below.

Chapter 2.1. elucidates the successful fabrication of composites comprising Bi_3TaO_7 and Bi_4TaO_8X (X= Cl and Br) through ambient air treatment of precursors, demonstrating significantly enhanced photocatalytic Rhodamine B degradation (RhB, a toxic pollutant) activity compared to pure Bi_3TaO_7 and Bi_4TaO_8X . Incorporating minute amounts of noble metals into these composites suppresses the recombination of photo-generated excitons, enhancing photocatalytic RhB degradation performance. The outstanding resilience of these catalysts against harsh conditions underscores their potential for environmental remediation applications.

Chapter 2.2 realizes the concept of converting the toxic pollutant Rhodamine B (RhB) into a widely used pro-fluorophore and biologically important Rhodamine 110 (Rh110) which is recently used in SARS-CoV-2 research. Current commercial Rh110 production methods involve high-temperature condensation, resulting in complex side product separations, reduced purity, and high costs. This research demonstrates an economically viable method to convert RhB into Rh110 using Bi₃TaO₇-Bi₄TaO₈Br heterostructures as photocatalysts. These heterostructures efficiently deprotect inexpensive RhB's amino groups to yield pure Rh110 (a thousand times more expensive than RhB). A noteworthy discovery is the self-activation of the catalyst during the reaction, enhancing catalytic efficiency without the typical deactivation observed in photocatalysts over cycles. This study carries practical implications and historical significance by revitalizing the commercial value of Rh110 as a degradation intermediate in an environmentally sustainable manner, adding substantial worth to this well-established reaction.

Chapter 2.3 introduces the synthesis of highly active nanoplates of the double-layered Sillen Aurivillius phase $Sr_2Bi_3Ta_2O_{11}Cl$ through the flux method, a feat not easily accomplished through the traditional solid-state method. $Sr_2Bi_3Ta_2O_{11}Cl$ nanoplates have remarkable potential for the photocatalytic production of green and high energy density liquid fuel i.e., hydrogen peroxide (H₂O₂). Additionally, it also unveils a rare and highly pertinent self-activation property in double layered sillen Aurivillius phase, which is thoroughly examined. Its sustainable and efficient H₂O₂ production capabilities hold the potential to supplant conventional methods, representing a significant advancement in the field.

Chapter 2.4 is dedicated to the thorough exploration of double-layered Sillen Aurivillius phase Sr₂Bi₃Ta₂O₁₁Cl nanoplates for other critical catalytic applications. It highlights their efficiency in producing the highly valuable and important pro-fluorophore Rh110. This research stands out for its remarkable achievements, including an impressive 54% yield of Rh110 within just 180 minutes during the initial catalytic cycle. Equally noteworthy is the observation of an unprecedented self-activation rate, resulting in 100% efficiency by the 11th cycle, surpassing the performance of Bi₃TaO₇-Bi₄TaO₈Br heterostructures. This underscores the substantial potential of Bi₃TaO₇-Bi₄TaO₈Br heterostructures for significant Rh110 production using these nanoplates.

Future Outlook

Sillen Aurivillius phases have garnered significant attention as potential photocatalysts for various applications, primarily due to their remarkable intrinsic stability. The key to their outstanding performance lies in the hybridization of post-transition metal S orbitals, such as the Bi 6s orbital, and O 2p orbitals. This interaction leads to a unique electronic structure that marks Sillen Aurivillus as exceptionally photostable, a phenomenon elucidated by the revised lone pair effect. Over the years, researchers have dedicated significant efforts to enhance the photocatalytic activity of these phases. While their primary application has been in oxygen evolution photocatalysis, there is a growing interest in extending their use to other crucial photocatalytic reactions, including photocatalytic nitrogen fixation, carbon dioxide reduction, and various organic transformations. To fully explore the potential of Sillen Aurivillius phases in different photocatalytic reactions, a comprehensive understanding of their photoelectric properties is imperative. However, despite the progress made, several key aspects remain elusive and require further clarification. These aspects include: the absorption coefficient,

charge carrier lifetime, mobility of photoexcited charge carriers, differentiation of defect concentrations within the bulk and at the surface, and quantification of active sites on the surface. A deeper understanding of these factors is indispensable to unlock the full efficiency potential of Sillen Aurivillius phases as photocatalysts. This knowledge will not only enhance their performance but also facilitate their practical application in a variety of important photocatalytic reactions, contributing to advancements in sustainable energy and organic synthesis.

Part 3

Piezocatalytic Investigation of sillen Aurivillus

CHAPTER 3.1.

Bi₄TaO₈Cl as a New Class of Layered Perovskite Oxyhalide Materials for Piezopotential Driven Efficient Seawater Splitting



Summery

Piezocatalytic water splitting is an emerging approach to generate "green hydrogen" that can address several drawbacks of photocatalytic and electrocatalytic approaches. However, existing piezocatalysts are few and with minimal structural flexibility for engineering properties. Moreover, the scope of utilizing unprocessed water is yet unknown and may widely differ from competing techniques due to the constantly varying nature of surface potential. Herein, we present Bi₄TaO₈Cl as a representative of a class of layered perovskite Oxyhalide piezocatalysts with high hydrogen production efficiency and exciting tailorable features including the layer number, multiple cation–anion combination options, etc. In the absence of any co-catalyst and scavenger, an ultrahigh production rate is achievable (1.5 mmol g⁻¹ h⁻¹), along with simultaneous generation of value-added H₂O₂. The production by most oxides as well as piezocatalysts and has been illustrated using a double-layer model for further development.

A Manuscript based on this work has appeared in Nano Lett. 2022, 22, 22, 8867-8874

3.1.1. Introduction

A midst the growing energy and environmental crisis, the production of green hydrogen using different forms of renewable energies is fast emerging as a promising alternative.^{1–3} Piezocatalysis, a newly developed technology has demonstrated tremendous promise for hydrogen production due to many inherent benefits.⁴ Piezoelectrics are a class of materials with non-centrosymmetric crystal structures. Under external mechanical force, their constituting atoms get displaced within the unit cell to induce a mismatch of the cation and anion centers, resulting in polarization. Such piezopotential serves as a driving force for effective charge separation in the material.⁵ In contrast to photocatalysis, therein, an appropriate band-edge position is not required since band tilting under the piezoelectric field makes the conduction and valence bands appropriate for water splitting. High electrical conductivity is also not required as in the case of electrocatalysis.^{6.7}

In a pioneering work, ZnO nanowires were first used to establish the idea of a piezoelectric nanogenerator.⁸ Recently, piezoelectric materials such as perovskites (BaTiO₃), 2D (MoS₂ and C₃N₄),^{4,9} and bismuth-based layered materials (BiFeO₃, BiOCl, etc.)^{10,11} that were formerly employed as sensors, transducers, etc. have now found a new purpose in piezocatalysis. Novel strategies such as polarization enhancement by crystal and phase-boundary engineering, vacancy creation, etc. have been adapted to enhance their performances.³

3.1.2. Scope of the present investigation

In this scenario, two important factors may be considered to impede the growth and diversification of this technology. First, considering that most materials allow transient symmetry breaking in some of the crystallographic directions for use in piezocatalysis, the number of such phases explored so far has remained minuscule and crystallographically simple. As the strategies to improve their performances are diverse, complex materials with multiple flexible structural and compositional features can highly augment rational design and performance control strategies. For example, the Sillen Aurivillius phases enable the intergrowth of two structurally distinct families of crystals into one in a layered fashion where each family can be individually tuned by varying the number of layers and choosing from multiple cation/anion options,¹² providing ample scope for engineering properties such as piezoelectric constant-free charge carriers, ionic conductivity, under pressure stability, etc.¹³

Second, it is unsustainable to utilize ultrapure water for hydrogen generation. On the other hand, seawater accounts for ~97% of all water resources, which has led to enormous interest in seawater splitting by other means such as photocatalysis.^{14–16} Oceans also offer a diverse spectrum of frequencies, some closely matching those used in piezocatalysis. Shipping takes up the low-frequency range (10–500 Hz), sonars contribute to the medium-frequency range (0.5–25 kHz), while thermal noise dominates the high frequencies (>25 kHz) and is harvested using piezoelectric materials.¹⁰ However, the prospects of using seawater in piezocatalysis have never been explored. Importantly, considering the dynamic nature of piezoelectric charge density and its screening possibility by ions to profoundly influence piezocatalysis, seawater splitting efficiency in the presence of high salt concentrations may be very different and not predictable.

Herein, we report on the single-crystalline Bi_4TaO_8Cl nanoplates, a member of the structurally diverse Sillen Aurivillius phases, as a piezocatalyst to split water with remarkably high efficiency even without the assistance of any cocatalyst and scavenger to produce H_2 and value-added H_2O_2 simultaneously. The amount of H_2 generated at 37 kHz frequency is 1.5 mmol/g/h and further improves in the presence of charge-trapping agents. Importantly, we report for the first time on the scope of seawater splitting through piezocatalysis using these nanoplates with a hydrogen production rate of 854 µmol/g/h, which is appreciably superior to photocatalytic H_2 production by other oxides and many piezocatalysts using pure water. We evidence the differences with photocatalytic splitting of seawater that would streamline the use of unprocessed water during piezocatalytic water splitting.

3.1.3. Methods

3.1.3.1. Catalyst Synthesis

Synthesis of Bi₄TaO₈Cl nanoplates: The flux approach was used to synthesize Bi_4TaO_8Cl nanoplates by taking a stoichiometric molar ratio of Bi_2O_3 , BiOCl, and Ta_2O_5 (3:2:1) at a solute concentration of ($Bi_4TaO_8Cl / (Bi_4TaO_8Cl + flux)$) of 3.2 mol%. A molten salt of an alkali metal chloride (eutectic mixture (1:1) of NaCl and KCl) was used as the flux. The mixture was first grounded using a motor and pestle then transferred onto a silica boat followed by heating at 750 °C with a heating rate of 3 °C min⁻¹ for 4 h in a muffle furnace. The

products were thoroughly washed with deionized water more than five times to remove the flux after cooling at room temperature, collected by filtration, and dried at 60 $^{\circ}$ C for 10 h.¹

3.1.3.2. Photocatalytic reactions

Piezocatalytic hydrogen evolution experiments: In a typical experiment, 10 mg of the Bi₄TaO₈Cl nanoplate was dispersed in 30 mL of pure water. The solid solution sealed in a 500 ml RB was evacuated by purging the solution with N₂ for an hour to completely remove the air. The RB was then placed in the center of an ultrasonic bath (ELMA Elmasonic P300H with a power of 110W and two ultrasonic switchable frequencies i.e. 37 kHz and 80 kHz) and then exposed to different ultrasonic vibrations. The temperature of the piezo-catalytic system was controlled at 30 °C using a circulating water-cooling system. The gas thus produced was periodically withdrawn with a gas-tight syringe and examined by gas chromatography (GC). For seawater splitting, simulated seawater i.e. an aqueous solution prepared by dissolving 27.21 g of NaCl, 3.81 g of MgCl₂, 1.66 g of MgSO₄, 1.404 g of CaSO₄, 0.577 g of K₂SO₄, 0.2124 g of K₂CO₃, and 0.08 g of MgBr₂ in 1 L of distilled water was used.³

Charge trapping experiments: For the charge trapping experiments, 0.05 M AgNO₃ and 10 vol% lactic acid were used as the trapping agents for piezoelectrically-induced negative and positive charges respectively. 10 mg of the Bi₄TaO₈Cl nanoplate dispersed in 30 mL of pure water along with trapping agents AgNO₃ or lactic acid was used to check hydrogen production.

 H_2O_2 and •OH measurement: The piezocatalytic generation of H_2O_2 and •OH in pure and seawater were detected by the iodide titration method and terephthalic acid photon fluorescence method, respectively. The quantity of H_2O_2 formed in this process was determined by taking 500 µl of an aliquot from the reaction solution in every 60 min time interval and then treating it with 2 ml 0.1 M KI solution and 50 ml 0.01 M $H_{32}Mo_7N_6O_{28}$ solution. The concentration of H_2O_2 was obtained by evaluating the absorbance of the KI/ $H_{32}Mo_7N_6O_{28}$ combination at 352 nm by UV-Vis. spectroscopy.

For •OH detection, $(0.5 \times 10^{-3} \text{ M})$ terephthalic acid solution along with 10 mg of catalyst was dispersed in 30 ml of water. The homogeneous suspension was then exposed to ultrasonic irradiation. After every 60 min interval, about 1 ml of the suspension was analyzed by fluorescence spectrophotometer. The amount of •OH radicals was determined by measuring the fluorescence intensity at 425 nm with the excitation wavelength of 315 nm in a fluorescence spectrophotometer.
$O^{2^{\circ}}$ measurement: The piezocatalytic superoxide radical detection was done by taking 10 mg of Bi₄TaO₈Cl dispersed in 30 ml of nitro blue tetrazolium (NBT, conc. 0.025×10^{-3} m) aqueous solution. The homogenous suspension was sealed in a 500 ml round bottom flask (RB) and evacuated by purging the solution with N₂ for an hour to completely remove dissolved oxygen.⁵ The RB was then placed in the center of an ultrasonic bath (ELMA Elmasonic P300H) and then exposed to ultrasonic vibrations. The temperature of the piezo-catalytic system was controlled at 30 °C using a circulating water-cooling system. After every 1h interval, about 1 mL of the aliquot was taken and centrifuged to remove the catalyst. Then, the clear solution was analyzed on a UV-lambda 365 spectrophotometer.

Measurement of oxygen evolution: The sensing patch was attached to the inner wall of the flask in such a way that it is immersed in the reaction aliquot and can measure dissolved oxygen. To study oxygen evolution, first, the amount of oxygen dissolved in water was measured (317 μ mol/L) which further increased to 371 μ mol/L with the addition of 10 mg Bi₄TaO₈Cl.^{4,5} To check the amount of oxygen that evolved during catalysis, the reaction mixture was first degassed by nitrogen purging for 1 h, then subjected to ultrasonic irradiation for 4h. The oxygen was measured every 1 hour.

3.1.3.3. Characterization

All the characterization techniques are discussed in chapter 1.2.

3.1.4. Results and Discussion

3.1.4.1. Catalyst Characterization

Figure 3.1.1. a, b, and c show the crystal structure of layered bismuth-based oxyhalides, Bi₄MO₈X (M = Nb, Ta; X = Cl/Br), a member of the Sillen Aurivillius phases with the general formula $[A_{n-1}B_nO_{3n+1}]$ [Bi₂O₂] [X]_m, where n represents the number of perovskite layers.¹⁷ It consists of halide (X), fluorite (Bi₂O₂), and perovskite (MO₄) layers. As illustrated by Kageyama and co-workers recently, Bi₄MO₈X exhibits spontaneous polarization along the aaxis and the c-axis due to Bi³⁺ stereochemically active lone pair electrons and second-order John-Teller effect around M.¹⁸ Its band structure supports an enormously stable oxygen evolution in photocatalysis but is not suitable for hydrogen evolution due to poor band alignment.¹⁹ Single-crystalline Bi₄TaO₈Cl nanoplates were prepared using a eutectic flux of NaCl and KCl.²⁰ The crystallinity of the product was analyzed by powder X-ray diffraction

(XRD, **Figure 3.1.2. a**), where all diffraction peaks are assigned to pure Bi₄TaO₈Cl with the lattice constants of a = 5.54 Å, b = 5.6 Å, and c = 29.8 Å (ICDS# 89-009-3557), confirming purity.



Figure 3.1.1. Crystal structure seen from the (**a**) ac plane and (**b**) ab plane. Blue, brown, pink, and green balls represent Bi, Ta, O, and Cl atoms, respectively. (**c**) Single MO4 layer is seen from the ab plane where the arrows show the displacement of oxygen atoms from the non-titted perovskite under pressure that contributes to the polarization along the a-axis. The dotted lines represent the unit cell axis.

Scanning electron microscopy (SEM) images (**Figure 3.1.2. b**) show that the sample consists of rectangular-shaped nanoplates with an edge length of $\sim 1 \pm 0.25 \,\mu$ m. Their thicknesses are $\sim 100-120$ nm and contain smooth surfaces (**Figure 3.1.2. c**). High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED)

analysis were carried out to check the orientation and crystalline nature of the individual nanoplates (**Figure 3.1.2. d, e, f**) show TEM and HRTEM images, suggesting that each nanoplate is single-crystalline and enclosed by $\{100\}$, $\{010\}$, and $\{001\}$ facets, where the $\{001\}$ facets are dominantly exposed. The lattice fringes of 0.38 and 0.28 nm are consistent with the (110) and (020) planes, respectively, inferring that the basal facet of nanoplates is $\{001\}$. The [001] zone axis of the SAED pattern confirms dominant exposure of the $\{001\}$ facets (**Figure 3.1.2. g**) and single-crystallinity of individual plates.



Figure 3.1.2. (a) Powder XRD pattern and (b) field emission scanning electron microscopy image of the nanoplates. (c) Atomic force microscopy image and the corresponding height profile (inset) of a nanoplate, (d–f) TEM and HRTEM images and (g) single-crystalline SAED pattern acquired on a single nanoplate. Inset in (g) shows the crystal facets enclosing a nanoplate.

X-ray photoelectron spectroscopy (XPS) was performed to verify the surface elemental composition and their oxidation states in the nanoplates (**Figure 3.1.3. a**). The high-resolution Bi 4f XPS spectrum (**Figure 3.1.3. b**) is fitted with peaks at the binding energies of 159.4 and 164.6 eV corresponding to the $4f_{7/2}$ and Bi $4f_{5/2}$ states, respectively of Bi³⁺ ions. Ta 4f peaks however overlap with the Bi 5d peaks (**Figure 3.1.3. c**). The symmetrical O 1s spectrum at 529.8 eV (**Figure 3.1.3. d**) represents the lattice oxygen moieties alone. In addition, the two split-peaks of chlorine at 197.7 and 199.5 eV represent Cl 2p3/2 and Cl 2p1/2, respectively, and correspond to a Bi/Cl % abundance ratio of 75.2:24.8, confirming the pure surface

composition of Bi₄TaO₈Cl (**Figure 3.1.3. e, f**) also matched by SEM-dispersive X-ray spectroscopy analysis (**Figure 3.1.3. g**).



Figure 3.1.3. (a) XPS survey spectrum, (b) high-resolution XPS spectra of Bi 4f, (c) Bi-5d and Ta-4f (peaks at 26.7 & 24.84 eV correspond to $Ta^{5+} 4f_{7/2}$ and $Ta^{5+} 4f_{5/2}$ while the peak at 25.6 & 28.6 eV belongs to Bi³⁺ 5d_{5/2} and Bi³⁺ 5d_{3/2}), (d) O1s, and (e) Cl 2p (f) Plot showing percentage abundance of Bi with respect to chlorine in the Bi₄TaO₈Cl nanoplates.(g) FE-SEM EDS spectrum of Bi₄TaO₈Cl (h) UV-Vis diffuse reflectance spectroscopy of Bi₄TaO₈Cl (inset is corresponding Tauc Plot) (i) Mott–Schottky plots of Bi₄TaO₈Cl measured at 500 and 1000 Hz.

The electronic band structure was investigated by UV–vis absorption spectroscopy and Mott–Schottky measurements (**Figure 3.1.3. h, i**). UV–Vis diffuse reflectance spectrum of Bi_4TaO_8Cl exhibiting a steep absorption edge starting at 498 nm, in agreement with previous findings. The corresponding optical bandgap was estimated as 2.55 eV from the Tauc plot using

the equation $(\alpha h\nu) = A (h\nu - Eg)$ n where Eg = optical bandgap energy, hv = light energy, A = constant, α = absorption coefficient and n = 2 considering an indirect bandgap.1 From the x-axis intercepts, the flat potentials of Bi₄TaO₈Cl were obtained at -0.3 V versus NHE, as established in the literatures. Combined with the band gap value of 2.55 eV obtained from the Tauc plot, the VB position of Bi₄TaO₈Cl was estimated at +2.25 V.



Figure 3.1.4. (a) Resonant peaks on a nanoplate recorded during PFM for different applied voltages showing a (b) linear correlation between the operating voltage and the amplitude. (c-e) Topography, amplitude, and phase images, respectively, of a Bi₄TaO₈Cl nanoplate. (f, g) Displacement–voltage curve and phase curve of Bi₄TaO₈Cl. (h, i) KPFM potential mapping image of Bi₄TaO₈Cl in the dark and the corresponding surface potential.

The piezoelectric properties of the nanoplates were characterized by piezoelectric force microscopy (PFM) and Kelvin probe force microscopy (KPFM). The pronounced resonance peaks at 322 kHz reflect the linear piezoelectric response at various voltages (Figure **3.1.4. a**, **b**) on a 100 nm thick nanoplate, as shown in Figure 3.1.4. **c** and exhibit a close match of the topography image to the corresponding phase and amplitude images (Figure 3.1.4. d, e). The local piezoresponse hysteresis loops were acquired by sweeping the DC bias from -10to 10 V and simultaneously measuring the phase and amplitude responses. We observed a clear butterfly-shaped amplitude loop (Figure 3.1.4. f) with a maximum effective piezoelectric coefficient determined as 53.6 pm/V (a deviation of ~10% in various nanoplates), indicating that the Bi4TaO8Cl nanoplate has pronounced piezoelectric properties. In addition, in the corresponding phase-angle-voltage hysteresis plot (Figure 3.1.4. g), a shift of 180° under the reversal of the DC bias confirmed polarization switching within the nanoplate. For a better comprehension of charge transport, a piezoelectric potential map (Figure 3.1.4. h, i) was acquired by scanning the KPFM cantilever over the nanoplate, and a contact potential difference (CPD) between the tip and the nanoplate was measured, revealing a surface potential of -18 mV. The work function φ was be determined by the equation:²¹

$$\frac{\varphi_{tip}-\varphi_{sample}}{e} = V_{CDP}$$

Where V_{CPD} is the CPD between tip and sample, φ_{tip} and φ_{sample} are the work function of the tip and the sample, respectively, and e represents elementary charge. Highly oriented pyrolytic graphite (HOPG, $\varphi = 4.66 \text{ eV}$) was used as a reference for calibrating φ_{tip} , and the work function of the nanoplate was estimated as 5.142 eV. Under sonication, however, the individual nanoplates may position themselves exposing different facets to sonic waves, giving rise to transient piezopotentials in all such facets. This is different from the potential developed under light irradiation where subsequent exciton transfer to the catalyst surface occurs in certain crystallographic directions only.^{22,23} In Bi₄TaO₈Cl, the photogenerated electrons were shown to migrate to the {100} and {010} facets only to facilitate their participation in reductive reactions in a facet-selective manner. To verify the extent of piezopotential generation under sonication, we attempted to piezocatalytically reduce Pt⁴⁺ and Ag⁺ on the nanoplates with the assumption that their reduction requires a potential higher than that for protons, and successful deposition will guarantee H₂ evolution in all facets, a huge advantage over the photocatalytic approach (in addition to "not needing" cocatalysts and scavengers). **Figure 3.1.5. a, b, c** shows

exposed facets of the nanoplates showing that the piezopotential generated is not facetselective. The same was the case for Pt, too (**Figure 3.1.5. d and inset**). Therefore, the random generation of piezopotential on the catalyst surface (**Figure 3.1.5. e**) is expected to enrich the number of reductive reactive sites leading to an improved hydrogen generation efficiency.



Figure 3.1.5. (a) FE-SEM image, (b) Schematic showing Piezocatalytic Ag loading on all facets of the nanoplate. (c) FE-SEM EDS data showing the presence of Ag. (d) SEM image showing deposition of Pt on all (inset show schematic for Pt deposition on all facets under ultra-sonication). (e) Schematic showing generation of polarization in different directions in the nanoplate.

3.1.4.2. Piezocatalytic Hydrogen Generation

To explore the Piezocatalytic efficiency of the bare Bi_4TaO_8Cl nanoplates, the splitting of water was carried out under ultrasonic vibrations using different frequencies and power. Notably, no hole scavengers were used, unlike photocatalytic approaches, since their use can be considered to be a disadvantage due to cost and usage in large quantities as compared to the amount of hydrogen produced. Similarly, no Pt-based cocatalyst was used either. **Figure 3.1.6. a** shows the typical hydrogen production rates under different conditions, i.e., in the presence or the absence of a catalyst. As observed earlier, too, we found that ultrasound alone can split water to produce a trace amount of hydrogen (1.92 µmol in 4 h).²⁴ This is unlike in the presence of the catalyst where hydrogen production continuously increases in significantly larger quantities (50 μ mol in 4 h or 1.508 mmol g⁻¹ h⁻¹ of catalyst), establishing that the co-catalyst-free Bi₄TaO₈Cl nanoplates play an important role in ultrasonic water splitting under scavenger-free conditions. Moreover, the oxidation of water simultaneously produces value-added H₂O₂ as a counter-reaction, inferring that the piezopotential-induced positive charges oxidize the OH⁻ ions to H₂O₂. The production rate of H₂O₂ is 399 μ mol g⁻¹ h⁻¹ (**Figure 3.1.6. b**). Note that we have also observed oxygen evolution (**Figure 3.1.6. c, d**), which can evolve either from the oxidation of water or from the decomposition of H₂O₂. To investigate the active species responsible for water splitting, Piezocatalytic experiments were carried out using lactic acid



Figure 3.1.6. (a) Ultrasound irradiation-induced H₂ production rate in the presence or absence of a piezocatalyst. (b) UV-Vis. absorbance plot showing the formation of H₂O₂ during H₂ production.(c) Plot showing oxygen evolution under ultrasonication over Bi₄TaO₈Cl, the amount of oxygen increases with increasing the ultrasonication time with an evolution rate of 69 μ mol/h/g (standard deviation ~ 10%) (Note that oxygen evolution is in addition to H₂O₂ generation) (d) UV-Vis. absorption spectra of nitro blue tetrazolium (NBT) over Bi4TaO8Cl under sonication confirming superoxide radical formation. 1 mole of NBT can react with 4 mol of \cdot O2 – and display a maximum in UV-Vis. absorbance spectrum at 259 nm. (e) Plot showing the effect of trapping agents on H₂ production. (f) Fluorescence spectra of TA solution over Bi4TaO₈Cl during ultrasonic irradiation.

and AgNO₃ as positive and negative charge-trapping reagents, respectively (**Figure 3.1.6. e**). In the presence of lactic acid, the recombination of the induced charges was significantly suppressed due to scavenging of positive charges, leading to an increase in the lifetime of the surface negative charges and 14% increase in H₂ generation.²² Conversely, H₂ generation was highly suppressed in the presence of AgNO₃, suggesting that the induced negative charges are its primary active species.⁹ To verify that the surface positive charges oxidize the OH to • OH radicals during H₂O₂ production, we further detected these radicals using terephthalic acid (**Figure 3.1.6. f**).²² The strong photoluminescence peak at 425 nm confirms that Bi₄TaO₈Cl generates a large amount of • OH under ultrasonic agitation. However, the molar ratio of H₂ and H₂O₂ thus produced is not 1:1, which may result from the incomplete •OH conversion,



Figure 3.1.7. (a, b) Hydrogen production as a function of ultrasonic frequency and power respectively. (c) H₂ production by the same Bi₄TaO₈Cl powder in seven successive cycles.

back reaction, and two-step reactions of water oxidation decreasing the H_2O_2 production rate. We subsequently investigated the effect of frequency and power on hydrogen production. As shown in **Figure 3.1.7. a**, hydrogen production is high at 37 kHz compared to 80 kHz probably due to proximity to the resonance frequency of the catalyst.10 **Figure 3.1.7. b** shows the influence of ultrasonic power on hydrogen production at 37 kHz. The rate increases with the increasing power from 40% (44 W) to 100% (110 W). However, the increase is nonlinear, and the yield of hydrogen increases nearly by 2.5, 6.5, and 18 times when power was raised from 40% to 60, 80, and 100%, respectively. The relationship between the piezoelectric charge density (Qp), piezoelectric coefficient (d), and external stress (T) can be described as Qp= dT. Higher vibrational power leads to higher T and more piezoelectric charges, resulting in a higher

hydrogen production rate. While such an increase in the H₂ yield is quite encouraging, little is known about the stress transfer mechanisms and surface structural integrity during piezocatalysis to justify the nonlinear increase, and a comprehensive understanding should lead to rational improvement strategies. The H₂ evolution rate for Bi₄TaO₈Cl remains almost constant over seven consecutive cycles for a total of 28 h (**Figure 3.1.7. c**), indicating that the highly stability of the catalyst (also confirmed by PXRD, TEM, HRTEM and BET seen in **Figure 3.1.8. a, b, c, d** respectively). The comparison of the specific surface area and XRD pattern of the fresh and the used catalysts show that there are no appreciable changes in their physical properties. The TEM analysis of the used sample showed that the morphology of the sample did not change, confirming high stability.



Figure 3.1.8. (a) Powder XRD patterns of Bi₄TaO₈Cl nanoplates before and after catalysis. (b) TEM and HRTEM image of the Bi₄TaO₈Cl nanoplates after catalysis. (c) BET surface area measurements of the Bi₄TaO₈Cl nanoplates before and after catalysis.



3.1.4.3. Seawater Splitting Prospects Using Piezocatalysis

Figure 3.1.9. (a) Comparison of H₂ production from pure and simulated seawater by $Bi_4TaO_8Cl.$ (b) UV-Vis. absorption spectra of KI/ $H_{32}Mo_7N_6O_{28}$ at 352 nm showing the formation of H_2O_2 in seawater. (c, d) Comparison of H₂ production performance of Bi_4TaO_8Cl in pure water and seawater with the photocatalytic activity of Sillen Aurivillius phases and other reported piezocatalysts (including those employing further activation strategies by using scavengers, co-catalysts, and light), respectively.

Intrigued by high simultaneous production of H_2 and H_2O_2 using the nanoplates, we investigated the prospects of piezocatalytic seawater splitting, which is characterized by the presence of large concentrations of different salts, including the most common Na⁺, Mg²⁺, Ca²⁺, K⁺, Cl⁻, and SO₄ ²⁻ accounting for >90% of the total salt content.²⁵ We used a combination of various salts (NaCl, MgCl₂, MgSO₄, CaSO₄, K₂SO₄, K₂CO₃, and MgBr₂) in predetermined concentrations to check the piezocatalytic seawater splitting efficiency (**Figure 3.1.9 a, b**). The H₂ and H₂O₂ production rate of the nanoplates in simulated seawater is 854 and 282 µmol g⁻¹ h⁻¹, respectively. It is encouraging that, despite some decrease, the H₂ generation rates from seawater are quite superior to (i) photocatalytic H₂ production by the co-catalyst-loaded Sillen

Catalyst	Energy Source	$H_2 \ (\mu mol/h/g)$	Scavenger	Reference			
Piezocatalysis							
Bi ₄ TaO ₈ Cl	110 W, 37 kHz	1500 (Pure water)	No Scavenger	This work			
		854 (Souvetor)					
Sr _{0.5} Ba _{0.5} Nb ₂ O ₆	110 W, 40 kHz	109.4	TEOA 5%Vol	7			
SnSe NS	100 W, 45 kHz	48.4	Glucose (0.1 M)	8			
Ni/GaN Nw	110 W, 40 kHz	88.3	TEOA 15% Vol	9			
BiFeO ₃ NS	100 W, 45 kHz	124.1	Na ₂ SO ₃ (0.05 M)	10			
Di Na TiO	40 HU- 100 W	506.70	McOII 109/ 351	11			
B1 _{1/2} Na _{1/2} 110 ₃	40 KH2, 100 W	500.70	MeOH 10% WI	11			
Photocatalysis							
Pt (0.5Wt%)	Xe lamp 300 W	1	Methanol 20 vol%	12			
Bi ₄ NbO ₈ Cl							
Pt(0.5wt%)	Xe lamp 300 W	0.75	Methanol 20 vol%	13			
Bi ₄ TaO ₈ Br							
Pt(0.5wt%)	Xe lamp 300 W	1.25	Methanol 20 vol%	14			
Bi ₄ TaO ₈ Cl							
Pt(1wt%)	Xe lamp 300 W	10	Methanol 20 vol%	14			
BaBisTisOuCl							
Pt(1wt%)	Xe lamp 300 W	30	Methanol 20 vol%	14			
Ba-Bi-Ti-OCl							
Pt(1wt%)	Xe lamp 300 W	90	Methanol 20 vol%	14			
Ba-Bi-Ti-O-Cl							
Bi ₄ TaO ₈ Cl/graphene	Xe lamp 200 W	12	Methanol 10 vol%	15			
Piezo-photocatalysis							
Pt/Bi _{0.5} Na _{0.5} TiO ₃	110 W, 40 kHz	158	TEOA 15% Vol	16			
	Xe lamp 300 W						
ZnSnO ₃ NW	250 W, 40 kHz	857	Alcohol 50% Vol	17			
	Xelamp 150 W						
Pt-KNbO ₃ /MoS ₂	110 W, 40 kHz	96	TEOA 15% vol	18			
	Xalamp 200 W						
(NBT-BNT)/CODs	200 W, 40 kHz	747	TEOA 15% Vol	19			
	N 1						
TEOA-T	TEOA-Triethanolamine NBT-BNT-(NaBi)TiO ₂ -BaTiO ₂						

Table 3.1.1. Comparison table showing piezocatalytic H₂ evolution activity of Bi₄TaO₈Cl as compared to other reported photocatalysts, piezocatalysts, and photo piezo catalysts.

Aurivillius phases and some other oxides as well as (ii) several previously reported piezocatalysts using ultrapure water.^{13,26–31} Photocatalytic H₂ evolution by Bi₄TaO₈Cl nanoplates has barely been investigated so far and is unlikely to be good, even though very tiny amounts of H₂ evolution (5–100 μ mol g⁻¹ h⁻¹) using various other Sillen Aurivillius phases were observed occasionally, but only after Pt loading (**Figure 3.1.9 c**). In that sense, it is remarkable that, under piezocatalytic conditions, all facets develop enriched reductive sites, resulting in significant hydrogen production. Moreover, the production in this study outperforms all previously reported oxide piezocatalysts in terms of the H2 generation rate (**Figure 3.1.9 d and Table 3.1.1.**) including coveted materials such as PZT.

3.1.4.4. Mechanism of Piezocatalysis and Influencing Factors in Seawater Splitting

To understand the mechanism more clearly, we can approximate the piezocatalytic system to a conventional electrocatalytic system where an external electric potential is applied for driving electron transfer reactions. In piezocatalysis, the external power source is replaced by an internal piezoelectric potential developed from stress. When a strained piezoelectric material is placed within an aqueous medium of finite conductivity and polarizability, its piezoelectricity-induced surface charges can be diminished in two ways: (i) capacitive current, leading to the formation of double layers around piezoelectric surfaces, thus screening surface potential and reducing the probability of a redox reaction; (ii) faradic current, the other fraction of the charges that transfer between the solution and piezoelectric surfaces and thus inducing a redox reaction. A fast charge transfer between the piezoelectric and electroactive species is crucial for the available piezo-induced surface charges to completely participate in the process. Otherwise, the direction of the generated piezoelectric field changes frequently in the ultrasonic process, resulting in substantial recombination of piezoelectric charges. As shown Figure **3.1.10. a**, **b** a steady electrochemical equilibrium between Bi₄TaO₈Cl and the solution is achievable in a solution. However, when stress is applied to the nanoplate by the implosive collapse of a cavitation bubble during piezocatalysis, the nanoplate deforms and creates a favorable energetics landscape for H2 evolution at the negatively charged side by the transfer of electrons from its valence band to species in solution.



Figure 3.1.10. (a, b) Energy band diagram of unstrained and strained Bi_4TaO_8Cl showing band bending and charge transfer during piezocatalysis. (c) Schematic illustration of the hydrogen and H_2O_2 production under piezocatalytic conditions over a polarized Bi_4TaO_8Cl nanoplate. Inset shows the polarization direction along the [001] crystal axis with maximal surface exposure19 (color codes for the atoms are kept the same as in Figure 7.1.). (d, e) Schematic of

the impeded H_2 evolution process within the double layer while having high electrolyte concentrations as in seawater.

Simultaneously, on the positive side of the nanoplate, water oxidation takes place with a net electron flow into the piezocatalysts conduction band. **Figure 3.1.10. c** schematically depicts the process of hydrogen and H_2O_2 production over Bi₄TaO₈Cl nanoplates, where piezoelectric modulation of charge carriers naturally allows the enhancement of electrochemical-equivalent processes occurring at the piezoelectric material and solution interface, while charge-carrier conduction during conventional photocatalysis is rather poor in Bi₄TaO₈Cl. The H₂ production from the piezocatalytic splitting of seawater decreases as compared to pure water. Consider the following equation:⁶

$$\Delta Q_p = \int I_f \mathrm{dt} + C_d V_d$$

Where ΔQ_p is the piezoelectricity-induced surface charge, If is the faradic current, and CdVd is related to the capacitive current (Ic = dCdVd/dt, in which Cd and Vd are the double-layer capacitance and voltage-drop across the double layer). A high Cd would potentially affect piezocatalytic efficiency by diminishing If. As such, concentrated electrolytes in piezocatalytic seawater splitting systems may severely restrict the efficacy of the piezocatalytic process by increasing Cd and screening the piezoelectric potential by draining the free energy available for driving redox reaction.⁶ **Figure 3.1.10. d, e** schematically illustrates the decrease in H₂ production by Bi₄TaO₈Cl in high electrolyte concentration (seawater) due to this effect. Interestingly, it is widely reported in electrocatalytic seawater splitting literature that the reduced H₂ evolution activity in saline conditions is attributable to the blocking of active sites.^{32,33} Several cations present in saline water are known to undergo either electrodeposition through reduction or are deposited as hydroxides at the cathode under reductive conditions to decrease faradic efficiency, and similar effects may arise during piezocatalysis.^{34,35}

3.1.5. Conclusion

In conclusion, we present Bi_4TaO_8Cl as a member of a new class of layered perovskite oxyhalide materials with highly efficient piezocatalytic hydrogen production efficiency even in the absence of any cocatalyst and scavenger. As a counterreaction, the process also generates value-added H_2O_2 simultaneously. We have further explored the scope of using seawater for piezocatalytic hydrogen generation for the first time. Even though the efficiency is somewhat less, it is appreciably superior to photocatalytic H_2 production by most oxide materials and piezocatalysts. A double-layer model has been proposed to illustrate the effects that would auger further developments of new piezocatalytic phases and the use of unprocessed water in this emerging approach.

Bibliography:

(1) Chen, S.; Takata, T.; Domen, K. Particulate Photocatalysts for Overall Water Splitting. Nat. Rev. Mater. 2017, 2, 1–17. https://doi.org/10.1038/natrevmats.2017.50.

(2) Zhou, Z.; Pei, Z.; Wei, L.; Zhao, S.; Jian, X.; Chen, Y. Electrocatalytic Hydrogen Evolution under Neutral PH Conditions: Current Understandings, Recent Advances, and Future Prospects. Energy Environ. Sci. 2020, 13 (10), 3185–3206. https://doi.org/10.1039/d0ee01856b.

(3) Tu, S.; Guo, Y.; Zhang, Y.; Hu, C.; Zhang, T.; Ma, T.; Huang, H. Piezocatalysis and Piezo-Photocatalysis: Catalysts Classification and Modification Strategy, Reaction Mechanism, and Practical Application. Adv. Funct. Mater. 2020, 30 (48), 1–31. https://doi.org/10.1002/adfm.202005158.

(4) Hong, K. S.; Xu, H.; Konishi, H.; Li, X. Direct Water Splitting through Vibrating Piezoelectric Microfibers in Water. J. Phys. Chem. Lett. 2010, 1 (6), 997–1002. https://doi.org/10.1021/jz100027t.

(5) Yan, X.; Li, G.; Wang, Z.; Yu, Z.; Wang, K.; Wu, Y. Recent Progress on Piezoelectric Materials for Renewable Energy Conversion. Nano Energy 2020, 77 (May), 105180. https://doi.org/10.1016/j.nanoen.2020.105180.

Wang, K.; Han, C.; Li, J.; Qiu, J.; Sunarso, J.; Liu, S. The Mechanism of Piezocatalysis:
Energy Band Theory or Screening Charge Effect? Angew. Chemie - Int. Ed. 2022, 61 (6).
https://doi.org/10.1002/anie.202110429.

 (7) Starr, M. B.; Wang, X. Fundamental Analysis of Piezocatalysis Process on the Surfaces of Strained Piezoelectric Materials. Sci. Rep. 2013, 3 (1), 1–8. https://doi.org/10.1038/srep02160.

(8) Wang, Z. L.; Song, J. Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays. Science (80-.). 2006, 312 (5771), 242–246. https://doi.org/10.1126/science.1124005.

(9) Hu, C.; Chen, F.; Wang, Y.; Tian, N.; Ma, T.; Zhang, Y.; Huang, H. Exceptional Cocatalyst-Free Photo-Enhanced Piezocatalytic Hydrogen Evolution of Carbon Nitride Nanosheets from Strong In-Plane Polarization. Adv. Mater. 2021, 33 (24), 1–9. https://doi.org/10.1002/adma.202101751.

176

You, H.; Wu, Z.; Zhang, L.; Ying, Y.; Liu, Y.; Fei, L.; Chen, X.; Jia, Y.; Wang, Y.;
Wang, F.; Ju, S.; Qiao, J.; Lam, C.; Huang, H. Harvesting the Vibration Energy of BiFeO 3
Nanosheets for Hydrogen Evolution . Angew. Chemie 2019, 131 (34), 11905–11910.
https://doi.org/10.1002/ange.201906181.

(11) Zhou, X.; Yan, F.; Wu, S.; Shen, B.; Zeng, H.; Zhai, J. Remarkable Piezophoto Coupling Catalysis Behavior of BiOX/BaTiO3 (X = Cl, Br, Cl0.166Br0.834) Piezoelectric Composites. Small 2020, 16 (26), 1–15. https://doi.org/10.1002/smll.202001573.

(12) Li, L.; Han, Q.; Tang, L.; Zhang, Y.; Li, P.; Zhou, Y.; Zou, Z. Flux Synthesis of Regular Bi4TaO8Cl Square Nanoplates Exhibiting Dominant Exposure Surfaces of {001} Crystal Facets for Photocatalytic Reduction of CO2 to Methane. Nanoscale 2018, 10 (4), 1905–1911. https://doi.org/10.1039/c7nr06279f.

(13) Ozaki, D.; Suzuki, H.; Ogawa, K.; Sakamoto, R.; Inaguma, Y.; Nakashima, K.; Tomita,
O.; Kageyama, H.; Abe, R. Synthesis, Band Structure and Photocatalytic Properties of Sillén-Aurivillius Oxychlorides BaBi5Ti3O14Cl, Ba2Bi5Ti4O17Cl and Ba3Bi5Ti5O20Cl with Triple-, Quadruple- And Quintuple-Perovskite Layers. J. Mater. Chem. A 2021, 9 (13), 8332– 8340. https://doi.org/10.1039/d0ta12550d.

(14) Xu, W.; Zhao, X.; An, X.; Wang, S.; Zhang, J.; Li, Z.; Wu, W.; Wu, M. Alkali Halide
Boost of Carbon Nitride for Photocatalytic H2 Evolution in Seawater. ACS Appl. Mater.
Interfaces 2020, 12 (43), 48526–48532. https://doi.org/10.1021/acsami.0c13060.

(15) Wu, Q.; Cao, J.; Wang, X.; Liu, Y.; Zhao, Y.; Wang, H.; Liu, Y.; Huang, H.; Liao, F.;
Shao, M.; Kang, Z. A Metal-Free Photocatalyst for Highly Efficient Hydrogen Peroxide
Photoproduction in Real Seawater. Nat. Commun. 2021, 12 (1).
https://doi.org/10.1038/s41467-020-20823-8.

(16) Dang, H. Van; Wang, Y. H.; Wu, J. C. S. Z-Scheme Photocatalyst Pt/GaP-TiO2-SiO2:Rh for the Separated H2 Evolution from Photocatalytic Seawater Splitting. Appl. Catal. B Environ. 2021, 296 (April). https://doi.org/10.1016/j.apcatb.2021.120339.

(17) Chatterjee, K.; Banoo, M.; Mondal, S.; Sahoo, L.; Gautam, U. K. Synthesis of Bi3TaO7-Bi4TaO8Br Composites in Ambient Air and Their High Photocatalytic Activity upon Metal Loading. Dalt. Trans. 2019, 48 (21), 7110–7116. https://doi.org/10.1039/c9dt00068b.

(18) Zhong, C.; Ishii, Y.; Tassel, C.; Zhu, T.; Kato, D.; Kurushima, K.; Fujibayashi, Y.; Saito, T.; Ogawa, T.; Kuwabara, A.; Mori, S.; Kageyama, H. Lone-Pair-Induced Intra- and Interlayer Polarizations in Sillén-Aurivillius Layered Perovskite Bi4NbO8Br. Inorg. Chem. 2022, 61 (25), 9816–9822. https://doi.org/10.1021/acs.inorgchem.2c01358.

(19) Zhong, C.; Mizushima, D.; Hirata, K.; Ishii, Y.; Kurushima, K.; Kato, D.; Nakajima, H.; Mori, S.; Suzuki, H.; Ogawa, K.; Abe, R.; Fukuma, T.; Kageyama, H. Domain Observation in the Visible-Light Photocatalyst Bi4NbO8Br with the Layered Perovskite Structure. Appl. Phys. Express 2020, 13 (9). https://doi.org/10.35848/1882-0786/abb287.

Banoo, M.; Chatterjee, K.; Mondal, S.;Vinod, C.P.; Gautam, U. K. A 'self-activating'
Bi3TaO7–Bi4TaO8Br photocatalyst and its use in the sustainable production of profluorophoric rhodamine-110.Green Chem., 2022, 24, 5514-5523.
https://doi.org/10.1039/D2GC01574A

(22) Hu, C.; Huang, H.; Chen, F.; Zhang, Y.; Yu, H.; Ma, T. Coupling Piezocatalysis and Photocatalysis in Bi4NbO8X (X = Cl, Br) Polar Single Crystals. Adv. Funct. Mater. 2020, 30 (7), 1–10. https://doi.org/10.1002/adfm.201908168.

(23) Takata, T.; Jiang, J.; Sakata, Y.; Nakabayashi, M.; Shibata, N.; Nandal, V.; Seki, K.; Hisatomi, T.; Domen, K. Photocatalytic Water Splitting with a Quantum Efficiency of Almost Unity. Nature 2020, 581 (7809), 411–414. https://doi.org/10.1038/s41586-020-2278-9.

(24) Zhao, Y.; Huang, X.; Gao, F.; Zhang, L.; Tian, Q.; Fang, Z. Bin; Liu, P. Study on Water Splitting Characteristics of CdS Nanosheets Driven by the Coupling Effect between Photocatalysis and Piezoelectricity. Nanoscale 2019, 11 (18), 9085–9090. https://doi.org/10.1039/c9nr01676g.

(25) Ji, S. M.; Jun, H.; Jang, J. S.; Son, H. C.; Borse, P. H.; Lee, J. S. Photocatalytic Hydrogen Production from Natural Seawater. J. Photochem. Photobiol. A Chem. 2007, 189
(1), 141–144. https://doi.org/10.1016/j.jphotochem.2007.01.011.

(26) Tao, X.; Zhao, Y.; Mu, L.; Wang, S.; Li, R.; Li, C. Bismuth Tantalum Oxyhalogen: A Promising Candidate Photocatalyst for Solar Water Splitting. Adv. Energy Mater. 2018, 8 (1), 1–7. https://doi.org/10.1002/aenm.201701392.

(27) Fujito, H.; Kunioku, H.; Kato, D.; Suzuki, H.; Higashi, M.; Kageyama, H.; Abe, R. Layered Perovskite Oxychloride Bi4NbO8Cl: A Stable Visible Light Responsive Photocatalyst for Water Splitting. J. Am. Chem. Soc. 2016, 138 (7), 2082–2085. https://doi.org/10.1021/jacs.5b11191.

(28) Zhang, Y.; Thuy Phuong, P. T.; Hoang Duy, N. P.; Roake, E.; Khanbareh, H.; Hopkins, M.; Zhou, X.; Zhang, D.; Zhou, K.; Bowen, C. Polarisation Tuneable Piezo-Catalytic Activity of Nb-Doped PZT with Low Curie Temperature for Efficient CO2reduction and H2generation. Nanoscale Adv. 2021, 3 (5), 1362–1374. https://doi.org/10.1039/d1na00013f.

(29) Zhang, M.; Zhao, S.; Zhao, Z.; Li, S.; Wang, F. Piezocatalytic Effect Induced Hydrogen Production from Water over Non-Noble Metal Ni Deposited Ultralong GaN Nanowires. ACS Appl. Mater. Interfaces 2021, 13 (9), 10916–10924. https://doi.org/10.1021/acsami.0c21976.

(30) Xiao, H.; He, J.; Lu, X.; Wang, F.; Guo, Y. Bandgap-Engineered Ferroelectric Single-Crystalline NBT-BT Based Nanocomposites with Excellent Visible Light-Ultrasound Catalytic Performance. Chemosphere 2022, 306 (June), 135543. https://doi.org/10.1016/j.chemosphere.2022.135543.

(31) Razavi-Khosroshahi, H.; Mohammadzadeh, S.; Fuji, M. Bi4TaO8Cl/Graphene Nanocomposite for Photocatalytic Water Splitting. Adv. Powder Technol. 2020, 31 (1), 381–386. https://doi.org/10.1016/j.apt.2019.10.030.

(32) Wang, C.; Shang, H.; Jin, L.; Xu, H.; Du, Y. Advances in Hydrogen Production from Electrocatalytic Seawater Splitting. Nanoscale 2021, 13 (17), 7897–7912. https://doi.org/10.1039/d1nr00784j.

(33) Xiao, X.; Yang, L.; Sun, W.; Chen, Y.; Yu, H.; Li, K.; Jia, B.; Zhang, L.; Ma, T. Electrocatalytic Water Splitting: From Harsh and Mild Conditions to Natural Seawater. Small 2022, 18 (11), 1–16. https://doi.org/10.1002/smll.202105830.

(34) Khatun, S.; Hirani, H.; Roy, P. Seawater Electrocatalysis: Activity and Selectivity. J. Mater. Chem. A 2021, 9 (1), 74–86. https://doi.org/10.1039/d0ta08709b.

(35) Ke, S. C.; Chen, R.; Chen, G. H.; Ma, X. L. Mini Review on Electrocatalyst Design for Seawater Splitting: Recent Progress and Perspectives. Energy and Fuels 2021, 35 (16), 12948– 12956. <u>https://doi.org/10.1021/acs.energyfuels.1c02056</u>.

References of Table 7.1.

 Li, L.; Han, Q.; Tang, L.; Zhang, Y.; Li, P.; Zhou, Y.; Zou, Z. Flux Synthesis of Regular Bi4TaO8Cl Square Nanoplates Exhibiting Dominant Exposure Surfaces of {001} Crystal Facets for Photocatalytic Reduction of CO2 to Methane. Nanoscale 2018, 10 (4), 1905–1911. https://doi.org/10.1039/c7nr06279f.

Moun, M.; Vasdev, A.; Pujar, R.; Priya Madhuri, K.; Mogera, U.; John, N. S.; Kulkarni,
G. U.; Sheet, G. Enhanced Electrical Transport through Wrinkles in Turbostratic Graphene
Films. Appl. Phys. Lett. 2021, 119 (3) 033102. https://doi.org/10.1063/5.0056212.

(3) Ji, S. M.; Jun, H.; Jang, J. S.; Son, H. C.; Borse, P. H.; Lee, J. S. Photocatalytic Hydrogen Production from Natural Seawater. J. Photochem. Photobiol. A Chem. 2007, 189
(1), 141–144. https://doi.org/10.1016/j.jphotochem.2007.01.011.

(4) Kanan, M. W.; Nocera, D. G. In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co2+. Science (80-.). 2008, 321 (5892), 1072–1075. https://doi.org/10.1126/science.1162018.

(5) Mondal, S.; Karthik, P. E.; Sahoo, L.; Chatterjee, K.; Sathish, M.; Gautam, U. K. High and Reversible Oxygen Uptake in Carbon Dot Solutions Generated from Polyethylene Facilitating Reactant-Enhanced Solar Light Harvesting. Nanoscale 2020, 12 (19), 10480–10490. https://doi.org/10.1039/d0nr00266f.

(6) Tao, X.; Shi, W.; Zeng, B.; Zhao, Y.; Ta, N.; Wang, S.; Adenle, A. A.; Li, R.; Li, C. Photoinduced Surface Activation of Semiconductor Photocatalysts under Reaction Conditions: A Commonly Overlooked Phenomenon in Photocatalysis. ACS Catal. 2020, 10 (10), 5941–5948. https://doi.org/10.1021/acscatal.0c00462.

(7) Dai, J.; Shao, N.; Zhang, S.; Zhao, Z.; Long, Y.; Zhao, S.; Li, S.; Zhao, C.; Zhang, Z.; Liu, W. Enhanced Piezocatalytic Activity of Sr0.5Ba0.5Nb2O6Nanostructures by Engineering Surface Oxygen Vacancies and Self-Generated Heterojunctions. ACS Appl. Mater. Interfaces 2021, 13 (6), 7259–7267. https://doi.org/10.1021/acsami.0c21202.

Li, S.; Zhao, Z.; Li, J.; Liu, H.; Liu, M.; Zhang, Y.; Su, L.; Pérez-Jiménez, A. I.; Guo,
Y.; Yang, F.; Liu, Y.; Zhao, J.; Zhang, J.; Zhao, L. D.; Lin, Y. Mechanically Induced Highly
Efficient Hydrogen Evolution from Water over Piezoelectric SnSe Nanosheets. Small 2022, 18
(29), 1–9. https://doi.org/10.1002/smll.202202507.

(9) Zhang, M.; Zhao, S.; Zhao, Z.; Li, S.; Wang, F. Piezocatalytic Effect Induced Hydrogen
 Production from Water over Non-Noble Metal Ni Deposited Ultralong GaN Nanowires. ACS
 Appl. Mater. Interfaces 2021, 13 (9), 10916–10924. https://doi.org/10.1021/acsami.0c21976.

You, H.; Wu, Z.; Zhang, L.; Ying, Y.; Liu, Y.; Fei, L.; Chen, X.; Jia, Y.; Wang, Y.; Wang, F.; Ju, S.; Qiao, J.; Lam, C. H.; Huang, H. Harvesting the Vibration Energy of BiFeO3 Nanosheets for Hydrogen Evolution. Angew. Chemie - Int. Ed. 2019, 58 (34), 11779–11784. https://doi.org/10.1002/anie.201906181.

(11) Ranjan, A.; Hsiao, K. Y.; Lin, C. Y.; Tseng, Y. H.; Lu, M. Y. Enhanced Piezocatalytic Activity in Bi1/2Na1/2TiO3for Water Splitting by Oxygen Vacancy Engineering. ACS Appl. Mater. Interfaces 2022, 14 (31), 35635–35644. https://doi.org/10.1021/acsami.2c07817.

(12) Fujito, H.; Kunioku, H.; Kato, D.; Suzuki, H.; Higashi, M.; Kageyama, H.; Abe, R. Layered Perovskite Oxychloride Bi4NbO8Cl: A Stable Visible Light Responsive Photocatalyst for Water Splitting. J. Am. Chem. Soc. 2016, 138 (7), 2082–2085. https://doi.org/10.1021/jacs.5b11191.

(13) Tao, X.; Zhao, Y.; Mu, L.; Wang, S.; Li, R.; Li, C. Bismuth Tantalum Oxyhalogen: A Promising Candidate Photocatalyst for Solar Water Splitting. Adv. Energy Mater. 2018, 8 (1), 1–7. https://doi.org/10.1002/aenm.201701392.

(14) Ozaki, D.; Suzuki, H.; Ogawa, K.; Sakamoto, R.; Inaguma, Y.; Nakashima, K.; Tomita,
O.; Kageyama, H.; Abe, R. Synthesis, Band Structure and Photocatalytic Properties of Sillén-Aurivillius Oxychlorides BaBi5Ti3O14Cl, Ba2Bi5Ti4O17Cl and Ba3Bi5Ti5O20Cl with Triple-, Quadruple- And Quintuple-Perovskite Layers. J. Mater. Chem. A 2021, 9 (13), 8332– 8340. https://doi.org/10.1039/d0ta12550d.

(15) Razavi-Khosroshahi, H.; Mohammadzadeh, S.; Fuji, M. Bi4TaO8Cl/Graphene Nanocomposite for Photocatalytic Water Splitting. Adv. Powder Technol. 2020, 31 (1), 381– 386. https://doi.org/10.1016/j.apt.2019.10.030.

(16) Zhao, Z.; Wei, L.; Li, S.; Zhu, L.; Su, Y.; Liu, Y.; Bu, Y.; Lin, Y.; Liu, W.; Zhang, Z.
Exclusive Enhancement of Catalytic Activity in Bi0.5Na0.5TiO3nanostructures: New Insights into the Design of Efficient Piezocatalysts and Piezo-Photocatalysts. J. Mater. Chem. A 2020, 8 (32), 16238–16245. https://doi.org/10.1039/c9ta14007g.

(17) Wang, Y. C.; Wu, J. M. Effect of Controlled Oxygen Vacancy on H2-Production through the Piezocatalysis and Piezophototronics of Ferroelectric R3C ZnSnO3 Nanowires. Adv. Funct. Mater. 2020, 30 (5), 1–12. https://doi.org/10.1002/adfm.201907619.

(18) Jia, S.; Su, Y.; Zhang, B.; Zhao, Z.; Li, S.; Zhang, Y.; Li, P.; Xu, M.; Ren, R. Few-Layer MoS2 Nanosheet-Coated KNbO3 Nanowire Heterostructures: Piezo-Photocatalytic Effect Enhanced Hydrogen Production and Organic Pollutant Degradation. Nanoscale 2019, 11 (16), 7690–7700. https://doi.org/10.1039/c9nr00246d.

(19) Xiao, H.; He, J.; Lu, X.; Wang, F.; Guo, Y. Bandgap-Engineered Ferroelectric Single-Crystalline NBT-BT Based Nanocomposites with Excellent Visible Light-Ultrasound Catalytic Performance. Chemosphere 2022, 306 (June), 135543.
<u>https://doi.org/10.1016/j.chemosphere.2022.135543</u>.

CHAPTER 3.2.

Unusual structural phase transition in BiOBr under high pressure and ultrahigh bifunctional fuel generation efficiency under piezocatalytic conditions



Summary

Conventionally, piezoelectric materials have required non-centrosymmetric crystal structures, posing a century-old challenge. However, we overcame this limitation by inducing polarization in centrosymmetric BiOBr through the creation of oxygen vacancies, which was confirmed by multiple studies. The piezoelectric property of BiOBr was evaluated using piezoelectric force microscopy (PFM), unveiling unexpected piezoelectric behavior with a piezoelectric constant of 93 pm/V. Furthermore, BiOBr displayed remarkable bifunctional piezocatalytic activity for complete water splitting, concurrently producing H₂ and H₂O₂ without requiring co-catalysts or scavengers. To assess their impact on crystal structure, a high-pressure synchrotron X-ray diffraction investigation was conducted within a pressure range of 0.048 to 42.48 GPa, closely resembling piezocatalytic conditions. Remarkably, BiOBr underwent a distinctive isostructural phase transition under high pressure, all while maintaining crystallographic symmetry. These findings provide opportunities to design piezoelectric materials beyond centrosymmetric ones.

3.2.1. Introduction

Catalytic water splitting technology is a possible solution to tackle the global energy and environmental crises since it converts different forms of renewable energies into H₂ with a high energy capacity (143 MJ kg⁻¹) and benign O₂ as a byproduct.¹⁻⁴ However, the necessity for separating these gases, the sluggish kinetics of the four-electron O₂ evolution process, and the unavoidable reverse reaction are major obstacles that must be resolved for its commercial implementation. Therefore, the two-electron pathways that result in the production of H₂O₂, besides H₂ is a better alternative to improve the viability of the water-splitting process. This approach not only can address the aforementioned challenges but also yield more valuable H₂O₂ which is a clean liquid fuel and a versatile industrial chemical.⁵⁻⁷ The commercial production of hydrogen peroxide involves the anthraquinone oxidation process. However, due to reliance on energy-intensive multi-step reactions and the safety challenges associated with handling high-pressure hydrogen, makes this process environmentally non-beneficial. In this context, the simultaneous production of green H₂ and H₂O₂ using renewable energy is a highly desirable alternative.⁸⁻¹⁰

3.2.2. Scope of Investigation

Piezocatalysis is an emerging approach for fuel production by utilizing waste mechanical energy to induce atomic displacement and polarization within a catalyst material, which in turn facilitates effective charge separation.¹¹ Unlike traditional photocatalysis, piezocatalysis doesn't rely on precise band-edge positions because the piezoelectric effect can naturally bend the conduction and valence bands. ^{12,13} Furthermore, it can work effectively in materials with lower electrical conductivity, expanding the pool of suitable materials, and doesn't require an external voltage source, as in electrocatalysis.¹⁴ A number of piezocatalysts have been developed recently with H₂ production efficiencies per gram of the catalyst surpassing those in the photocatalytic approach, despite not using any noble metal cocatalysts and hole scavengers. In a few cases, minuscule amounts of H₂O₂ production have also been observed. The H₂O₂ production can, in certain cases, negatively impact the overall efficiency because the same upon decomposition generates molecular O₂ which scavenges the negative charges on the catalyst to form H₂O₂ again, and the cycle reduces both the H₂ and H₂O₂ production.^{1,15,16} Therefore, designing new catalysts with improved efficiencies for the simultaneous production of these two fuels is critical for realizing waste mechanical energy harvesting for fuel generation.

However, a major challenge in designing piezoelectric catalyst materials is that they must possess a crystal structure devoid of a center of symmetry, or else, the pressure-induced polarization in the unit half-cells cancels each other to severely limit the choice of a catalyst.^{17,18} Therefore, it is essential to explore and develop materials that do not rely on an overall non-centrosymmetric structure alone to develop piezoelectric charges. Herein we demonstrate that centrosymmetric defect-rich BiOBr can act as a highly efficient bifunctional catalyst for two-electron overall pure water splitting with simultaneous evolution of H₂ evolution and H₂O₂ under ultrasonic treatment in the absence of any co-catalyst and scavenger. The hydrogen evolution rate of 2.7 mmol h⁻¹ g⁻¹ is significantly higher than most of the recently developed piezocatalysts and photocatalysts that use noble metals as cocatalysts and scavengers for hole annihilation. The simultaneous H₂O₂ generation rate of 462 µmol h⁻¹ g⁻¹ is also the highest known to date when considering all metal-based catalysts and the fact that only the hydroxyl oxidation route is active for its generation, as the reaction is carried out under an inert atmosphere.

Even though a BiOBr crystal being centrosymmetric is not expected to exhibit piezocatalytic behavior,¹⁹ our measurements established that their microparticles prepared under hydrothermal process are highly piezoelectric. We, therefore, explored the possibility of any changes in its crystal structure up to 42.5 GPa pressure for the first time matching those in the piezocatalytic conditions using synchrotron radiation X-ray diffraction measurements, which revealed an interesting, previously unknown phase transition, but remained centrosymmetric throughout.²⁰ We subsequently explored the possibility of local symmetry breaking in the crystal leading to polarization due to the presence of oxygen vacancies, which are usually present in these phases.^{21,22} Very recently, such vacancies have been shown to lead to giant piezoelectricity in other oxide phases.²³ Chemical analysis of our sample confirmed oxygen sub-stoichiometry and the presence of such vacancies. we systematically varied the oxygen vacancy concentration in the sample. The vacancy concentration was confirmed from positron annihilation spectroscopy and revealed that increasing its concentration improves fuel generation efficiency. Finally, we have noted that since no excitons are involved, BiOBr remains highly stable under the catalytic conditions. This is critically important because even though BiOBr/Cl has been thoroughly explored for its high efficiency in photocatalytic reactions, it remained unusable due to its instability against chlorine evolution because of its unique band structure.

3.2.3. Methods

3.2.3.1. Synthesis of BiOBr: The BiOBr samples were prepared by a one-pot solvothermal method. In a typical synthesis, $Bi(NO_3)_3.5H_2O$ precursor was added to an ethylene glycol solution having KBr with Bi/Br molar ratio of 1. The mixture was stirred for 30 min and then transferred into a Teflon-lined autoclave. The autoclave was heated at a temperature of 160 °C for 12 h under autogenous pressure and then air cooled to room temperature. The resulting precipitate was collected by centrifugation and dried at room temperature after washing them with ethanol and distilled water repeatedly.²⁴

To reduce the oxygen vacancy concentration in the as-synthesized BiOBr sample, 250 mg of the catalyst was treated by using 15 ml of 15 wt% hydrogen peroxide (H_2O_2) solution for approximately two hours. To further decrease the oxygen vacancy concentration, an additional 250 mg of the catalyst was treated with another 15 ml of 30 wt% H_2O_2 solution for two hours.

3.2.3.2. Piezocatalytic Hydrogen Evolution: piezocatalytic water splitting was done by dispersing 10 mg of BiOBr in 30 ml of pure water. The suspension was sealed and then evacuated by purging with N₂ for an hour to completely remove air. The reactor was then exposed to ultrasonic vibration by using an ELMA Elmasonic P300H bath sonicator with a power of 110W and two ultrasonic switchable frequencies i.e., 37 kHz and 80 kHz. The temperature of the reaction system was controlled at 30 °C by using a water circulating system. The gas produced was withdrawn periodically with by gas-tight syringe and examined by gas chromatography (GC).

3.2.3.3. Hydrogen peroxide measurement: The amount of H_2O_2 produced during piezocatalytic water splitting is detected by the iodide titration method. 500 µl of suspension was taken after every 30 min interval and treated with 2 ml 0.1 M KI solution, and 50 ml 0.01 M $H_{32}Mo_7N_6O_{28}$ solution after centrifugation. After being reacted for 10 min, the concentration of H2O2 was determined by evaluating the absorbance of the KI/ $H_{32}Mo_7N_6O_{28}$ mixture at 325 nm by UV-Vis. spectroscopy.

3.2.3.4. Measurement of oxygen evolution: A sensor patch was affixed to the inner surface of a flask, ensuring it was submerged in the reaction solution to monitor the dissolved oxygen levels. To assess the amount of oxygen produced during the catalytic process, the reaction mixture was first purged with nitrogen for an hour to remove any dissolved oxygen.

Subsequently, the mixture was exposed to ultrasonic irradiation for a total of 4 hours, and measurements of oxygen levels were taken at hourly intervals.

3.2.3.5. Characterization

All the characterization techniques are discussed in chapter 1.2.

3.2.4. Result and Discussion

BiOBr belongs to the Sillen phases with a general formula of $[Bi_2O_2]^{2+}[X_2]^{2-}$, consisting of stacked sheets of [Br-Bi-O-Bi-Br] (**Figure 3.2.1. a**) within the non-polar P4/nmm space group, where the mono $[Bi_2O_2]$ layers alternate with double layers of Br along the *c*-axis. A Bi atom is coordinated by four oxygen and four bromine ions on either side, forming a Bi $[O_4Br_4]$ decahedron with a net polarization vector pointing towards oxygen. The polarization is however neutralized by neighboring polyhedral along the *c*-axis due to its center of symmetry. The [Br-Bi-O-Bi-Br] sheets are held together by van der Waals forces between Bi & Br from the adjacent sheets leading to high compressibility under pressure. Thus there are two distinct distances between Bi and Br ion within a Bi-O-Br (intra)layer, represented by Bi-Br(I), whereas the same in the two neighboring Bi-O-Br (inter)layers along the [100] direction is represented by Bi-Br(II).²⁵

The purity of the BiOBr particles obtained by the hydrothermal synthesis was confirmed by powder X-ray diffraction (XRD, **Figure 3.2.1. b**, a = b = 3.92 Å, and c = 8.39 Å (ICDS#98-001-1207)). Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analysis revealed that BiOBr consists of nanoplates that are radially aligned and tightly packed, forming a hierarchical microsphere with a diameter of ~2-3 µm (**Figure 3.2.1. c** and **inset, Figure 3.2.1. d**). The lattice fringes in a nanoplate with 0.28 nm spacing (high-resolution TEM image, **Figure 3.2.1. e**) correspond to the (110) plane of BiOBr.¹⁹ The packing of the nanoplates leads to a mesoporous structure (type-IV N₂ adsorption-desorption isotherm, **Figure 3.2.1. f**) having an average pore size of 20 nm and a surface area of 6.9 m²/g. Elemental composition and oxidation states of the surface atoms were confirmed by X-ray photoelectron spectroscopy (XPS). The analysis of the high-resolution Bi-4*f* XPS spectrum reveals peaks centered at 159.4 and 164.6 eV that correspond to the Bi 4*f*_{7/2} and Bi 4*f*_{5/2} states, respectively, indicating the presence of Bi³⁺ ions (**Figure 3.2.1. g**). The bromine peaks were observed at 67.8 and 68.9 eV, representing Br 3*d*_{5/2} and Br 3*d*_{3/2}, respectively (**Figure 3.2.1.**



h). In the O 1*s* XPS spectrum (**Figure 3.2.1. i**), three distinct peaks at 529.2, 530.6, and 531.9 eV can be discerned, representing lattice oxygen (O_L , O^{2-}) in BiOBr, oxygen atoms adjacent to

Figure 3.2.1. Crystal characterization (a) Crystal structure from the [001] direction (dark purple, purple, and blue spheres represent Br, O, and Bi atoms respectively). (b) Powder XRD pattern, (c) SEM, (d) TEM, and (e) HRTEM images of the BiOBr microsphere. (f) N_2 adsorption isotherm and pore-size analysis in the inset. (g) High-resolution XPS spectra of O1s of the BiOBr sample. (h, i) Amplitude, and phase images, respectively, of a BiOBr microsphere. (j, k) Displacement–voltage and phase curves of the microsphere. (l, m) KPFM potential mapping image of a microsphere in the dark and the corresponding surface potential.

oxygen vacancies (Ov), and adsorbed O₂ molecules (O_{add}), respectively.^{21,26,27} It provides confirmation evidence for the presence of oxygen vacancies in the sample. The valance band maximum (VBM) and the conduction band minimum (CBM) positions were estimated at 2.17 and 0.47 eV vs. NHE by relating an average bandgap of the microspheres (2.64 eV) from the observed at 67.8 and 68.9 eV, representing Br $3d_{5/2}$ and Br $3d_{3/2}$, respectively (**Figure 3.2.1. h**). In the O 1s XPS spectrum (**Figure 3.2.1. i**), three distinct peaks at 529.2, 530.6, and 531.9 eV can be discerned, representing lattice oxygen (O_L, O²⁻) in BiOBr, oxygen atoms adjacent to oxygen vacancies (O_V), and adsorbed O₂ molecules (O_{add}), respectively.^{21,26,27} It provides confirmation evidence for the presence of oxygen vacancies in the sample. The valance band maximum (VBM) and the conduction band minimum (CBM) positions were estimated at 2.17 and 0.47 eV vs. NHE by relating an average bandgap of the microspheres (2.64 eV) from the Tauc plot to a flat band potential of -0.47 V obtained from Mott–Schottky measurements (**Figure 3.2.2.**).²⁸



Figure 3.2.2. (a) UV-Vis diffuse reflectance spectroscopy of BiOBr and its corresponding (b) Tauc Plot (c) Mott–Schottky plots of BiOBr measured at 500 and 1000 Hz (d) Schematic showing the determined energy levels of BiOBr microspheres.



Figure 3.2.3. Piezoelectric properties of BiOBr (a) Resonant peaks on BiOBr microsphere recorded during PFM for different applied voltages showing a (b) linear correlation between the operating voltage and the amplitude. (c–e) Topography, amplitude, and phase images, respectively, of a BiOBr microsphere. (f, g) Displacement–voltage and phase curves of the microsphere. (h, i) KPFM potential mapping image of a microsphere in the dark and the corresponding surface potential.

The unusual piezoelectric properties of the centrosymmetric BiOBr microsphere were confirmed using piezoelectric force microscopy (PFM) and Kelvin probe force microscopy (KPFM). The microspheres exhibited resonance peaks at 263 kHz with a linear piezoelectric response across various applied voltages (**Figure 3.2.3. a and b**). The topography image

(**Figure 3.2.3. c**) is in agreement with the corresponding phase and amplitude images to show an apparent uniform response from the sphere (**Figure 3.2.3. d e**). The local piezoresponse hysteresis loops were obtained by sweeping the DC bias from -15 V to +15 V while simultaneously recording the phase and amplitude responses. A maximum effective piezoelectric coefficient of 63.29 pm/V (with a deviation of approximately 10%) was determined from the distinctive butterfly-shaped amplitude loop, underscoring the piezoelectric nature of the BiOBr microspheres (**Figure 3.2.3. f**). Notably, the phase-anglevoltage hysteresis plot exhibited a 180° shift upon reversing the DC bias due to polarization switching within the subject (**Figure 3.2.3. g**). To understand the nature of the surface charge, a piezoelectric potential map was acquired by scanning the KPFM cantilever over the nanoplate. The contact potential difference (CPD) between the tip and the nanoplate unveiled a surface potential of 42 mV (**Figure 3.2.3. h, i**). Furthermore, the work function, φ , was determined by using a Highly Ordered Pyrolytic Graphite substrate (HOPG, with φ of 4.688 eV) as a reference and using the equation below,

$$\varphi_{\text{tip}}$$
- $\varphi_{\text{sample}} = eV_{\text{CPD}}$

Where φ_{tip} , φ_{sample} , and *e* represent the work functions of the tip and the sample, and elementary charge respectively.

3.2.4.1. Piezocatalytic Hydrogen Generation

To assess the piezocatalytic efficiency of the BiOBr microspheres, the splitting of pure water was performed under ultrasonic vibrations without any scavenger or co-catalyst. Notably, a negligible amount of H₂ was also detected (~33.6 micromoles g^-12h^{-1} that does not change with time, **Figure 3.2.4. a**) under identical conditions but in the absence of the catalyst. On the other hand, a pronounced H₂ evolution rate of ~6 millimole $g^{-1} 2h^{-1}$ establishes that the cocatalystfree BiOBr plays an important role in ultrasonic water splitting from the reduction of protons by its surface potential developed under ultrasonic pressure in the scavenger-free conditions. The effect of catalyst loading on H₂ generation was examined (5 to 15 mg range, **Figure 3.2.4. b**) to find that increasing catalyst dosage reduces H₂ generation per gram of the catalyst, attributed to the agglomeration of particles at higher dosages, reducing the effective acoustic power experienced by catalyst particles.¹⁷ We further conducted trapping experiments to determine the active species responsible for water splitting by using lactic acid as positive and AgNO₃ as negative charge-trapping reagents respectively (**Figure 3.2.4. c**). It revealed that positive charge scavenging further increases H₂ generation, due to suppression of the recombination of induced charges resulting in an increased lifetime of negative charges.¹ Conversely, the introduction of AgNO₃ noticeably inhibited the H_2 generation rate, confirming that the induced negative charges are the primary active species for H_2 evolution.



Figure 3.2.4. Piezocatalytic activity of BiOBr (a) Ultrasound irradiation-induced H_2 production rate in the presence or absence of piezocatalysts. (b) Effect of catalyst dosage on H_2 production. (c) Plot showing the effect of trapping agents on H_2 production. (d, e) Hydrogen production as a function of ultrasonic frequency and power respectively. (f) Comparative previous studies. (g) Plot showing the comparison of H_2O_2 production performance of BiOBr evaluation of the hydrogen production efficiency of BiOBr with other piezocatalysts from with other reports

Catalyst	Energy Sources	$H_2 \ (\mu mol \ g^{-1} \ h^{-1})$	Scavenger	Reference
BiOBr	110W, 37KHz	2724	No scavenger	
BiFeO3 NS	100W, 45KHz	124	Na ₂ SO ₃ (0.05 M)	1
BaTiO3 NPs	60 kHz	655	-	2
MOS2	110 W, 40KHZ	29.1	-	3
$\begin{array}{l} Sr_{0.5}Ba_{0.5}Nb_2O_6/Sr_2Nb_2\\ O_7 \text{ nanocomposites} \end{array}$		109.4	methanol	4
BiFeO ₃ @COF Z- Scheme Heterostructures	40 kHz, 100 W visible light ($\lambda \ge 420$ nm)	1416.4	-	5
Ni/GaN NW	110 W, 40KHZ	88	TEOA	6
SnSe Nw	100 W, 45KHZ	48	Glucose (0.1M)	7
TiO ₂ /BiOBr (3:1)	300 W Xe lamp	472.7	-	8
Bi _{1/2} Na _{1/2} TiO ₃	40 kHz 100 W	506.70	-	9
ZnS nanosheets	27kHz	1080	-	10
La ₂ NiO ₄ nanoplates	40 kHz 100 W, 300 W Xe lamp	1097	-	11
ZnSO3 Nw	250W, 40kHz, Xe lamp 150W	857	Alcohol (50vol%)	12
Pt/ Bi0.5Na0.5TiO3	110W, 40KHz, Xe lamp 300W	158	TEOA (15vol %)	13
Pt/Bi ₃ Bi ₅ Ta ₅ O ₂₀ Cl	Xe lamp 300W	90	20vol% methanol	14

Table 3.2.1. A comparison table showing piezocatalytic H_2 evolution activity of BiOBr as compared to other reported piezo catalysts.

We also explored the impact of ultrasonication frequency and power on catalytic efficacy. H₂ production is high when a frequency of 37 kHz is used as compared to 80 kHz, owing to proximity to the resonance frequency of the catalyst (**Figure 3.2.4. d**).¹¹ Additionally, the production rate at 37 kHz increases as power is increased from 40% (44 W) to 100% (110 W, **Figure 3.2.4. e**), where the increase is rather nonlinear with an initial rate of

392 µmol h⁻¹ g⁻¹ improving enormously to 2.7 mmol h⁻¹ g⁻¹ at the end. The rate of 2.7 mmol h⁻¹ g⁻¹ is one of the best performances reported to date (**Figure 3.2.4. f, Table 3.2.1.**). Considering piezoelectric charges, $Q_p = dT$ (where *d* is the piezoelectric coefficient and T is external stress), higher vibrational power can lead to higher T, which induces more piezoelectric charges, resulting in a higher hydrogen production rate. However, the processes of transient stress accumulation and transfer within a particle, and also, surface structural changes during piezoeatalysis that are potentially responsible for the nonlinear increase are not well understood yet. In addition, we recently hypothesized that the fraction of the catalyst particles that are suitably exposed to ultrasonic pressure to experience sufficient band-bending for proton reduction may vary nonlinearly due to multiple bubbles bursting at higher power, leading to a non-linear effect.²⁹



Figure 3.2.5. (a) H_2 and H_2O_2 production by the same BiOBr powder for a continuous 8h. (b) PXRD pattern of fresh and used BiOBr microspheres. (c) TEM and (d) HRTEM image of the BiOBr after catalysis

Importantly, as a counter-reaction, the oxidation of water resulted in the concurrent generation of hydrogen peroxide (H₂O₂,), indicating that the positive charges induced by the piezopotential oxidize hydroxide ions (OH⁻) to produce H₂O₂. The H₂O₂ production rate was estimated to be 462 µmol h⁻¹ g⁻¹ (**Figure 3.2.4. g**), which is comparable in performance considering even those catalysts that are developed for H₂O₂ production alone (**Figure 3.2.4. h**). It may be noted that H₂O₂ production can be induced by the reduction of molecular O₂, which usually contributes majorly to its yield but competes with proton reduction to decrease the H₂ yield, H₂O₂ can also be generated by the oxidation of OH⁻ ions. In the present study, since no additional O₂ flow was used, the H₂O₂ production entirely occurs from OH⁻ oxidation. Thus, the ultrasonic process leads to the generation of two kinds of fuels with potentially no separation difficulties. However, since its production rate is somewhat lower than the H₂ production rate, we estimated the dissolved O₂ (DO) level in the reaction mixture, which might have been generated from H₂O₂ decomposition.³⁰ As seen in **Figure 3.2.4. i**, a gradual increase in the DO level confirms that a fraction of the produced H₂O₂ gets decomposed.

The structural integrity of the catalyst during its continuous use has been investigated thoroughly to find barely any changes in the catalyst activity and structure. (**Figure 3.2.5. a**) **shows** that there is almost no change in H₂ and H₂O₂ evolution. **Figure 3.2.5. b P-XRD**, **3.2.5. Figure 3.2.5. c TEM**, **Figure 3.2.5. d HRTEM** confirms structural stability. It is to be highlighted that BiOCl/Br has been widely used as a photocatalyst for renewable energy harvesting and has proven to be an important catalyst. However, its stability against photocorrosion remains a bottleneck, in which case the high stability of these materials under piezocatalytic conditions is a critical finding for its sustainable use. It may be noted that photocorrosion under photocatalytic conditions originates from populating the chloride subbands in the valance band by the excitonic hole that results in chlorine gas evolution.³¹ In that context, our high-pressure studies have demonstrated that under ultrasonic pressure, discussed vide infra, the contribution of oxygen to the valance band maximum significantly increases, which induces high stability of the lattice chloride against photo-corrosion. It may be highlighted that upon increasing O-contribution in the related Sillen Aurivillius phases, high stability has been demonstrated both experimentally and theoretically recently.
3.2.4.2. Structural Changes at High Pressure and Origin of Efficient Piezocatalysis

To probe the potential structural changes occurring in BiOBr under piezocatalytic conditions and to understand the origin of piezocatalysis, *in-situ* high-pressure powder X-ray diffraction measurements were performed. Even though such a correlation has not been established in piezocatalytic systems, conventional high-pressure studies on piezoelectric systems often indicate phase transitions under high pressure.²⁰ Our synchrotron measurements were conducted at room temperature and pressure values ranging from 0.248 GPA to 42.48 GPA, closely matching those under piezocatalytic conditions. Figure 3.2.6. a displays the evolution of the X-ray diffraction patterns throughout this pressure range, establishing interesting but unusual peak shifts for different crystal planes. A consistent broadening of all peaks was observed, as expected under high pressure.³² Notably, no appearances of extra peaks or disappearances of the existing Bragg peaks were observed, apart from some sharp peaks that emerged from 7.36 GPa onwards, corresponding to the crystallization of Ne, used as a pressuretransmitting medium.³³ By using Rietveld refinement, the diffraction patterns could be modeled using the tetragonal p4/nmm space group at all pressures, suggesting minimal changes in the relative orientation of the constituting atoms throughout the experiment. The atomic coordination parameters at different pressures are summarized in Table 3.2.2.

As seen in **Figure 3.2.6. b**, the variations in the *a* and the *c* parameters exhibited a noticeable discontinuity starting at ~16.24 GPa. A nearly linear decrease in the "*a*" parameter values undergoes a sudden change in slope from a higher decay rate to a lower one. On the other hand, the decrease in the "*c*" parameter can be fitted with an exponential decay until 16.24 GPa, beyond which the rate of shrinkage slows down. Concomitantly, the axis ratio, "*c/a*", exhibited a nonlinear decrease during the initial compression, indicating that the "*c*" parameter is more compressible than "*a*" (**Figure 3.2.6. c**) due to the weaker interlayer van der Waals forces relative to the stronger intralayer covalent bonding within the structure. Above 16.24 GPa, the '*c/a*' change rate followed a near-linear decrease, suggesting that the cell parameters '*a*' and '*c*' undergo nearly isotropic contractions in the high-pressure region. The Bi–O distance decreases with increasing pressure, with discontinuous evolution at 16.24 GPa. Similarly, The Bi–Br(I) decrease follows apparent linearity before and after 16.24GPa but with different rates, while Bi–Br(II) distances decrease exponentially and linearly before and after 16.24 GPa respectively, having relatively larger compression. Previously, similar

structural changes were observed in the case of BiOCl (p4/nmm space group) across ~17 GPa, attributed to an isostructural phase transition.²⁰ Accordingly, a low-pressure phase (LPP) and a high-pressure phase (HPP) is defined here for BiOBr too across ~16.24 GPa.



Figure 3.2.6. High-pressure phase transition in BiOBr (a) *In-situ* high-pressure synchrotron X-ray powder diffraction of BiOBr at room temperature up to 42.48 GPa. Pressure dependences of (b) lattice parameters, (c) the *c* to *a* ratio, (d) unit cell volume, V (the V–P relationship are fitted according to the BM-EoS equation of state), and (e) Bound distance of BiOBr up to 42.48 GPa.

The pressure-volume (P–V) data fits well to a third-order Birch–Murnaghan equation of state (BM-EoS, **Figure 3.2.6. d**) to obtain the zero-pressure volume (V₀), bulk modulus (B₀), and its pressure derivative (B₀'). The bulk modulus B₀ is estimated as 47.31 and 150 GPa for the LPP and HPP respectively, with a first-order pressure derivative B₀ of 9 and 7.05, respectively. The respective ambient unit cell volumes (V₀) of these two phases are 122 and 112 Å³ which are

higher by 10.2 and 0.5 value than BiOCl in the lower-pressure region and higher-pressure region respectively. The increased bulk modulus of the HPP is mainly due to the shrinkage of the Bi-Br (II) distance between the two neighboring Bi-O-Br layers upon compression. (**Figure 3.2.6.e**)

Pressure (GPa)	Lattice Parameter (a)	Lattice parameter (c)	Volume	R _{Wp}	χ^2
0.28	3.9195(8)	8.0811(28)	124.15(8)	0.06867	0.624
2.14	3.9022(6)	7.7514(29)	118.03(7)	0.03904	0.347
3.88	3.8875(7)	7.5686(24)	114.38(7)	0.06538	0.588
4.44	3.8854(9)	7.5320(26)	113.70(7)	0.06524	0.573
5.91	3.8753(8)	7.4576(24)	112.00(7)	0.06679	0.603
7.36	3.8642(8)	7.3906(23)	110.36(7)	0.06820	0.620
8.83	3.8555(9)	7.3378(19)	109.08(6)	0.01090	0.262
10.44	3.8459(10)	7.2834(25)	107.73(8)	0.06978	0.630
12.36	3.8342(12)	7.2223(28)	106.17(9)	0.07410	0.666
14.6	3.8233(13)	7.1728(31)	104.85(10)	0.07632	0.694
16.24	3.8139(13)	7.1225(29)	103.60(9)	0.07109	0.637
19.89	3.8031(15)	7.064(3)	102.18(11)	0.07392	0.669
23.56	3.7886(14)	7.0026(31)	100.51(10)	0.05931	0.536
26.97	3.7809(19)	6.979(4)	99.77(13)	0.07799	0.699
31.16	3.7700(19)	6.947(4)	98.73(13)	0.07510	0.674
38.76	3.7480(23)	6.870(5)	96.50(15)	0.07720	0.689
42.48	3.7344(20)	6.847(4)	95.49(14)	0.07360	0.664

Table 3.2.2. the atomic coordination parameters of BiOBr at different pressures.

Generally, it is expected that a centrosymmetric space group would not exhibit piezoelectricity. Additionally, the aforementioned synchrotron X-ray conducted under high pressure confirms that there is no evidence of crystallographic symmetry breakage in centrosymmetric BiOBr under high pressure, almost similar to piezocatalytic conditions. However, both Piezoresponse force microscopy (PFM) and piezocatalytic investigations have demonstrated that centrosymmetric BiOBr does respond to external pressure by concurrently producing H₂ and H₂O₂, thereby confirming its piezocatalytic characteristics.

A growing number of studies propose that oxygen vacancies in centrosymmetric crystal structures can lead to the generation of piezoelectric responses in these materials. For instance, D.S. Park et al. observed an exceptionally large piezoelectric response in centrosymmetric cubic fluorite gadolinium-doped CeO_{2-x} films. This response was found to be two orders of magnitude larger than the responses observed in the best-known lead-based piezoelectric relaxor–ferroelectric oxide at kilohertz frequencies.²³ The introduction of oxygen vacancies results in a chemical expansion of the films. Consequently, this creates a piezoelectric effect. Furthermore, Wang and colleagues observed the piezocatalytic degradation capability of organic dyes using BiOBr.³⁴5 However, the sources of polarization in centrosymmetric BiOBr have yet to be explored.

Sample	$ au_1(ps)$	I ₁ (%)	$\tau_2(ps)$	I ₂ (%)	$ au_3(ps)$	I ₃ (%)
BiOBr- fresh	100 ± 2	15 ± 1	308 ± 1	84 ± 1	1888 ± 48	1 ± 0.06
BiOBr-dil.	100 ± 5	17 ± 1	308 ± 1	82 ± 1	1896 ± 42	1 ± 0.1
BiOBr-Conc.	105 ± 5	22 ± 1	330 ± 2	76 ± 1	1979 ± 60	2 ± 0.06

Table 3.2.3. Positron lifetime parameters of the BiOBr-fresh, BiOBr-diluted, and BiOBr-concentrated H_2O_2 treated samples.

To elucidate the origin of polarization in centrosymmetric BiOBr we conducted a series of experiments involving the generation of three samples with varying oxygen vacancies by subjecting an initially synthesized oxygen vacancy-rich BiOBr sample to oxidation using hydrogen peroxide at room temperature. These samples were characterized through various analytical techniques, including powder-XRD pattern analysis (as shown in **Figure 3.2.7. a**), which confirmed the sample's stability at the bulk level even after the H_2O_2 treatment. **Figure 3.2.7. b** displays high-resolution XPS data of O1s for all three samples. The O1s peak area,

corresponding to oxygen atoms proximate to oxygen vacancies, decreased, while the lattice oxygen peak increased as we progressed from the fresh BiOBr to the samples treated with diluted and concentrated H_2O_2 . This indicates a reduction in the abundance of oxygen vacancies (**Figure 3.2.7. c**). EPR spectroscopy (**Figure 3.2.7. d**) revealed a distinctive peak at a g-factor of 2.002, which is associated with oxygen vacancies. The decreasing intensity of this peak as we transitioned from fresh BiOBr to dilute and then to concentrated H_2O_2 -treated BiOBr clearly indicates the diminishing presence of oxygen vacancies. PAS characterize the type and concentration of vacancies. The positron annihilation lifetime spectra (PAL, **Table 3.2.3**.) were analyzed, revealing three distinct lifetime components. The longest component



Figure 3.2.7. (a) Powdered X-ray Diffraction (XRD) pattern, revealing the stability of oxidized samples at the bulk level. (b) High-resolution spectra of O1s showcasing the reduction in oxygen vacancies as the oxidation of fresh BiOBr increases. (c) Plot illustrating the diminishing abundance of oxygen vacancies. (d) The Electron Paramagnetic Resonance (EPR) plot (e) CDB spectra (e) further confirms the decrease in oxygen vacancy levels as the oxidation of BiOBr microspheres progresses (f) Plot showing a reduction in hydrogen (H₂) production in correlation with decreasing oxygen vacancy concentrations.

(τ 3), approximately 1888 ps in duration with a minor intensity (~2%), represents positronium atom pick-off annihilation. The shortest component $\tau 1$ represents the free annihilation of positrons in a defect-free state. The $\tau 2$ component, which is much longer than $\tau 1$ lifetimes, is attributed to oxygen vacancies. Notably, the contribution of $\tau 2$ was relatively high in all three samples, suggesting that oxygen vacancies predominantly constitute the defect structure in the BiOBr microspheres. Furthermore, with an increasing concentration of H₂O₂ treatment, the relative intensity of $\tau 2$ increased, while $\tau 1$ decreased, indicating a progressive reduction in oxygen vacancies with H₂O₂ treatment.³⁵ Coincidence Doppler broadening (CDB, Figure **3.2.7.** e) spectra were analyzed by calculating point-by-point intensity ratios using a 99.9999% pure aluminum single crystal as a reference. The ratio curve of CDB for all three samples exhibited a distinct peak at $pL = 11 \times 10-3 \times m0c$, which can be attributed to the positron annihilation with oxygen anions' 2p electrons. The reduction in peak intensity from fresh to diluted H_2O_2 treated and then to concentrated H_2O_2 confirmed the decrease in vacancy with an increase in H₂O₂ treatment. In conclusion, all the above characterization provides strong evidence for the reduction in oxygen vacancy concentration when the as-synthesized fresh BiOBr is treated with an increasing concentration of H₂O₂.

The piezocatalytic hydrogen evolution of these catalysts was further evaluated, as shown in **Figure 3.2.7. f.** It is evident from the data that the hydrogen evolution decreases with increasing oxygen vacancy concentration, confirming the role of oxygen vacancies as the origin of piezocatalysis in centrosymmetric BiOBr microspheres.

3.2.5. Conclusion

In summary, we have successfully induced piezoelectricity in centrosymmetric BiOBr, thus overcoming a century-old challenge that required non-centrosymmetric crystal structures for piezoelectric materials. Our comprehensive assessment of BiOBr's piezoelectric properties via piezoelectric force microscopy (PFM) unveiled an unexpected piezoelectric behavior characterized by a remarkable piezoelectric constant of 93 pm/V. Moreover, we extended our exploration to BiOBr microspheres, which serve as highly efficient bifunctional piezocatalysts for complete water splitting. These microspheres concurrently generate H₂ and H₂O₂ without the need for co-catalysts or scavengers. To comprehend the influence of high pressure on the crystal structure, we conducted high-pressure synchrotron X-ray diffraction, in a pressure range 0.048 to 42.48 GPa, closely resembling the conditions of piezocatalysis. Notably, BiOBr

underwent a distinctive isostructural phase transition under high pressure while preserving its crystallographic symmetry. We additionally substantiated the role of oxygen vacancies as the origin of piezoelectricity by deliberately reducing the quantity of oxygen vacancies in the originally synthesized oxygen vacancy-enriched BiOBr. This reduction was achieved through treatment with H₂O₂, and we conducted a comprehensive characterization of the modified material using various analytical techniques. Furthermore, our investigations revealed that the efficiency of piezocatalytic hydrogen evolution decreases proportionally with an increasing concentration of oxygen vacancies conforming oxygen vacancy as origin of piezoelectricity in centrosymmetric BiOBr.

Bibliography:

- Hu, C.; Chen, F.; Wang, Y.; Tian, N.; Ma, T.; Zhang, Y.; Huang, H. Exceptional Cocatalyst-Free Photo-Enhanced Piezocatalytic Hydrogen Evolution of Carbon Nitride Nanosheets from Strong In-Plane Polarization. *Adv. Mater.* 2021, *33* (24), 1–9. https://doi.org/10.1002/adma.202101751.
- Wang, L.; Zhang, Y.; Chen, L.; Xu, H.; Xiong, Y. 2D Polymers as Emerging Materials for Photocatalytic Overall Water Splitting. *Adv. Mater.* 2018, *30* (48), 1–12. https://doi.org/10.1002/adma.201801955.
- (3) Oshima, T.; Lu, D.; Ishitani, O.; Maeda, K. Intercalation of Highly Dispersed Metal Nanoclusters into a Layered Metal Oxide for Photocatalytic Overall Water Splitting. *Angew. Chemie* 2015, *127* (9), 2736–2740. https://doi.org/10.1002/ange.201411494.
- Wan, G.; Yin, L.; Chen, X.; Xu, X.; Huang, J.; Zhen, C.; Zhu, H.; Huang, B.; Hu, W.; Ren, Z.; Tian, H.; Wang, L.; Liu, G.; Cheng, H. M. Photocatalytic Overall Water Splitting over PbTiO3Modulated by Oxygen Vacancy and Ferroelectric Polarization. *J. Am. Chem. Soc.* 2022, *144* (44), 20342–20350. https://doi.org/10.1021/jacs.2c08177.
- Hu, C.; Hu, J.; Zhu, Z.; Lu, Y.; Chu, S.; Ma, T.; Zhang, Y.; Huang, H. Orthogonal Charge Transfer by Precise Positioning of Silver Single Atoms and Clusters on Carbon Nitride for Efficient Piezocatalytic Pure Water Splitting. *Angew. Chemie - Int. Ed.* 2022, *61* (43). https://doi.org/10.1002/anie.202212397.
- (6) He, J.; Gao, F.; Wang, H.; Liu, F.; Lin, J.; Wang, B.; Liu, C.; Huang, F.; Lin, Z.;
 Wang, M. C-Doped KNbO3 Single Crystals for Enhanced Piezocatalytic Intermediate
 Water Splitting. *Environ. Sci. Nano* 2022, 9 (6), 1952–1960.
 https://doi.org/10.1039/d2en00244b.
- Xue, F.; Si, Y.; Wang, M.; Liu, M.; Guo, L. Toward Efficient Photocatalytic Pure Water Splitting for Simultaneous H2 and H2O2 Production. *Nano Energy* 2019, 62, 823–831. https://doi.org/10.1016/j.nanoen.2019.05.086.
- Wu, S.; Yu, H.; Chen, S.; Quan, X. Enhanced Photocatalytic H2O2 Production over Carbon Nitride by Doping and Defect Engineering. *ACS Catal.* 2020, *10* (24), 14380– 14389. https://doi.org/10.1021/acscatal.0c03359.
- (9) Wang, L.; Zhang, J.; Zhang, Y.; Yu, H.; Qu, Y.; Yu, J. Inorganic Metal-Oxide

Photocatalyst for H2O2 Production. *Small* **2022**, *18* (8). https://doi.org/10.1002/smll.202104561.

- (10) Zhou, X.; Yan, F.; Lyubartsev, A.; Shen, B.; Zhai, J.; Conesa, J. C.; Hedin, N.
 Efficient Production of Solar Hydrogen Peroxide Using Piezoelectric Polarization and Photoinduced Charge Transfer of Nanopiezoelectrics Sensitized by Carbon Quantum Dots. *Adv. Sci.* 2022, 9 (18), 1–13. https://doi.org/10.1002/advs.202105792.
- Banoo, M.; Roy, R. S.; Bhakar, M.; Kaur, J.; Jaiswal, A.; Sheet, G.; Gautam, U. K. Bi4TaO8Cl as a New Class of Layered Perovskite Oxyhalide Materials for Piezopotential Driven Efficient Seawater Splitting. *Nano Lett.* 2022, 22 (22), 8867– 8874. https://doi.org/10.1021/acs.nanolett.2c02900.
- Tu, S.; Guo, Y.; Zhang, Y.; Hu, C.; Zhang, T.; Ma, T.; Huang, H. Piezocatalysis and Piezo-Photocatalysis: Catalysts Classification and Modification Strategy, Reaction Mechanism, and Practical Application. *Adv. Funct. Mater.* 2020, *30* (48), 1–31. https://doi.org/10.1002/adfm.202005158.
- Wang, K.; Han, C.; Li, J.; Qiu, J.; Sunarso, J.; Liu, S. The Mechanism of Piezocatalysis: Energy Band Theory or Screening Charge Effect? *Angew. Chemie - Int. Ed.* 2022, *61* (6). https://doi.org/10.1002/anie.202110429.
- (14) Starr, M. B.; Wang, X. Fundamental Analysis of Piezocatalysis Process on the Surfaces of Strained Piezoelectric Materials. *Sci. Rep.* 2013, *3* (1), 1–8. https://doi.org/10.1038/srep02160.
- Wang, C.; Hu, C.; Chen, F.; Li, H.; Zhang, Y.; Ma, T.; Huang, H. Polar Layered Bismuth-Rich Oxyhalide Piezoelectrics Bi4O5X2 ((Formula Presented.), I): Efficient Piezocatalytic Pure Water Splitting and Interlayer Anion-Dependent Activity. *Adv. Funct. Mater.* 2023, 2, 1–12. https://doi.org/10.1002/adfm.202301144.
- (16) Feng, W.; Yuan, J.; Zhang, L.; Hu, W.; Wu, Z.; Wang, X.; Huang, X.; Liu, P.; Zhang, S. Atomically Thin ZnS Nanosheets: Facile Synthesis and Superior Piezocatalytic H2 Production from Pure H2O. *Appl. Catal. B Environ.* 2020, 277 (March 2020), 119250. https://doi.org/10.1016/j.apcatb.2020.119250.
- (17) Zhang, Y.; Khanbareh, H.; Dunn, S.; Bowen, C. R.; Gong, H.; Duy, N. P. H.; Phuong,P. T. T. High Efficiency Water Splitting Using Ultrasound Coupled to a BaTiO3

Nanofluid. Adv. Sci. 2022, 9 (9), 1–11. https://doi.org/10.1002/advs.202105248.

- (18) Su, R.; Hsain, H. A.; Wu, M.; Zhang, D.; Hu, X.; Wang, Z.; Wang, X.; Li, F. tang; Chen, X.; Zhu, L.; Yang, Y.; Yang, Y.; Lou, X.; Pennycook, S. J. Nano-Ferroelectric for High Efficiency Overall Water Splitting under Ultrasonic Vibration. *Angew. Chemie - Int. Ed.* **2019**, *58* (42), 15076–15081. https://doi.org/10.1002/anie.201907695.
- (19) Cao, X.; Huang, A.; Liang, C.; Chen, H. C.; Han, T.; Lin, R.; Peng, Q.; Zhuang, Z.; Shen, R.; Chen, H. M.; Yu, Y.; Chen, C.; Li, Y. Engineering Lattice Disorder on a Photocatalyst: Photochromic BiOBr Nanosheets Enhance Activation of Aromatic C-H Bonds via Water Oxidation. *J. Am. Chem. Soc.* 2022, *144* (8), 3386–3397. https://doi.org/10.1021/jacs.1c10112.
- (20) Zhao, J.; Xu, L.; Liu, Y.; Yu, Z.; Li, C.; Wang, Y.; Liu, Z. Isostructural Phase Transition in Bismuth Oxide Chloride Induced by Redistribution of Charge under High Pressure. J. Phys. Chem. C 2015, 119 (49), 27657–27665. https://doi.org/10.1021/acs.jpcc.5b07180.
- (21) Shen, Z.; Luo, Z.; Chen, J.; Li, Y. Oxygen Vacancy-Mediated Exciton Effect in Hierarchical BiOBr Enables Dichotomy of Energy Transfer and Electron Transfer in Photocatalysis. *Adv. Funct. Mater.* 2023, *33* (10). https://doi.org/10.1002/adfm.202213935.
- Wang, H.; Yong, D.; Chen, S.; Jiang, S.; Zhang, X.; Shao, W.; Zhang, Q.; Yan, W.;
 Pan, B.; Xie, Y. Oxygen-Vacancy-Mediated Exciton Dissociation in Biobr for
 Boosting Charge-Carrier-Involved Molecular Oxygen Activation. *J. Am. Chem. Soc.* **2018**, *140* (5), 1760–1766. https://doi.org/10.1021/jacs.7b10997.
- (23) Park, D. S.; Hadad, M.; Riemer, L. M.; Ignatans, R.; Spirito, D.; Esposito, V.; Tileli, V.; Gauquelin, N.; Chezganov, D.; Jannis, D.; Verbeeck, J.; Gorfman, S.; Pryds, N.; Muralt, P.; Damjanovic, D. Induced Giant Piezoelectricity in Centrosymmetric Oxides. *Science (80-.).* 2022, *375* (6581), 653–657. https://doi.org/10.1126/science.abm7497.
- (24) Chatterjee, K.; Banoo, M.; Mondal, S.; Sahoo, L.; Gautam, U. K. Synthesis of Bi3TaO7-Bi4TaO8Br Composites in Ambient Air and Their High Photocatalytic Activity upon Metal Loading. *Dalt. Trans.* 2019, 48 (21), 7110–7116. https://doi.org/10.1039/c9dt00068b.

- (25) Tang, Z. K.; Yin, W. J.; Le Zhang; Wen, B.; Zhang, D. Y.; Liu, L. M.; Lau, W. M. Spatial Separation of Photo-Generated Electron-Hole Pairs in BiOBr/BiOI Bilayer to Facilitate Water Splitting. *Sci. Rep.* 2016, 6 (June), 1–9. https://doi.org/10.1038/srep32764.
- Banoo, M.; Chatterjee, K.; Mondal, S.; Vinod, C. P.; Gautam, U. K. A 'Self-Activating' Bi3TaO7-Bi4TaO8Br Photocatalyst and Its Use in the Sustainable Production of pro-Fluorophoric Rhodamine-110. *Green Chem.* 2022, 24 (14), 5514–5523. https://doi.org/10.1039/d2gc01574a.
- Wang, X. J.; Zhao, Y.; Li, F. T.; Dou, L. J.; Li, Y. P.; Zhao, J.; Hao, Y. J. A Chelation Strategy for In-Situ Constructing Surface Oxygen Vacancy on {001} Facets Exposed BiOBr Nanosheets. *Sci. Rep.* 2016, *6* (April), 1–11. https://doi.org/10.1038/srep24918.
- (28) Li, Y.; Jiang, H.; Wang, X.; Hong, X.; Liang, B. Recent Advances in Bismuth Oxyhalide Photocatalysts for Degradation of Organic Pollutants in Wastewater. *RSC Adv.* 2021, *11* (43), 26855–26875. https://doi.org/10.1039/d1ra05796k.
- Banoo, M.; Kaur, J.; Sah, A. K.; Roy, R. S.; Bhakar, M.; Kommula, B.; Sheet, G.;
 Gautam, U. K. Universal Piezo-Photocatalytic Wastewater Treatment on Realistic
 Pollutant Feedstocks by Bi4TaO8Cl: Origin of High Efficiency and Adjustable
 Synergy. ACS Appl. Mater. Interfaces 2023, 15 (27), 32425–32435.
 https://doi.org/10.1021/acsami.3c04959.
- (30) Shiraishi, Y.; Ueda, Y.; Soramoto, A.; Hinokuma, S.; Hirai, T. Photocatalytic Hydrogen Peroxide Splitting on Metal-Free Powders Assisted by Phosphoric Acid as a Stabilizer. *Nat. Commun.* 2020, *11* (1), 1–9. https://doi.org/10.1038/s41467-020-17216-2.
- (31) Fujito, H.; Kunioku, H.; Kato, D.; Suzuki, H.; Higashi, M.; Kageyama, H.; Abe, R. Layered Perovskite Oxychloride Bi4NbO8Cl: A Stable Visible Light Responsive Photocatalyst for Water Splitting. *J. Am. Chem. Soc.* 2016, *138* (7), 2082–2085. https://doi.org/10.1021/jacs.5b11191.
- Wang, X.; Chen, X.; Zhou, Y.; Park, C.; An, C.; Zhou, Y.; Zhang, R.; Gu, C.; Yang, W.; Yang, Z. Pressure-Induced Iso-Structural Phase Transition and Metallization in WSe2. *Sci. Rep.* 2017, 7 (May), 2–10. https://doi.org/10.1038/srep46694.

- (33) Finger, L. W.; Hazen, R. M.; Zou, G.; Mao, H. K.; Bell, P. M. Structure and Compression of Crystalline Argon and Neon at High Pressure and Room Temperature. *Appl. Phys. Lett.* **1981**, *39* (11), 892–894. https://doi.org/10.1063/1.92597.
- Li, L.; Boda, M. A.; Chen, C.; Wang, F.; Liu, Y.; Yi, Z. BiOBr Micro-Nanosheets: Controllable Synthesis and Piezoelectric and Photoelectric Properties. *Cryst. Growth Des.* 2021, 21 (12), 7179–7185. https://doi.org/10.1021/acs.cgd.1c01026.
- (35) Yang, B.; Wang, W.; Hu, Z.; Shen, B.; Guo, S. Q. Vacancy Pairs Regulate BiOBr Microstructure for Efficient Dimethyl Phthalate Removal under Visible Light Irradiation. J. Hazard. Mater. 2023, 458 (July), 132008. https://doi.org/10.1016/j.jhazmat.2023.132008.

Part 4

Piezo-photocatalytic Investigation of sillen Aurivillus

Chapter 4.1.

Universal piezo-photocatalytic wastewater treatment at realistic pollutant feed-stocks by Bi₄TaO₈Cl: Origin of high efficiency and adjustable synergy



Summary

Clean water is a fundamental human right but millions struggle for it daily. Herein, we demonstrate a new piezo-photocatalyst with immense structural diversity for universal wastewater decontamination. The single-crystalline Bi₄TaO₈Cl nanoplates with exposed piezoelectric facets exhibit visible-light response, piezoelectric behaviour with coercive voltages of ±5 V yielding 0.35% crystal deformation, and pressure-induced band-bending of >2.5 eV. Using five common contaminants of textile and pharmaceutical industries, we show that the nanoplates can mineralize them in all piezocatalytic, photocatalytic as well as piezophotocatalytic approaches with efficiencies higher than most catalysts developed for just one contaminant. Their efficiencies for feedstocks differing over 2 orders of magnitude in concentrations, the highest to date, are also demonstrated to simulate real-life situations. These extensive studies established that combining piezocatalytic and photocatalytic approaches can lead to a tremendous synergy exceeding >45%. The origin of synergy has been illustrated for the first-time using band-bending models and improved charge transfer from valance and conduction band electronic surfaces. We further quantified synergy across reactants, concentrations, and ultrasonic frequency and power to demonstrate its versatility and unpredictability. Finally, seven parameters that contribute to the synergy but create unpredictability have been identified for the rational design of piezo-photocatalysts for wastewater treatment.

A Manuscript based on this work has appeared in ACS Appl. Mater. Interfaces 2023, 15, 27, 32425–3243

4.1.1. Introduction

Nearly 800 km³ of freshwater is used by industries annually, whose effluents cause irreversible damage to water bodies.¹ Textile and pharmaceutical industries are the major contributors to water pollution due to the low biodegradability of pharmaceuticals. Also, ~15% of the 700 million Kg of dyes is released as undesirable effluents annually.² This inspired intense research activities for decades seeking materials that can remove the pollutants, but with only limited success. There are by and large two aspects crucial for real-life implementation that remain unaddressed: (i) developing materials to act universally across a range of pollutants since large wastewater pools contain multiple contaminants whose response to the material is not guaranteed due to diversity in their chemical interactions and (ii) performance evaluation at realistic concentrations that can be orders of magnitude higher than lab-scale investigations.

4.1.2. Scope of the present investigation

Harvesting carbon-neutral renewable energies are advantageous for wastewater treatment, leading to a tremendous surge in developing solar-responsive photocatalysts.^{3–5} However, the strategy relies inordinately on the suitable alignment of the redox potentials of pollutants to those of a catalyst, limiting the choice of materials severely. Besides, the intrinsic re-emitting of energy by the material further limits its effectiveness. In this context, very recently, piezocatalysis as a way of harvesting mechanical energy such as ultrasound noise is fast emerging as a highly promising strategy due to several additional advantages such as the (i) non-requirement of band-alignment conditions as in photocatalysis, (ii) therefore, a much larger choice of materials, and (iii) the possibility of integrating with photocatalysis.^{6–8}

Piezopotential resulting from external stress can generate an energy shift in the occupied and unoccupied electronic states of a catalytic material and efficiently drive the redox reaction.⁹ In addition, ultrasound scrub cleans the catalyst surface intermittently to remove poisoning reaction intermediates that were adsorbed on the surface due to a developing surface charge, reducing their catalyst poisoning effect. Solitarily piezocatalysis is, however, challenged by low efficiency due to the need for high built-in electric fields to provide sufficient activation for electron transfer.^{10,11} Typical band bending requirements for oxides, for example, are of the order of 2-3.5 V which would require a pressure of 10⁸-10⁹ pascal.^{12,13} A major fraction of the catalyst particles may not experience such pressure due to inappropriate orientation to the cavitation bubbles. But this can be changed since many semiconducting materials exhibit both piezoelectric and light absorption properties.^{7,14} In such materials, the

efficiency can be improved by adopting a piezo-photocatalytic approach so that the piezoinactive particles can still participate in a photocatalytic pathway. Piezocatalysis involving the valence band electrons of the catalyst and photocatalysis involving the excited ones can work in tandem, but with additional benefits to yield synergy discussed *vide infra*.¹⁵

Herein we report on the Bi₄TaO₈Cl nanoplates, a member of the family of layered Sillen Aurivillius (SA) phases, as a universal catalyst for wastewater treatment under photocatalytic, piezocatalytic, and photo-piezocatalytic conditions and also at industrially relevant organic contaminant concentrations. As compared to usual piezocatalytic compounds such as ZnO, BaTiO₃, etc.,^{12,14} SA phases are advantageous as it belongs to the family of layered materials consisting of the alternate Sillen and Aurivillius layers and has large material design flexibility originating from the choice of modulating each phase independently. SA phases consist of halide (X), fluorite Bi₂O₂, and perovskite MO₄ (M=Ta, Nb, etc.) slabs with a general formula of $[Bi_2O_2]$ $[A_{n-1}B_nO_{3n+1}]$ $[Bi_2O_2]$ $[X]_m$ where n represents the number of perovskite layers and are highly responsive to visible light.^{16,17} It has a polar space group, with spontaneous polarization along both the *a*-axis and *c*-axis.^{18,19} Our single-crystalline Bi₄TaO₈Cl nanoplates, unlike traditional high-temperature synthesized powders, are well-defined in shape with exposed facets along the piezoactive a- and c-axis. We found them to have a rare, universal piezocatalytic degradation efficiency under photoirradiation towards both cationic and anionic dye contaminants as well as towards some of the most stubborn antibiotics, with a performance outwitting most previously known catalysts designed for just a single pollutant. The same was then tested in pollutant concentrations ranging 2 orders of magnitude for the first time with some remarkable deviation from expectation.

We further bring forth an important scenario during piezo-photocatalysis that can tremendously improve efficiency by considering photo-excitons in those catalyst particles exposed to insufficient ultrasonic stress. Such excited electrons and holes feel the piezo-generated field gradient and effectively separate towards the oppositely polarized particle facets, leading to synergy. Such improvement has been observed recently, though its origin remains unclear. We quantify and landscape synergistic improvements across all pollutants and under high feedstock to demonstrate its benefits. We show that synergy is universal for all pollutants but unpredictable, ranging within 1- 44.6% in the lab scale concentrations and 25–39% in the varying feedstock. The origin of synergy diversity and unpredictability has been illustrated by proposing a gear interlock of nearly independent contributing factors that would help the rational design of highly active catalysts.

4.1.3. Methods

4.1.3.1. Catalyst Synthesis

Synthesis of Bi₄TaO₈Cl nanoplates: Bi₄TaO₈Cl nanoplates have been synthesized by taking a stoichiometric molar ratio of (3:2:1) Bi₂O₃, BiOCl, and Ta₂O₅ precursors. The mixture was first grounded and then added to a eutectic mixture of an alkali metal chlorides (1:1) NaCl and KCl as a flux at a solute concentration of (Bi₄TaO₈Cl/(Bi₄TaO₈Cl+flux)) of 3.2 mol percent. Once again, the mixture was grounded before being transferred to a silica boat and heated for 4 hours in a muffle furnace at 700 °C with a heating rate of 3 °C min⁻¹. After cooling to ambient temperature, the product was cleaned with deionized water five times to eliminate the flux, collected by centrifugation, and dried at 60 °C for 10 hours.

4.1.3.2. Photocatalytic reactions

Photocatalytic, Piezocatalytic, and Piezo–Photocatalytic Degradation Measurements.

Dye Degradation: For a typical dye degradation experiment, 40 mg of Bi₄TaO₈Cl sample was dispersed in 25 mL of dye solution (20 μ M for RhB and MB; and 10 μ M for MO). Before irradiation, an adsorption–desorption equilibrium was obtained by stirring the solution in dark for about 30 min. Afterward, the system was subjected to particular irradiation using a bath sonicator and xenon lamp as ultrasound and light sources respectively. The aliquot was periodically collected and centrifuged for the kinetic study of the dye degradation using UV-Vis. spectrometer. RhB absorbs at 553 nm, MB and MO adsorb at 664 nm, and 464 nm respectively. (Note: High-concentration studies were carried out by taking 500 and 1000 μ M RhB dye solution, with other conditions remaining the same.)

Pharmaceutical Degradation: Piezo-photocatalytic pharmaceutical degradation performance of Bi_4TaO_8Cl was done by taking two-model pharmaceuticals (antibiotics): tetracycline and ciprofloxacin. 0.2 mM tetracycline and 0.1 mL of ciprofloxacin solutions containing 0.3% w/v ciprofloxacin and 0.01% w/v benzalkonium chloride diluted in 80 mL of distilled water were taken as initial concentration. To make a homogenous suspension both pharmaceutical solutions are sonicated for one hour. The catalytic experiment was done by taking 10 ml of suspension and irradiating it with both ultrasound and light simultaneously. The aliquots were collected after each 2 min and the degradation was analyzed from decreases

in the solution absorbance at 375 nm and 277 nm for tetracycline and ciprofloxacin respectively by UV-Vis. spectroscopy after centrifugation.

Trapping Experiments: The trapping experiments were done by using several scavengers. 2 ml Isopropyl alcohol (IPA), 1.5 ml (10^{-2} g/mol) benzoquinone (BQ), and 2ml (0.05 mM) Ammonium Oxalate (AO) solutions were added respectively into the reaction system i.e 25 ml of 20 μ M rhodamine solution having 40 mg of Bi₄TaO₈Cl. The solution was stirred in the dark for 30 min to attain adsorption-desorption equilibrium. Subsequently, the reaction system was subjected to simultaneous irradiation of light and ultrasound. The degradation was analyzed by recording a decrease in absorbance at 553 nm by UV-Vis. spectroscopy.

Detection of Superoxide and Hydroxyl Radical: Superoxide radicals and hydroxyl radicals were quantified by dispersing 40 mg of Bi₄TaO₈Cl nanoplates into 25 mL of nitro blue tetrazolium (NBT) (0.025×10^{-3} M) and the terephthalic acid (0.5 mM) aqueous solution respectively. The reaction mixture was irradiated with light for 2 h and the aliquots were analyzed by UV-Vis. absorption spectroscopy at maximum absorbance of 259 nm for superoxide radical and fluorescence spectra at 425 nm for hydroxyl radical.

4.1.3.3. Characterization:

All the characterization techniques are discussed in chapter 1.2.

4.1.4. Results and Discussion

4.1.4.1. Catalyst Characterization

Single crystalline Bi₄TaO₈Cl nanoplates with exposed piezoactive facets were prepared by using a eutectic mixture of NaCl and KCl flux. Bi₄TaO₈Cl crystal consists of the [Bi₂O₂], [TaO₄], and [Cl] layers (**Figure 4.1.1. a**), with high polarization along the *a*-axis arising from the displacement of Bi³⁺ and octahedral off-centering of Ta⁺⁵ (**Figure 4.1.1. b** and **c**) due to the *pseudo-John-Teller effect*, while polarization along the *c*-axis is ascribed to an anisotropic coordination around Bi³⁺.¹⁹ The phase purity of the product nanoplates was confirmed by powder X-ray diffraction (XRD) pattern (**Figure 4.1.1. d**, ICDS#89-009-3557), and Energy-dispersive X-ray spectroscopy (SEM-EDS, **Figure 4.1.1. e**). The surface chemical composition and oxidation states were investigated with X-ray photoelectron spectroscopy. The high-resolution Bi-4f spectrum (**Figure 4.1.2. a**) can be fitted with two peaks centered at 159.40 eV

and ~164.60 eV corresponding to the Bi4f_{7/2} and Bi 4f_{5/2} states respectively of Bi³⁺ ions. The peak centered at 531.10 eV in the O-1s spectrum originates from oxygen moieties within the Bi₄TaO₈Cl crystal (**Figure 4.1.2. b**). Note that the Ta 4f spectrum overlaps with the Bi-5d spectrum, and therefore the same has been deconvoluted into four peaks (**Figure 4.1.2. c**). The two peaks at 26.70 and 24.85 eV are attributed to Ta-4f_{7/2} and Ta-4f_{5/2} states of Ta⁺⁵ species, while the other two peaks at 28.60 eV and 25.60 eV correspond to Bi-5d_{5/2} and Bi-5d_{3/2} states of Bi³⁺. Finally, the two peaks with binding energies at 199.80 and 198.33 eV are attributed to Cl-2p_{1/2} and Cl-2p_{3/2} respectively of Cl⁻ in the Bi₄TaO₈Cl lattice (**Figure 4.1.2. d**).



Figure 4.1.1. (a) Crystal structure of Bi_4TaO_8Cl , red, green, purple, and blue balls represent Ta, Bi, O, and Cl atoms respectively. (b, c) TaO_6 octahedral unit showing the offset of Ta along the *a*-axis. (d) Powder XRD pattern of Bi_4TaO_8Cl . (e) FE-SEM EDS spectrum of Bi_4TaO_8Cl Nanoplate.

The product powder is composed of morphology pure, square- or rectangular-shaped ~1±0.5 μ m wide nanoplates (**Figure 4.1.3 a, b**). **Figure 4.1.3. c** is a high-resolution transmission electron microscopy (HRTEM) image of a nanoplate revealing the lattice fringes of 0.38 nm and 0.28 nm corresponding to the (110) and (020) planes respectively and suggesting the basal facet of the square nanoplate as {001}. The corresponding selected area diffraction (SAED)

pattern along the [001] zone axis confirms its single crystalline nature along with the dominant exposure of the $\{001\}$ facets (**Figure 4.1.3. d**). The other facets enclosing the nanoplate thus appear to be the $\{001\}$ analogs. But careful observation of these facets has revealed the presence of numerous steps, kinks, and uncoordinated atoms all along, increasing its surface area and potentially the catalytic activities (**Figure 4.1.3. e**).



Figure 4.1.2. (a, b) High-resolution Bi-4f and O-1s XPS spectra of the sample. (c) High-resolution XPS spectra of Bi-5d (red peaks at 25.6 & 28.6 eV belong to $Bi^{3+} 5d_{5/2}$ and $Bi^{3+} 5d_{3/2}$) and Ta-4f (purple peaks at 26.7 & 24.84 eV correspond to $Ta^{5+} 4f_{7/2}$ and $Ta^{5+} 4f_{5/2}$). (d) XPS spectrum of Cl-2p.



Figure 4.1.3. (a) FE-SEM and (b) TEM image showing Bi₄TaO₈Cl nanoplates with a width of ~0.5-1um (c) HRTEM image and (d) SAED pattern confirming single crystalline nature of Bi₄TaO₈Cl nanoplates. (e) HRTEM image showing numerous steps, kinks, and uncoordinated atoms at the edge of nanoplate.

The specific surface area of these nanoplates is indeed nearly double (7.2 m²/g) of those obtained by the solid-state approach (**Figure 4.1.4. a**).²⁰ Furthermore, UV–Vis diffuse reflectance spectroscopy (DRS) was used to investigate the optical properties of Bi₄TaO₈Cl nanoplates.²¹ The sample exhibited an absorption edge at 510 nm. A bandgap energy of ~2.5 eV was determined by Kubelka–Munk function shown below (**Figure 4.1.4. b and inset**):

$$(\alpha h\nu) = A (h\nu - Eg)^n$$

Where Eg = optical bandgap energy, hv = photon energy, A = constant, a = absorption coefficient, and *n* depends on the nature of transition, here n = 2 considering an indirect bandgap. The valance band of Bi₄TaO₈Cl was determined by Mott-Schottky analysis performed in 0.5 M NaSO₄ solution at 500 kHz frequency. As shown in **Figure 4.1.4. c**, it exhibits *n*-type characteristics with a flat band potential of -0.3 eV vs. RHE.



Figure 4.1.4. (a) N_2 adsorption isotherms of Bi₄TaO₈Cl nanoplates synthesized by the Flux method. (b) DRS plots and the corresponding Tauc plot (inset), (c) Mott–Schottky plot of Bi₄TaO₈Cl measured at 500 kHz.



Figure 4.1.5. (a) Topography image of a Bi_4TaO_8Cl nanoplate with height information in (b). (c, d) The corresponding amplitude and phase images. (e) Piezoelectric force spectroscopy measurement of the displacement-voltage curve, and (f) the phase curve-voltage curve recorded on the nanoplate.

The piezoelectric properties of nanoplates were investigated by using piezoelectric force microscopy (PFM) by applying an AC voltage coupled with a sweeping DC voltage to the tip. A topographic image with a typical Bi₄TaO₈Cl nanoplate of ~100 nm height and the corresponding piezoresponse amplitude and phase images are seen in **Figure 4.1.5. a, b, c, and d.** The local piezoresponse hysteresis loops were recorded by sweeping the DC voltage within -10 V to +10 V. A clear butterfly-shaped amplitude loop was observed (**Figure 4.1.5. e**) with forward and reverse coercive voltages of 5 V and -5 V, and the highest amplitude of 350 pm, indicating the pronounced piezoelectric properties of the nanoplate. Besides, a 180-degree shift in the corresponding phase-angle-voltage hysteresis plot under DC bias reversal confirmed polarization switching within the nanoplates (**Figure 4.1.5. f**).

4.1.4.2. Synergistically improved piezo-photocatalytic efficiency of Bi₄TaO₈Cl nanoplates

The excellent piezoelectric and light absorption properties of the Bi₄TaO₈Cl nanoplates inspired us to investigate their piezo-photocatalytic properties with the anticipation of markedly



Figure 4.1.6. Temporal variation in UV-Vis. absorption spectra of RhB solution under (a) photocatalytic, (b) piezocatalytic, and (c) piezo-photocatalytic conditions. The UV-vis absorption spectra presented in (d), (e), and (f) demonstrate the degradation of the dye under light irradiation (photo), ultrasonication (piezo), and a combination of both (piezo-photo), respectively, in absence of the catalyst.

enhanced the catalytic activity originating from a synergy of the two processes (as elaborated in the mechanism section). The catalytic performance was investigated using the mineralization of several common pollutants such as antibiotics (ciprofloxacin and tetracycline) and dyes (methylene blue, methyl orange, and Rh B (RhB)). Under the photo, piezo, and piezophotocatalysis conditions, complete mineralization of a RhB (Conversion of RhB to carbondioxide solution and water) took 105, 25, and 12 min respectively (**Figure 4.1.6. a, b, and c**). In order to investigate the significance of the catalyst, RhB degradation was also performed without Bi₄TaO₈Cl nanoplates. As shows in (**Figure 4.1.6. d, e, f)**, only 5%, 10%, and 15% RhB undergoes degradation under photoirradiation, ultrasonication, and combined piezo-photoirradiation respectively without catalyst. In **Figure 4.1.7. a**, we show the rate constants (k) under all conditions considering pseudo-first-order kinetics with a rate equation,

$$(-\ln(C/C_0) = kt) \qquad \text{eq-1}$$

where C_0 and C are the dye concentrations initially and at time t.²² The k values during photo and piezocatalysis are 0.0339 min⁻¹ and 0.1153 min⁻¹, which in piezo-photocatalysis conditions, quite impressively, increases by a staggering ~10 and ~3 times respectively to 0.2694 min⁻¹. This activity was found to be highly dependent on ultrasound frequency (**Figure 4.1.7. b**), and the highest activity was achieved at 37 kHz which was used for the remaining studies. Moreover, a higher vibrational power should lead to higher stress (T) and more piezoelectric charge density (Q_p) on the catalyst's surface, resulting in higher catalytic efficiency following the relationship,

$$Q_p = d_{33} T \qquad eq-2$$

where d_{33} is the piezoelectric coefficient of the nanoplates.²³ The efficiency indeed varied with ultrasonic power (**Figure 4.1.7. c**), but with nonlinear increments. The mineralization rate disproportionately increased from 0.07 min⁻¹ to 0.11, 0.148, and 0.284 min⁻¹ when the power was increased from 40% to 60%, 80%, and 100 % respectively.

The rate constant values estimated under the different conditions in this study were compared with the recent literature to realize that Bi_4TaO_8Cl nanoplates are perhaps the most efficient ones among the *state-of-the-art* piezo-photocatalyst (**Table 4.1.1**.).^{24–27} We further investigated the catalyst stability and found that the catalyst maintained similar activity for up to 5 cycles without exhibiting structural deformations (**Figure 4.1.7.d**).



Figure 4.1.7. (a) Plot showing degradation rate for RhB solution under photo, piezo, and piezo-photocatalytic conditions. (b, c) Rate of piezo-photocatalytic RhB degradation as a function of frequency and pressure. (d) Reusability of the catalyst under piezo-photocatalysis for five consecutive cycles.

The enormous enhancement in catalytic activity in piezo-photocatalytic conditions as compared to the photocatalytic and piezocatalytic conditions respectively can be attributed to the synergistic effects originating from the coupling of photo and piezocatalytic approaches. A synergistic factor and % synergy can be defined as below:

Synergy factor =
$$\frac{k(piezophoto)}{k(piezo) + k(photo)}$$
 eq-3

$$% Synergy = \frac{k(piezophoto) - (k(piezo) + k(photo))}{k(piezophoto)} * 100$$
 eq-3

Thus, the improved degradation efficiency in piezo-photocatalysis characterized by a %synergy and synergy factor of 44.6 and 1.8 respectively.



4.1.4.3. Band-bending, exciton separation as the origin of synergy

Figure 4.1.8. UV-Vis absorption spectra and the corresponding rate constant plots showing the effect of various scavengers on the RhB dye degradation through (a,b,c,d,e,f) piezo-photo, (g,h,i,j,k,l) piezo, and (m,n,o,p,q,r) photocatalysis over Bi₄TaO₈Cl nanoplates.

We explored the reaction mechanism using several controlled experiments to establish that the electron transfer pathways are heavily influenced by band-bending under piezo-photocatalytic conditions which lead to unprecedented synergistic improvements in the reaction rate. We further establish the contributing factors to the synergy that can influence catalyst performance while using in industry-relevant concentrations. We first examined the reactive species responsible for dye degradation under piezo, photo, and piezo-photocatalytic conditions using reactive species scavenging experiments (Figure 4.1.8.). Isopropyl alcohol (IPA), benzoquinone (BQ), and triethanolamine (TEOA) were used as a scavenger for •OH, •O2-, and holes (h+) respectively. Triethanolamine has a minor impact on the degradation efficiency in all photo, piezo, and piezo-photocatalytic conditions whereas the addition of IPA and BQ considerably reduces the efficiency in piezo and piezo-photocatalytic conditions. However, in the case of photocatalysis, there is a negligible effect of BQ on degradation efficiency. The result demonstrated that both \cdot OH and \cdot O²⁻, are the active species in the degradation of RhB dve over Bi₄TaO₈Cl nanoplates under piezocatalysis and piezo-photocatalysis. whereas •OH is the only active species in photocatalysis indicating a profound influence of pressure-induced band-bending. Figure 4.1.9. a shows the band positions of Bi₄TaO₈Cl in ambient pressure and the redox potentials of various active species to support these observations.²¹¹⁵ With a band gap (Eg) value of 2.5 eV, Bi₄TaO₈Cl can harvest visible light during photocatalysis to excite electrons to the CB, leaving a hole behind in the VB. The holes oxidize water to form ·OH radicals, which subsequently degrade RhB. However, the CB edge is not sufficiently negative to facilitate the reduction of adsorbed oxygen (-0.33eV vs NHE) to form the superoxide radicals.

Unlike photocatalysis which requires suitable band edge positions for active species generation, piezocatalysis can have an advantage because pressure can forcefully align the band positions to enable charge transfer to active species. Under piezocatalytic conditions, the ultrasound waves provoke cavitation bubble formation. When such a bubble collapses, the rushing molecules on the exterior of the bubble exert tremendous pressure, transiently, on the floating catalyst particles causing its deformation and generation of piezo-potential on its surfaces.²⁸ The oppositely polarized surfaces of such a Bi₄TaO₈Cl nanoplates then create a favourable energy landscape for active radical species formation, as shown **in Figure 4.1.9. b** (**i**). Under sufficient pressure, the conduction band becomes more negative than the reduction potential of molecular oxygen and favours superoxide radical formation which can induce RhB

degradation. The degradation by ·OH radical pathway remains intact, thus providing more pathways for RhB degradation than in photocatalysis.



Figure 4.1.9. Energy band diagram of Bi_4TaO_8Cl nanoplates under the (a) photo, (b) piezo, and (c) piezo-photocatalytic conditions. (d, e) Schematic showing the formation of reactive oxygen species during photo and piezo-photocatalysis. (f, g, h) UV-Vis. absorption spectra showing the formation of superoxide radicals during photo, piezo, and piezo-photocatalysis respectively.

In this scenario, there is a situation that can lead to synergy. The extent of band bending is correlated to the deformation of a Bi_4TaO_8Cl nanoplate or how much pressure it experiences. For superoxide radical formation, the band has to bend by more than 2.5 eV. However, all nanoplates may not experience sufficient deformation due to their spatial positioning with respect to the bursting bubble and may refrain from catalysing the reaction (**Figure 4.1.9. b** (ii)). In that case, piezo-photocatalytic conditions have an advantage that leads to extra efficiency in two ways: (i) By forcefully adjusting the redox potentials of catalyst and reactants to induce photocatalysis. Note that even under partial band bending (piezo-inactive) conditions

such as in **Figure 4.1.9. b** (ii), light irradiation enables its participation due to the generation of excited electrons in the conduction band, as shown in **Figure 4.1.9. c**, and (ii) by improved exciton separation since the piezopotential on nanoplate surfaces causing band-bending as in **Figure 4.1.9. b** (i, ii) can also serve as a driving force for the separation of photogenerated charge carriers.^{29,30} Accordingly, a schematic of the reaction mechanism under photocatalytic and piezo-photocatalytic conditions is shown in **Figure 4.1.9. d & 4e**.

To establish this hypothesis, we quantified the superoxide radicals and hydroxyl radical formed under different conditions. As seen in **Figure 4.1.9. f, g, and h,** superoxide radical formation during photocatalysis is indeed negligible, whereas its quantity increases from 55 μ mol/h/g to 105 μ mol/h/g in piezocatalysis and piezo-photocatalysis respectively. Similarly, the fluorescence spectra of 2-hydroxy terephthalic acid at 425 nm (**Figure 4.1.10.**) depicts the formation of hydroxyl radical (61.5, 99, and 141 μ mol/h/g in photocatalysis, piezo catalysis, and photo-piezo catalysis, respectively), confirming the proposed mechanism.^{31,32}



Figure 4.1.10. UV-Vis. absorption spectra showing the formation of Hydroxyl radicals during the (a) photo, (b) piezo, and (c) piezo-photocatalysis respectively

4.1.4.4. Universality, diversifying synergy, and high concentration contaminant degradation efficiency

A crucial aspect of catalyst development for wastewater treatment is to evaluate its universality towards a diverse set of pollutants because, in actual conditions, water may contain multiple contaminants. However, a catalyst may not act on different pollutants effectively for reasons such as different conformations of pollutant molecules around the reactive oxygen species (ROS) attack center. Besides, the sorption strength of the pollutants on the catalyst surface as adjusted by the catalyst surface charge is also equally influencing. Pollutant molecules bind to the catalyst through electrostatic attraction, *H*-bonding, π - π interaction, or van der Waals force either exothermically or endothermically.³³ The situation becomes even more unpredictable since nothing much is known about the binding of degradation-intermediates and their

oxidation potentials during complete mineralization. Thus, quite similar molecules have been photodegraded by the same catalyst involving distinct electron and hole-mediated mechanisms.³⁴



Figure 4.1.11. (a) Plot showing the efficiency of Bi_4TaO_8Cl nanoplates to degrade both cationic (MB) and anionic (MO) dye. (b) Rate of pharmaceuticals degradation over Bi_4TaO_8Cl . (c) Degradation rate for different concentrations of dyes (rate constants of 20 μ M sample in the plot should be multiplied by 20). (d) Plot showing %synergy and amount of dye adsorbed per gram of the catalyst.

However, we anticipated that the situation may be significantly advantageous during piezo-photocatalysts due to the band-bending scenario described above, leading to the facile degradation of diverse pollutants. Barring a couple of reports with moderate performances, wastewater treatment has mainly been evaluated based on a single target pollutant only. We therefore further explored and observed that, as desirable, Bi₄TaO₈Cl nanoplates can degrade a wide range of pollutants, such as both cationic (RhB, Methylene blue (MB)) and anionic (methyl orange (MO)) dyes as well as widely used pharmaceuticals with very high efficiencies. These experiments also established that the synergy factors in all these reactions remain diverse and unpredictable, the origin of which will be discussed in the next section.

Catalyst	Energy source	Dye	Concentration µM	Rate constant (min ⁻¹)	Reference	
		Piezo-photo	catalysis			
		RhB	20	0.27		
			500	0.0076		
			1000	0.003]	
Bi ₄ TaO ₈ Cl Nanoplates	Ultrasonic: 110 W, 37kHz 400W Xe-lamp	MB	20	0.077	This work	
		MO	20	0.075		
		Ciprofloxacin	9000	0.0259		
		Tetracycline	200	0.01		
ZnO nanowires	Ultrasonic: 200 W 300 W Xe-lamp	MB	10	0.00213	1	
BT@TiO2 nanowires	Ultrasonic: 45 kHz, 200 W 300 W Xe-lamp	RhB	60	0.06	2	
Bi _{0.5} Na _{0.5} TiO ₃ @TiO ₂	Ultrasonic: 40 kHz, 100 W 300 W xenon lamp	RhB	100	0.034	3	
Ag ₂ O/BaTiO ₃	Ultrasound:45 kHz, 500 W 300 W xenon lamp	мо	6.5	0.019	4	
Bi ₄ Ti ₃ O ₁₂ nanoplates	Ultrasonic: 45 kHz, 300 W 300 W xenon lamp	RhB	10	0.144	5	
AgNbO ₃ –LiTaO ₃	Ultrasonic: 45 kHz, 300 W 300 W xenon lamp	RhB	10	0.026	6	
Bi ₂ VO ₅	Ultrasonic:150 W, 40 kHz Two Havells bulbs each 15W power	МВ	15	0.005	7	
		Piezoca	talysis			
	Ultrasonic: 110 W, 37kHz	RhB	20	0.1153	This work	
Bi₄TaO₀Cl		MB	20	0.048		
Nanoplates		MO	20	0.058		
		Ciprofloxacin	9000	0.0259		
		Tetracycline	200	0.01		
Ba _{0.8} Ca _{0.2} TiO ₃ nanowires	120 W, 40 kHz	MO	10	0.0281	8	
BaTiO ₃ nanowires	120 W, 40 kHz	мо	10	0.0164	9	
BiFeO ₃ nanowires	80 W, 132 kHz	RhB	10	0.0431	10	
ZnO rods	300 W, 40 kHz	MB	20	0.0149	11	
ZnO:Sb	1MHz; US power, 1.2 W cm-2	RhB	5	0.045	12	
Ag@LiNbO ₃ /PVDF	40 kHz,120 W	Tetracycline	0.2	0.00887	13	
BiOBr	40 kHz,120 W	RhB	20	0.005	14	
		Photocata	llysis			
		RhB	20	0.0339		
	300 W xenon lamp	MB	20	0.026		
Bi4T _a O ₈ Cl		мо	20	0.017	This work	
Nanopiates		Ciprofloxacin	9000	0.0259		
		Tetracycline	200	0.01		
Ag ₂ O/BaTiO ₃	500 W Xe Lamp	МО	6.5	0.015	4	
ZnO:Sb	500 W Xe lamp	RhB	5	0.048	12	
ZnO nanowires	500 W Xe lamp	МВ	10	0.00044	1	
BiOIO ₃	300 W Xe lamp	Ciprofloxacin	3	0.0083	15	
BaTiO ₃ @TiO ₂	300 W Xe lamp	RhB	20	0.023	2	

 Table 4.1.1 Comparison table showing photo, piezo, and piezo-photocatalytic pollutant degradation over Bi₄TaO₈Cl nanoplates as compared to other reported photocatalysts, piezocatalysts, and photo piezo catalysts.

Figure 4.1.11.a depict the degradation of MB and MO under all three conditions. Bi₄TaO₈Cl shows a rate constant of 0.038, 0.048, and 0.077 min⁻¹ for MB degradation and 0.016, 0.057, and 0.075 min⁻¹ for MO degradation under the photo, piezo, and piezo-photocatalysis respectively. In both cases activity enhanced in piezo-photocatalysis by 3.8 and 6.3 % synergy due to the synergistic effect of photocatalysis and piezocatalysis. Bi₄TaO₈Cl efficiency was further explored towards the degradation of pharmaceutical contaminants *viz*. widely used ciprofloxacin and tetracycline antibiotics that exist in zwitterionic forms at a neutral p*H*. Due to minimal bodily uptake, these are usually excreted in unchanged forms to harm biodiversity and create antibiotic resistance.³⁵ **Figure 4.1.11. b** shows the degradation efficiency of ciprofloxacin and tetracycline under a photo, piezo and piezo-photocatalytic condition over Bi₄TaO₈Cl. The corresponding first-order degradation rate constants are 0.026, 0.047, 0.117 min⁻¹ for ciprofloxacin and 0.010, 0.046, 0.070 min⁻¹ for tetracycline respectively. The respective % synergy values were estimated to be 37.7% and 20%.

> Mean Zeta Potential = -0.4 mV Peak 1 = -0.4 mV Peak 2 = -0.3 mV Standard Deviation =0.1 mV



Figure 4.1.12. Zeta potential data of Bi₄TaO₈Cl Nanoplates.

As in the case of RhB, a comparison of the other catalytic activities of the Bi_4TaO_8Cl nanoplates with literature reports showed that their activities towards all the pollutants are

significantly superior to most other catalysts including the ones containing noble metals, even though these reports are about single contaminants only.²⁶ The degradation efficiencies for different dyes and pharmaceuticals in this study are compared with the best-reported data in **Table 4.1.1.** For such efficient surface reactions, adequate adsorption of the reactive species is a prerequisite and the adsorption capacity is directly related to the surface charge of the catalyst, where a positive charge favors anionic dye adsorption and anionic surface-charged catalyst favors cationic dye adsorption. **Figure 4.1.12.** shows the zeta-potential plot for our Bi₄TaO₈Cl showing that the nanoplates have an average surface potential of just -0.4 mV. Therefore, both cationic and anionic dyes can find adsorptive sites on it for efficient degradation.

Finally, we used the Bi₄TaO₈Cl nanoplates to degrade RhB dyes dissolved in high concentrations mimicking those obtained in the industrial wastewater.³⁶ While the usual dye concentrations for lab demonstrations are ~10 -15 mg/L,³⁷ the nanoplates can degrade ~500 mg/L of RhB solution efficiently. The concentration is much higher than in a few previous reports using solutions of ~50-200 mg/L also (**Table 4.1.1.**). We systematically evaluated the degradation kinetics for 10, 375, and 500 mg/L RhB solution under photo, piezo, and piezo-photocatalysis (**Figure 4.1.11 c**). The average efficiency however decreases from k= 0.0339, 0.1153, 0.2694 min⁻¹ at 10 mg/L to 0.0006, 0.0018, 0.0032 at 500 mg/L respectively. The activity enhanced in piezo-photocatalytic conditions in all the cases due to the synergistic effects although the % synergy also reduced from 44.6% to 24% at the higher concentrations.

To explore the origin of the decrease in catalytic activity with increasing concentrations, the amount of dye adsorbed per unit mass of the catalyst (Q_e) (mg/g) was calculated as

$$Q_e = \frac{(C_o - C_t)}{W} * V \qquad \text{eq-5}$$

where C_o and C_t represent the initial concentration and the concentration at a time t (in mg/L), W is the catalyst amount (g), and V is the solution volume (L).³⁸ As shown in **Table 4.1.2.** and **Figure 4.1.11. d** Q_e and % synergy are oppositely related, i.e. Q_e increases with increasing RhB concentration, whereas the corresponding % synergy decreases, affirming that increasing dye concentration blocks the active sites from ROS formation and also screens the adsorption of photons and probably ultrasound energy to some extent by the nanoplate due to cushioning by the adsorbed layer.

Concentration (µM)	Rate Constant (min ⁻¹)			Q _e (mg/g)	Synergy	% Synergy
	Photo	Piezo	Piezo-Photo		Factor	
20	0.0339	0.115	0.2694	1.5	1.8	44.6
500	0.00168	0.0029	0.0076	18	1.6	38.8
1000	0.0006	0.0018	0.00323	59.6	1.3	25.7

Table 4.1.2. Table showing rate constant, synergy, and amount of dye adsorbed per unit mass

 of the catalyst under different concentrations of RhB dye.

4.1.4.5. Deviation from expected behaviour and the key synergy generator parameters: As in **Figure 4.1.11. c**, we found that despite being considered a pseudo-first-order reaction, the RhB degradation rates at industrial concentrations drastically deviate from lab scale concentrations. Such deviations during piezocatalysis have not been reported to date and the origin is hard to predict. In addition, the very high %synergy observed universally across a range of pollutants, but with drastic variations in %synergy in the different reactions, etc. indicate the interplay of several contributing factors to the catalyst performance acting simultaneously during the reaction, which can be tailored independently for better effectiveness. Herein, (**Figure 4.1.13. b**) we propose a performance gear-interlock for a piezo-photocatalysis approach involving seven nearly independent factors from the point of view of catalyst design while keeping the reaction mechanism described in **Figure 4.1.11.** in consideration.

i) Built-in electric field: Band-bending is critical and the extent of band-bending is dependent on the amplitude of the built-in electric field. Figure 4.1.11. b & c indicate band-bending hypothetically to the extent of ~2.5 and ~1.0 eV respectively. Not all bubbles implode to generate similar pressure, nor is each catalyst particle positioned appropriately to absorb the entire pressure. We can however estimate the possible extent of bending from the PFM measurements. The open-circuit voltage (V_p) created across the two (001) surfaces of the nanoplate under the mechanical deformation is related to the applied pressure (T_3) as:

$$V_p = \frac{W_3 T_3 d_{33}}{e_0 e_r}$$

where W_3 is the thickness of the nanoplate, d_{33} is the piezoelectric coefficient, e_0 is the permittivity of free space, and e_r is the relative permittivity in the *c* dimension.¹² Here, W_3 is ~100 nm (**Figure 4.1.5. b**), and the reported value for d_{33} is 53 pm/V.¹⁸ The e_r of the Bi₄TaO₈Cl has been considered as 150.³⁹ However, it is difficult to fix the T_3 values since the actual pressure generated under sonication is vaguely reported in the range of 0.1-10 GPa for a single bubble collapse.⁴⁰ If we consider T_3 = 1 GPa, the calculated opencircuit voltage across the Bi₄TaO₈Cl nanoplates is about 4.0 V and so is the band-bending potential. Therefore, band-bending by 2.5 eV requires a pressure of 6*10⁸ Pa which can be tuned either by changing W_3 or e_r , or d_{33} (hence intrinsic polarization).

Those nanoplates that do not generate a potential of 2.5 V can still contribute to synergy due to efficient charge separation as discussed below in (ii) below. The fraction of such nanoplates is expected to increase at higher ultrasound power due to a larger number of bubble formations leading to higher %synergy, as seen in **Figure 4.1.11. c** where it increases from 18% to 44.6% when power was changed from 40% to 100%.

- ii) *Improved exciton separation by piezopotential*: This improves the photocatalytic component of piezo-photocatalysis. The overall efficiency of the catalyst in a photocatalytic pathway depends on the separation and transportation of photogenerated charges to the active sites. A developing piezopotential can induce a better separation of the photogenerated holes and electrons due to a gradient field surrounding it and hence enhances overall efficiency.^{41,42}
- iii) Band positions of the catalyst: From (ii) and noting that (a) photocatalysis involves excited state electronic surfaces while piezocatalysis involves electrons in the ground state of the material,⁹ (b) all particles will not be appropriately positioned to adsorb entire pressure from bursting of a bubble (as in **Figure 4.1.13. a**), and (c) suitable band positions of the catalyst with respect to redox species are the minimum thermodynamic requirement for a photocatalyst to be active,⁴³ the fraction of the nanoplates that contribute to piezocatalysis/synergy can be altered by using a material with different band positions. Referring to **Figure 4.1.13.a**, a material with a minimal energy difference with the redox species needs a small band-bending to be piezoactive and hence most catalyst particles would participate in the reaction under sonication. But if this energy difference is high, only a smaller fraction will be piezoactive and then, by applying higher ultrasound power that generates more bubbles, the fraction of the catalyst particles that are photoactive due to more efficient exciton separation will significantly increase, leading to higher synergy.

- iv) Shielding of light: Light penetration throughout the reaction mixture depends upon the darkness of the solution or the dye concentration. Light shielding by highly concentrated dye solution will negatively influence the photocatalytic contribution and the overall efficiency of the catalyst, as evidenced in Figure 4.1.11.c. This need not necessarily affect the piezocatalytic contribution if the nature of the bubbles does not change. But it does (Figure 4.1.11.d) which is attributed to catalyst surface poisoning discussed below.
- *Poisoning of catalyst surface by reactant*: It again concerns the catalyst activity at high concentrations, where the reaction rate decreases drastically (Figure 4.1.11.c). Considering the photocatalytic part, the same can be attributed to reduced light penetration discussed in (iv). However, from the point of view of the catalyst, with increasing concentrations, excess reactant molecules adsorb on the nanoplates surface too (Figure 4.1.11.d) and block the active sites for molecular O₂ and hydroxide ions adsorption essential for the formation of reactive radicals that induce degradation. Besides, this may also (a) cushion the pressure exerted from the bubble bursting on the particle and (b) further reduce light absorption by it, reducing both photo and piezo contributions. Ideally, (b) should not affect %synergy, but since we observe it (Figure 4.1.11. d), the pressure cushioning effect is suggested to be prominent.

Variations in %synergy in comparable concentrations of different reactants can be attributed to their different redox potentials. Thus, these factors minimally sum up the way a catalyst particle experiences its environment to deliver piezo-photocatalytic efficiency. Two additional complications will arise when sensitization by some reactants such as dyes and their adsorption coefficients are considered that are well-studied for photocatalysis.^{44,45} Some of these factors may be made to act reasonably independent of each other to design catalysts with predictable synergy.


Figure 4.1.13. (a) Schematic showing the effect of band position on synergy for two catalysts with identical band-gap but hypothetically different band positions. (b) A gear interlock describing parameters associated with the extent of synergy during piezo-photocatalysis.

4.1.5. Conclusion

In conclusion, we demonstrate that rationally designed single-crystalline Bi₄TaO₈Cl nanoplates with exposed piezoactive facets can respond to ultrasound pressure with superior efficiency to develop piezopotential exceedingly at least 2.5 eV which can be used for universal wastewater decontamination considering several pervasive organic pollutants. We further establish that introducing renewable solar light during piezochemical decontamination process leads to excessive improvements in catalytic efficiencies originating from the synergy of photocatalytic and piezocatalytic processes. The synergy has been quantified for five structurally different contaminants, for concentrations ranging over two orders of magnitudes to mimic real-life situations and also under different ultrasonic power and frequencies to establish its tremendous unpredictability and diversity in the 1-45% range. While we establish such diversity for the

first time, the origin of synergy has also remained unexplained in a comprehensive manner until now. Landscaping from our vast range of experiments, we offer a sevenparameter synergy control model based on pressure-induced band-bending in the catalyst and the involvement of its ground state and excited state electrons to help understand the same and to rationally develop more efficient piezo-photocatalysts for wastewater management.

Bibliography

- Ahmed, J.; Thakur, A.; Goyal, A. And Its Toxic Effects. *Ind. Wastewater Its Toxic Eff.* 2022, No. 5, 1–14. https://doi.org/10.1039/9781839162794-00001.
- S.v., M.; Tripathy, B. K.; Kumar, M.; Pramod, S. Simultaneous Degradation of Anionic and Cationic Dyes from Multi-Dye Systems Using Falling Film Photoreactor: Performance Evaluation, Kinetic and Toxicity Analysis. *J. Environ. Chem. Eng.* 2020, 8 (6), 104486. https://doi.org/10.1016/j.jece.2020.104486.
- Cates, E. L. Photocatalytic Water Treatment: So Where Are We Going with This?
 Environ. Sci. Technol. 2017, *51* (2), 757–758. https://doi.org/10.1021/acs.est.6b06035.
- Jeon, T. H.; Koo, M. S.; Kim, H.; Choi, W. Dual-Functional Photocatalytic and Photoelectrocatalytic Systems for Energy- and Resource-Recovering Water Treatment. *ACS Catal.* 2018, 8 (12), 11542–11563. https://doi.org/10.1021/acscatal.8b03521.
- (5) Ayodhya, D.; Veerabhadram, G. A Review on Recent Advances in Photodegradation of Dyes Using Doped and Heterojunction Based Semiconductor Metal Sulfide Nanostructures for Environmental Protection. *Mater. Today Energy* 2018, *9*, 83–113. https://doi.org/10.1016/j.mtener.2018.05.007.
- Liu, Z.; Wang, L.; Yu, X.; Zhang, J.; Yang, R.; Zhang, X.; Ji, Y.; Wu, M.; Deng, L.;
 Li, L.; Wang, Z. L. Piezoelectric-Effect-Enhanced Full-Spectrum Photoelectrocatalysis in p–n Heterojunction. *Adv. Funct. Mater.* 2019, *29* (41), 1–8. https://doi.org/10.1002/adfm.201807279.
- Tu, S.; Guo, Y.; Zhang, Y.; Hu, C.; Zhang, T.; Ma, T.; Huang, H. Piezocatalysis and Piezo-Photocatalysis: Catalysts Classification and Modification Strategy, Reaction Mechanism, and Practical Application. *Adv. Funct. Mater.* 2020, *30* (48), 1–31. https://doi.org/10.1002/adfm.202005158.
- (8) Xiang, D.; Liu, Z.; Wu, M.; Liu, H.; Zhang, X.; Wang, Z.; Wang, Z. L.; Li, L. Enhanced Piezo-Photoelectric Catalysis with Oriented Carrier Migration in Asymmetric Au–ZnO Nanorod Array. *Small* 2020, *16* (18), 1–8. https://doi.org/10.1002/smll.201907603.
- (9) Starr, M. B.; Wang, X. Fundamental Analysis of Piezocatalysis Process on the Surfaces of Strained Piezoelectric Materials. *Sci. Rep.* 2013, *3* (1), 1–8.

https://doi.org/10.1038/srep02160.

- (10) Hu, C.; Chen, F.; Wang, Y.; Tian, N.; Ma, T.; Zhang, Y.; Huang, H. Exceptional Cocatalyst-Free Photo-Enhanced Piezocatalytic Hydrogen Evolution of Carbon Nitride Nanosheets from Strong In-Plane Polarization. *Adv. Mater.* 2021, *33* (24), 1–9. https://doi.org/10.1002/adma.202101751.
- (11) Lin, S.; Li, S.; Huang, H.; Yu, H.; Zhang, Y. Synergetic Piezo-Photocatalytic Hydrogen Evolution on CdxZn1-XS Solid-Solution 1D Nanorods. *Small* 2022, *18* (8), 1–11. https://doi.org/10.1002/smll.202106420.
- You, H.; Wu, Z.; Zhang, L.; Ying, Y.; Liu, Y.; Fei, L.; Chen, X.; Jia, Y.; Wang, Y.;
 Wang, F.; Ju, S.; Qiao, J.; Lam, C.; Huang, H. Harvesting the Vibration Energy of BiFeO 3 Nanosheets for Hydrogen Evolution . *Angew. Chemie* 2019, *131* (34), 11905– 11910. https://doi.org/10.1002/ange.201906181.
- (13) Starr, M. B.; Shi, J.; Wang, X. Piezopotential-Driven Redox Reactions at the Surface of Piezoelectric Materials. *Angew. Chemie Int. Ed.* 2012, *51* (24), 5962–5966. https://doi.org/10.1002/anie.201201424.
- Hong, K. S.; Xu, H.; Konishi, H.; Li, X. Direct Water Splitting through Vibrating Piezoelectric Microfibers in Water. J. Phys. Chem. Lett. 2010, 1 (6), 997–1002. https://doi.org/10.1021/jz100027t.
- (15) Hu, C.; Huang, H.; Chen, F.; Zhang, Y.; Yu, H.; Ma, T. Coupling Piezocatalysis and Photocatalysis in Bi4NbO8X (X = Cl, Br) Polar Single Crystals. *Adv. Funct. Mater.* 2020, *30* (7), 1–10. https://doi.org/10.1002/adfm.201908168.
- (16) Chatterjee, K.; Banoo, M.; Mondal, S.; Sahoo, L.; Gautam, U. K. Synthesis of Bi3TaO7-Bi4TaO8Br Composites in Ambient Air and Their High Photocatalytic Activity upon Metal Loading. *Dalt. Trans.* 2019, 48 (21), 7110–7116. https://doi.org/10.1039/c9dt00068b.
- Banoo, M.; Chatterjee, K.; Mondal, S.; Vinod, C. P.; Gautam, U. K. A 'Self-Activating' Bi3TaO7-Bi4TaO8Br Photocatalyst and Its Use in the Sustainable Production of pro-Fluorophoric Rhodamine-110. *Green Chem.* 2022, 24 (14), 5514–5523. https://doi.org/10.1039/d2gc01574a.
- (18) Banoo, M.; Roy, R. S.; Bhakar, M.; Kaur, J.; Jaiswal, A.; Sheet, G.; Gautam, U. K. Bi

4 TaO 8 Cl as a New Class of Layered Perovskite Oxyhalide Materials for Piezopotential Driven Efficient Seawater Splitting . *Nano Lett.* **2022**, 22, 22, 8867– 8874. https://doi.org/10.1021/acs.nanolett.2c02900.

- (19) Zhong, C.; Ishii, Y.; Tassel, C.; Zhu, T.; Kato, D.; Kurushima, K.; Fujibayashi, Y.;
 Saito, T.; Ogawa, T.; Kuwabara, A.; Mori, S.; Kageyama, H. Lone-Pair-Induced Intraand Interlayer Polarizations in Sillén-Aurivillius Layered Perovskite Bi4NbO8Br. *Inorg. Chem.* 2022, *61* (25), 9816–9822. https://doi.org/10.1021/acs.inorgchem.2c01358.
- Nakada, A.; Saeki, A.; Higashi, M.; Kageyama, H.; Abe, R. Two-Step Synthesis of Sillén-Aurivillius Type Oxychlorides to Enhance Their Photocatalytic Activity for Visible-Light-Induced Water Splitting. *J. Mater. Chem. A* 2018, 6 (23), 10909–10917. https://doi.org/10.1039/c8ta03321h.
- (21) Li, L.; Han, Q.; Tang, L.; Zhang, Y.; Li, P.; Zhou, Y.; Zou, Z. Flux Synthesis of Regular Bi4TaO8Cl Square Nanoplates Exhibiting Dominant Exposure Surfaces of {001} Crystal Facets for Photocatalytic Reduction of CO2 to Methane. *Nanoscale* 2018, 10 (4), 1905–1911. https://doi.org/10.1039/c7nr06279f.
- (22) Liu, D.; Jin, C.; Shan, F.; He, J.; Wang, F. Synthesizing BaTiO3 Nanostructures to Explore Morphological Influence, Kinetics, and Mechanism of Piezocatalytic Dye Degradation. ACS Appl. Mater. Interfaces 2020, 12 (15), 17443–17451. https://doi.org/10.1021/acsami.9b23351.
- (23) Su, R.; Hsain, H. A.; Wu, M.; Zhang, D.; Hu, X.; Wang, Z.; Wang, X.; Li, F. tang; Chen, X.; Zhu, L.; Yang, Y.; Yang, Y.; Lou, X.; Pennycook, S. J. Nano-Ferroelectric for High Efficiency Overall Water Splitting under Ultrasonic Vibration. *Angew. Chemie - Int. Ed.* **2019**, *58* (42), 15076–15081. https://doi.org/10.1002/anie.201907695.
- (24) Hong, D.; Zang, W.; Guo, X.; Fu, Y.; He, H.; Sun, J.; Xing, L.; Liu, B.; Xue, X. High Piezo-Photocatalytic Efficiency of CuS/ZnO Nanowires Using Both Solar and Mechanical Energy for Degrading Organic Dye. *ACS Appl. Mater. Interfaces* 2016, 8 (33), 21302–21314. https://doi.org/10.1021/acsami.6b05252.
- (25) Xu, X.; Lin, X.; Yang, F.; Huang, S.; Cheng, X. Piezo-Photocatalytic Activity of Bi0.5Na0.5TiO3@TiO2Composite Catalyst with Heterojunction for Degradation of

Organic Dye Molecule. *J. Phys. Chem. C* **2020**, *124* (44), 24126–24134. https://doi.org/10.1021/acs.jpcc.0c04700.

- (26) Singh, G.; Sharma, M.; Vaish, R. Flexible Ag@LiNbO3/PVDF Composite Film for Piezocatalytic Dye/Pharmaceutical Degradation and Bacterial Disinfection. ACS Appl. Mater. Interfaces 2021, 13 (19), 22914–22925. https://doi.org/10.1021/acsami.1c01314.
- (27) Laurenti, M.; Garino, N.; Garino, N.; Canavese, G.; Hernandéz, S.; Cauda, V. Piezo-And Photocatalytic Activity of Ferroelectric ZnO:Sb Thin Films for the Efficient Degradation of Rhodamine-β Dye Pollutant. *ACS Appl. Mater. Interfaces* 2020, *12* (23), 25798–25808. https://doi.org/10.1021/acsami.0c03787.
- (28) Shchukin, D. G.; Skorb, E.; Belova, V.; Möhwald, H. Ultrasonic Cavitation at Solid Surfaces. *Adv. Mater.* 2011, *23* (17), 1922–1934. https://doi.org/10.1002/adma.201004494.
- (29) Pan, L.; Sun, S.; Chen, Y.; Wang, P.; Wang, J.; Zhang, X.; Zou, J. J.; Wang, Z. L. Advances in Piezo-Phototronic Effect Enhanced Photocatalysis and Photoelectrocatalysis. *Adv. Energy Mater.* 2020, *10* (15), 1–25. https://doi.org/10.1002/aenm.202000214.
- Li, S.; Zhao, Z.; Zhao, J.; Zhang, Z.; Li, X.; Zhang, J. Recent Advances of Ferro-, Piezo-, and Pyroelectric Nanomaterials for Catalytic Applications. *ACS Appl. Nano Mater.* 2020, *3* (2), 1063–1079. https://doi.org/10.1021/acsanm.0c00039.
- (31) Wang, S.; Zhang, Y.; Zheng, Y.; Xu, Y.; Yang, G.; Zhong, S.; Zhao, Y.; Bai, S.
 Plasmonic Metal Mediated Charge Transfer in Stacked Core–Shell Semiconductor Heterojunction for Significantly Enhanced CO2 Photoreduction. *Small* 2023, 19 (2), 1–13. https://doi.org/10.1002/smll.202204774.
- Xi, Y.; Mo, W.; Fan, Z.; Hu, L.; Chen, W.; Zhang, Y.; Wang, P.; Zhong, S.; Zhao, Y.; Bai, S. A Mesh-like BiOBr/Bi2S3 Nanoarray Heterojunction with Hierarchical Pores and Oxygen Vacancies for Broadband CO2 Photoreduction. *J. Mater. Chem. A* 2022, *10* (39), 20934–20945. https://doi.org/10.1039/d2ta04278a.
- (33) Yang, J.; Wang, J.; Zhang, X.; Chen, M.; Tian, B.; Wang, N.; Huang, X.; Hao, H.Exploration of Hydrogen-Bonded Organic Framework (HOF) as Highly Efficient

Adsorbent for Rhodamine B and Methyl Orange. *Microporous Mesoporous Mater*. **2022**, *330*, 111624. https://doi.org/https://doi.org/10.1016/j.micromeso.2021.111624.

- (34) Yan, S. C.; Li, Z. S.; Zou, Z. G. Photodegradation of Rhodamine B and Methyl Orange over Boron-Doped g-C 3N4 under Visible Light Irradiation. *Langmuir* 2010, 26 (6), 3894–3901. https://doi.org/10.1021/la904023j.
- (35) Wang, Z.; Huo, B.; Wang, J.; Ma, W.; Qi, J.; Zhu, Z.; Meng, F.; Wang, Y. In Situ Synthesis of Flower-Structured ZnO@YFC for the Efficient Piezocatalytic Degradation of Tetracycline Wastewater: Degradation Mechanism and Toxicity Evolution. *Appl. Surf. Sci.* 2022, 602 (July), 154330. https://doi.org/10.1016/j.apsusc.2022.154330.
- (36) Yaseen, D. A.; Scholz, M. Textile Dye Wastewater Characteristics and Constituents of Synthetic Effluents: A Critical Review; Springer Berlin Heidelberg, 2019; Vol. 16, pages1193–1226. https://doi.org/10.1007/s13762-018-2130-z.
- (37) Liu, Q.; Zhai, D.; Xiao, Z.; Tang, C.; Sun, Q.; Bowen, C. R.; Luo, H.; Zhang, D.
 Piezo-Photoelectronic Coupling Effect of BaTiO3@TiO2 Nanowires for Highly
 Concentrated Dye Degradation. *Nano Energy* 2022, *92* (November 2021).
 https://doi.org/10.1016/j.nanoen.2021.106702.
- (38) Maruthapandi, M.; Kumar, V. B.; Luong, J. H. T.; Gedanken, A. Kinetics, Isotherm, and Thermodynamic Studies of Methylene Blue Adsorption on Polyaniline and Polypyrrole Macro-Nanoparticles Synthesized by C-Dot-Initiated Polymerization. ACS Omega 2018, 3 (7), 7196–7203. https://doi.org/10.1021/acsomega.8b00478.
- (39) Kusainova, A. M.; Stefanovich, S. Y.; Dolgikh, V. A.; Mosunov, A. V.; Hervoches, C. H.; Lightfoot, P. Dielectric Properties and Structure of Bi4NbO8Cl and Bi4TaO8Cl. J. *Mater. Chem.* 2001, 11 (4), 1141–1145. https://doi.org/10.1039/b008492l.
- (40) Sarkar, P.; Ghigliotti, G.; Fivel, M.; Franc, J. Numerical Investigation of the Dynamics of Pressure Loading on a Solid Boundary from a Collapsing Cavitation Bubble. *Proc. 10th Int. Symp. Cavitation* 2019, 765–770. https://doi.org/10.1115/1.861851_ch146.
- (41) Lin, S.; Li, S.; Huang, H.; Yu, H.; Zhang, Y. Synergetic Piezo-Photocatalytic Hydrogen Evolution on CdxZn1-XS Solid-Solution 1D Nanorods. *Small* 2022, *18* (8) 2106420. https://doi.org/10.1002/smll.202106420.

- (42) Yang, G.; Wang, S.; Wu, Y.; Zhou, H.; Zhao, W.; Zhong, S.; Liu, L.; Bai, S. Spatially Separated Redox Cocatalysts on Ferroelectric Nanoplates for Improved Piezophotocatalytic CO2 Reduction and H2O Oxidation. ACS Appl. Mater. Interfaces 2022, 14228–14239. https://doi.org/10.1021/acsami.2c20685.
- (43) Wang, K.; Han, C.; Li, J.; Qiu, J.; Sunarso, J.; Liu, S. The Mechanism of Piezocatalysis: Energy Band Theory or Screening Charge Effect? *Angew. Chemie - Int. Ed.* 2022, *61*, 202110429 (6). https://doi.org/10.1002/anie.202110429.
- (44) Latini, A.; Panetta, R. Test of Different Sensitizing Dyes in Dye-Sensitized Solar Cells Based on Nb2O5 Photoanodes. *Energies* 2018, 11 (4) 975. https://doi.org/10.3390/en11040975.
- (45) Chauhan, R.; Kushwaha, R.; Bahadur, L. Study of Light Harvesting Properties of Different Classes of Metal-Free Organic Dyes in TiO 2 Based Dye-Sensitized Solar Cells . J. Energy 2014, 2014 (1), 1–10. https://doi.org/10.1155/2014/517574.
- Ahmed, J.; Thakur, A.; Goyal, A. And Its Toxic Effects. *Ind. Wastewater Its Toxic Eff.* 2022, No. 5, 1–14. https://doi.org/10.1039/9781839162794-00001.
- S.v., M.; Tripathy, B. K.; Kumar, M.; Pramod, S. Simultaneous Degradation of Anionic and Cationic Dyes from Multi-Dye Systems Using Falling Film Photoreactor: Performance Evaluation, Kinetic and Toxicity Analysis. *J. Environ. Chem. Eng.* 2020, 8 (6), 104486. https://doi.org/10.1016/j.jece.2020.104486.
- Cates, E. L. Photocatalytic Water Treatment: So Where Are We Going with This?
 Environ. Sci. Technol. 2017, *51* (2), 757–758. https://doi.org/10.1021/acs.est.6b06035.
- Jeon, T. H.; Koo, M. S.; Kim, H.; Choi, W. Dual-Functional Photocatalytic and Photoelectrocatalytic Systems for Energy- and Resource-Recovering Water Treatment. *ACS Catal.* 2018, 8 (12), 11542–11563. https://doi.org/10.1021/acscatal.8b03521.
- (5) Ayodhya, D.; Veerabhadram, G. A Review on Recent Advances in Photodegradation of Dyes Using Doped and Heterojunction Based Semiconductor Metal Sulfide Nanostructures for Environmental Protection. *Mater. Today Energy* 2018, *9*, 83–113. https://doi.org/10.1016/j.mtener.2018.05.007.
- Liu, Z.; Wang, L.; Yu, X.; Zhang, J.; Yang, R.; Zhang, X.; Ji, Y.; Wu, M.; Deng, L.;
 Li, L.; Wang, Z. L. Piezoelectric-Effect-Enhanced Full-Spectrum Photoelectrocatalysis

in p–n Heterojunction. *Adv. Funct. Mater.* **2019**, *29* (41), 1–8. https://doi.org/10.1002/adfm.201807279.

- Tu, S.; Guo, Y.; Zhang, Y.; Hu, C.; Zhang, T.; Ma, T.; Huang, H. Piezocatalysis and Piezo-Photocatalysis: Catalysts Classification and Modification Strategy, Reaction Mechanism, and Practical Application. *Adv. Funct. Mater.* 2020, *30* (48), 1–31. https://doi.org/10.1002/adfm.202005158.
- (8) Xiang, D.; Liu, Z.; Wu, M.; Liu, H.; Zhang, X.; Wang, Z.; Wang, Z. L.; Li, L. Enhanced Piezo-Photoelectric Catalysis with Oriented Carrier Migration in Asymmetric Au–ZnO Nanorod Array. *Small* 2020, *16* (18), 1–8. https://doi.org/10.1002/smll.201907603.
- (9) Starr, M. B.; Wang, X. Fundamental Analysis of Piezocatalysis Process on the Surfaces of Strained Piezoelectric Materials. *Sci. Rep.* 2013, *3* (1), 1–8. https://doi.org/10.1038/srep02160.
- (10) Hu, C.; Chen, F.; Wang, Y.; Tian, N.; Ma, T.; Zhang, Y.; Huang, H. Exceptional Cocatalyst-Free Photo-Enhanced Piezocatalytic Hydrogen Evolution of Carbon Nitride Nanosheets from Strong In-Plane Polarization. *Adv. Mater.* 2021, *33* (24), 1–9. https://doi.org/10.1002/adma.202101751.
- (11) Lin, S.; Li, S.; Huang, H.; Yu, H.; Zhang, Y. Synergetic Piezo-Photocatalytic Hydrogen Evolution on CdxZn1-XS Solid-Solution 1D Nanorods. *Small* 2022, *18* (8), 1–11. https://doi.org/10.1002/smll.202106420.
- You, H.; Wu, Z.; Zhang, L.; Ying, Y.; Liu, Y.; Fei, L.; Chen, X.; Jia, Y.; Wang, Y.; Wang, F.; Ju, S.; Qiao, J.; Lam, C.; Huang, H. Harvesting the Vibration Energy of BiFeO 3 Nanosheets for Hydrogen Evolution . *Angew. Chemie* 2019, *131* (34), 11905–11910. https://doi.org/10.1002/ange.201906181.
- (13) Starr, M. B.; Shi, J.; Wang, X. Piezopotential-Driven Redox Reactions at the Surface of Piezoelectric Materials. *Angew. Chemie Int. Ed.* 2012, *51* (24), 5962–5966. https://doi.org/10.1002/anie.201201424.
- Hong, K. S.; Xu, H.; Konishi, H.; Li, X. Direct Water Splitting through Vibrating Piezoelectric Microfibers in Water. J. Phys. Chem. Lett. 2010, 1 (6), 997–1002. https://doi.org/10.1021/jz100027t.

- (15) Hu, C.; Huang, H.; Chen, F.; Zhang, Y.; Yu, H.; Ma, T. Coupling Piezocatalysis and Photocatalysis in Bi4NbO8X (X = Cl, Br) Polar Single Crystals. *Adv. Funct. Mater.* 2020, *30* (7), 1–10. https://doi.org/10.1002/adfm.201908168.
- (16) Chatterjee, K.; Banoo, M.; Mondal, S.; Sahoo, L.; Gautam, U. K. Synthesis of Bi3TaO7-Bi4TaO8Br Composites in Ambient Air and Their High Photocatalytic Activity upon Metal Loading. *Dalt. Trans.* 2019, 48 (21), 7110–7116. https://doi.org/10.1039/c9dt00068b.
- Banoo, M.; Chatterjee, K.; Mondal, S.; Vinod, C. P.; Gautam, U. K. A 'Self-Activating' Bi3TaO7-Bi4TaO8Br Photocatalyst and Its Use in the Sustainable Production of pro-Fluorophoric Rhodamine-110. *Green Chem.* 2022, 24 (14), 5514–5523. https://doi.org/10.1039/d2gc01574a.
- Banoo, M.; Roy, R. S.; Bhakar, M.; Kaur, J.; Jaiswal, A.; Sheet, G.; Gautam, U. K. Bi
 4 TaO 8 Cl as a New Class of Layered Perovskite Oxyhalide Materials for
 Piezopotential Driven Efficient Seawater Splitting . *Nano Lett.* 2022, 22, 22, 8867– 8874. https://doi.org/10.1021/acs.nanolett.2c02900.
- (19) Zhong, C.; Ishii, Y.; Tassel, C.; Zhu, T.; Kato, D.; Kurushima, K.; Fujibayashi, Y.;
 Saito, T.; Ogawa, T.; Kuwabara, A.; Mori, S.; Kageyama, H. Lone-Pair-Induced Intraand Interlayer Polarizations in Sillén-Aurivillius Layered Perovskite Bi4NbO8Br. *Inorg. Chem.* 2022, *61* (25), 9816–9822. https://doi.org/10.1021/acs.inorgchem.2c01358.
- (20) Nakada, A.; Saeki, A.; Higashi, M.; Kageyama, H.; Abe, R. Two-Step Synthesis of Sillén-Aurivillius Type Oxychlorides to Enhance Their Photocatalytic Activity for Visible-Light-Induced Water Splitting. J. Mater. Chem. A 2018, 6 (23), 10909–10917. https://doi.org/10.1039/c8ta03321h.
- (21) Li, L.; Han, Q.; Tang, L.; Zhang, Y.; Li, P.; Zhou, Y.; Zou, Z. Flux Synthesis of Regular Bi4TaO8Cl Square Nanoplates Exhibiting Dominant Exposure Surfaces of {001} Crystal Facets for Photocatalytic Reduction of CO2 to Methane. *Nanoscale* 2018, 10 (4), 1905–1911. https://doi.org/10.1039/c7nr06279f.
- (22) Liu, D.; Jin, C.; Shan, F.; He, J.; Wang, F. Synthesizing BaTiO3 Nanostructures to Explore Morphological Influence, Kinetics, and Mechanism of Piezocatalytic Dye Degradation. ACS Appl. Mater. Interfaces 2020, 12 (15), 17443–17451.

https://doi.org/10.1021/acsami.9b23351.

- (23) Su, R.; Hsain, H. A.; Wu, M.; Zhang, D.; Hu, X.; Wang, Z.; Wang, X.; Li, F. tang; Chen, X.; Zhu, L.; Yang, Y.; Yang, Y.; Lou, X.; Pennycook, S. J. Nano-Ferroelectric for High Efficiency Overall Water Splitting under Ultrasonic Vibration. *Angew. Chemie - Int. Ed.* **2019**, *58* (42), 15076–15081. https://doi.org/10.1002/anie.201907695.
- (24) Hong, D.; Zang, W.; Guo, X.; Fu, Y.; He, H.; Sun, J.; Xing, L.; Liu, B.; Xue, X. High Piezo-Photocatalytic Efficiency of CuS/ZnO Nanowires Using Both Solar and Mechanical Energy for Degrading Organic Dye. *ACS Appl. Mater. Interfaces* 2016, 8 (33), 21302–21314. https://doi.org/10.1021/acsami.6b05252.
- (25) Xu, X.; Lin, X.; Yang, F.; Huang, S.; Cheng, X. Piezo-Photocatalytic Activity of Bi0.5Na0.5TiO3@TiO2Composite Catalyst with Heterojunction for Degradation of Organic Dye Molecule. *J. Phys. Chem. C* 2020, *124* (44), 24126–24134. https://doi.org/10.1021/acs.jpcc.0c04700.
- (26) Singh, G.; Sharma, M.; Vaish, R. Flexible Ag@LiNbO3/PVDF Composite Film for Piezocatalytic Dye/Pharmaceutical Degradation and Bacterial Disinfection. ACS Appl. Mater. Interfaces 2021, 13 (19), 22914–22925. https://doi.org/10.1021/acsami.1c01314.
- (27) Laurenti, M.; Garino, N.; Garino, N.; Canavese, G.; Hernandéz, S.; Cauda, V. Piezo-And Photocatalytic Activity of Ferroelectric ZnO:Sb Thin Films for the Efficient Degradation of Rhodamine-β Dye Pollutant. *ACS Appl. Mater. Interfaces* 2020, *12* (23), 25798–25808. https://doi.org/10.1021/acsami.0c03787.
- (28) Shchukin, D. G.; Skorb, E.; Belova, V.; Möhwald, H. Ultrasonic Cavitation at Solid Surfaces. *Adv. Mater.* 2011, *23* (17), 1922–1934. https://doi.org/10.1002/adma.201004494.
- (29) Pan, L.; Sun, S.; Chen, Y.; Wang, P.; Wang, J.; Zhang, X.; Zou, J. J.; Wang, Z. L. Advances in Piezo-Phototronic Effect Enhanced Photocatalysis and Photoelectrocatalysis. *Adv. Energy Mater.* 2020, *10* (15), 1–25. https://doi.org/10.1002/aenm.202000214.
- (30) Li, S.; Zhao, Z.; Zhao, J.; Zhang, Z.; Li, X.; Zhang, J. Recent Advances of Ferro-,

Piezo-, and Pyroelectric Nanomaterials for Catalytic Applications. *ACS Appl. Nano Mater.* **2020**, *3* (2), 1063–1079. https://doi.org/10.1021/acsanm.0c00039.

- (31) Wang, S.; Zhang, Y.; Zheng, Y.; Xu, Y.; Yang, G.; Zhong, S.; Zhao, Y.; Bai, S.
 Plasmonic Metal Mediated Charge Transfer in Stacked Core–Shell Semiconductor Heterojunction for Significantly Enhanced CO2 Photoreduction. *Small* 2023, *19* (2), 1–13. https://doi.org/10.1002/smll.202204774.
- Xi, Y.; Mo, W.; Fan, Z.; Hu, L.; Chen, W.; Zhang, Y.; Wang, P.; Zhong, S.; Zhao, Y.; Bai, S. A Mesh-like BiOBr/Bi2S3 Nanoarray Heterojunction with Hierarchical Pores and Oxygen Vacancies for Broadband CO2 Photoreduction. *J. Mater. Chem. A* 2022, *10* (39), 20934–20945. https://doi.org/10.1039/d2ta04278a.
- (33) Yang, J.; Wang, J.; Zhang, X.; Chen, M.; Tian, B.; Wang, N.; Huang, X.; Hao, H. Exploration of Hydrogen-Bonded Organic Framework (HOF) as Highly Efficient Adsorbent for Rhodamine B and Methyl Orange. *Microporous Mesoporous Mater*. 2022, *330*, 111624. https://doi.org/https://doi.org/10.1016/j.micromeso.2021.111624.
- (34) Yan, S. C.; Li, Z. S.; Zou, Z. G. Photodegradation of Rhodamine B and Methyl Orange over Boron-Doped g-C 3N4 under Visible Light Irradiation. *Langmuir* 2010, 26 (6), 3894–3901. https://doi.org/10.1021/la904023j.
- (35) Wang, Z.; Huo, B.; Wang, J.; Ma, W.; Qi, J.; Zhu, Z.; Meng, F.; Wang, Y. In Situ Synthesis of Flower-Structured ZnO@YFC for the Efficient Piezocatalytic Degradation of Tetracycline Wastewater: Degradation Mechanism and Toxicity Evolution. *Appl. Surf. Sci.* 2022, 602 (July), 154330. https://doi.org/10.1016/j.apsusc.2022.154330.
- (36) Yaseen, D. A.; Scholz, M. Textile Dye Wastewater Characteristics and Constituents of Synthetic Effluents: A Critical Review; Springer Berlin Heidelberg, 2019; Vol. 16, pages1193–1226. https://doi.org/10.1007/s13762-018-2130-z.
- (37) Liu, Q.; Zhai, D.; Xiao, Z.; Tang, C.; Sun, Q.; Bowen, C. R.; Luo, H.; Zhang, D. Piezo-Photoelectronic Coupling Effect of BaTiO3@TiO2 Nanowires for Highly Concentrated Dye Degradation. *Nano Energy* 2022, *92* (November 2021). https://doi.org/10.1016/j.nanoen.2021.106702.
- (38) Maruthapandi, M.; Kumar, V. B.; Luong, J. H. T.; Gedanken, A. Kinetics, Isotherm,

and Thermodynamic Studies of Methylene Blue Adsorption on Polyaniline and Polypyrrole Macro-Nanoparticles Synthesized by C-Dot-Initiated Polymerization. *ACS Omega* **2018**, *3* (7), 7196–7203. https://doi.org/10.1021/acsomega.8b00478.

- (39) Kusainova, A. M.; Stefanovich, S. Y.; Dolgikh, V. A.; Mosunov, A. V.; Hervoches, C. H.; Lightfoot, P. Dielectric Properties and Structure of Bi4NbO8Cl and Bi4TaO8Cl. J. *Mater. Chem.* 2001, 11 (4), 1141–1145. https://doi.org/10.1039/b008492l.
- (40) Sarkar, P.; Ghigliotti, G.; Fivel, M.; Franc, J. Numerical Investigation of the Dynamics of Pressure Loading on a Solid Boundary from a Collapsing Cavitation Bubble. *Proc. 10th Int. Symp. Cavitation* 2019, 765–770. https://doi.org/10.1115/1.861851_ch146.
- (41) Lin, S.; Li, S.; Huang, H.; Yu, H.; Zhang, Y. Synergetic Piezo-Photocatalytic Hydrogen Evolution on CdxZn1-XS Solid-Solution 1D Nanorods. *Small* 2022, *18* (8) 2106420. https://doi.org/10.1002/smll.202106420.
- (42) Yang, G.; Wang, S.; Wu, Y.; Zhou, H.; Zhao, W.; Zhong, S.; Liu, L.; Bai, S. Spatially Separated Redox Cocatalysts on Ferroelectric Nanoplates for Improved Piezophotocatalytic CO2 Reduction and H2O Oxidation. *ACS Appl. Mater. Interfaces* 2022, 14228–14239. https://doi.org/10.1021/acsami.2c20685.
- (43) Wang, K.; Han, C.; Li, J.; Qiu, J.; Sunarso, J.; Liu, S. The Mechanism of Piezocatalysis: Energy Band Theory or Screening Charge Effect? *Angew. Chemie - Int. Ed.* 2022, *61*, 202110429 (6). https://doi.org/10.1002/anie.202110429.
- (44) Latini, A.; Panetta, R. Test of Different Sensitizing Dyes in Dye-Sensitized Solar Cells Based on Nb2O5 Photoanodes. *Energies* 2018, 11 (4) 975. https://doi.org/10.3390/en11040975.
- (45) Chauhan, R.; Kushwaha, R.; Bahadur, L. Study of Light Harvesting Properties of Different Classes of Metal-Free Organic Dyes in TiO 2 Based Dye-Sensitized Solar Cells . J. Energy 2014, 2014 (1), 1–10. https://doi.org/10.1155/2014/517574.

Bibliography of Table 4.1.1.

 Hong, D.; Zang, W.; Guo, X.; Fu, Y.; He, H.; Sun, J.; Xing, L.; Liu, B.; Xue, X. High Piezo-Photocatalytic Efficiency of CuS/ZnO Nanowires Using Both Solar and Mechanical Energy for Degrading Organic Dye. *ACS Appl. Mater. Interfaces* 2016, 8 (33), 21302–21314. https://doi.org/10.1021/acsami.6b05252.

- Liu, Q.; Zhai, D.; Xiao, Z.; Tang, C.; Sun, Q.; Bowen, C. R.; Luo, H.; Zhang, D.
 Piezo-Photoelectronic Coupling Effect of BaTiO3@TiO2 Nanowires for Highly
 Concentrated Dye Degradation. *Nano Energy* 2022, *92*, 106702.
 https://doi.org/https://doi.org/10.1016/j.nanoen.2021.106702.
- Xu, X.; Lin, X.; Yang, F.; Huang, S.; Cheng, X. Piezo-Photocatalytic Activity of Bi0.5Na0.5TiO3@TiO2Composite Catalyst with Heterojunction for Degradation of Organic Dye Molecule. J. Phys. Chem. C 2020, 124 (44), 24126–24134. https://doi.org/10.1021/acs.jpcc.0c04700.
- (4) Zhao, W.; Zhang, Q.; Wang, H.; Rong, J.; E, L.; Dai, Y. Enhanced Catalytic Performance of Ag2O/BaTiO3 Heterostructure Microspheres by the Piezo/Pyro-Phototronic Synergistic Effect. *Nano Energy* 2020, *73*, 104783. https://doi.org/https://doi.org/10.1016/j.nanoen.2020.104783.
- Xie, Z.; Tang, X.; Shi, J.; Wang, Y.; Yuan, G.; Liu, J.-M. Excellent Piezo-Photocatalytic Performance of Bi4Ti3O12 Nanoplates Synthesized by Molten-Salt Method. *Nano Energy* 2022, 98, 107247. https://doi.org/https://doi.org/10.1016/j.nanoen.2022.107247.
- (6) He, T.; Cao, Z.; Li, G.; Jia, Y.; Peng, B. High Efficiently Harvesting Visible Light and Vibration Energy in (1–x)AgNbO3–XLiTaO3 Solid Solution around Antiferroelectric–Ferroelectric Phase Boundary for Dye Degradation. *J. Adv. Ceram.* 2022, *11* (10), 1641–1653. https://doi.org/10.1007/s40145-022-0637-8.
- Kumar, M.; Vaish, R.; Elqahtani, Z. M.; Kebaili, I.; Al-Buriahi, M. S.; Sung, T. H.; Hwang, W.; Kumar, A. Piezo-Photocatalytic Activity of Bi2VO5.5 for Methylene Blue Dye Degradation. *J. Mater. Res. Technol.* 2022, *21*, 1998–2012. https://doi.org/https://doi.org/10.1016/j.jmrt.2022.09.130.
- Lin, E.; Wu, J.; Qin, N.; Yuan, B.; Kang, Z.; Bao, D. Enhanced Piezocatalytic, Photocatalytic and Piezo-/Photocatalytic Performance of Diphasic Ba1-: XCaxTiO3 Nanowires near a Solubility Limit. *Catal. Sci. Technol.* 2019, *9* (24), 6863–6874. https://doi.org/10.1039/c9cy01713e.
- (9) Singh, S.; Khare, N. Coupling of Piezoelectric, Semiconducting and Photoexcitation Properties in NaNbO3 Nanostructures for Controlling Electrical Transport: Realizing an Efficient Piezo-Photoanode and Piezo-Photocatalyst. *Nano Energy* 2017, *38*, 335– 341. https://doi.org/https://doi.org/10.1016/j.nanoen.2017.05.029.
- Mushtaq, F.; Chen, X.; Hoop, M.; Torlakcik, H.; Pellicer, E.; Sort, J.; Gattinoni, C.; Nelson, B. J.; Pané, S. Piezoelectrically Enhanced Photocatalysis with BiFeO3

Nanostructures for Efficient Water Remediation. *iScience* **2018**, *4*, 236–246. https://doi.org/https://doi.org/10.1016/j.isci.2018.06.003.

- He, X.; Yang, Y.; Li, Y.; Chen, J.; Yang, S.; Liu, R.; Xu, Z. Effects of Structure and Surface Properties on the Performance of ZnO towards Photocatalytic Degradation of Methylene Blue. *Appl. Surf. Sci.* 2022, *599*, 153898. https://doi.org/https://doi.org/10.1016/j.apsusc.2022.153898.
- (12) Laurenti, M.; Garino, N.; Garino, N.; Canavese, G.; Hernandéz, S.; Cauda, V. Piezo-And Photocatalytic Activity of Ferroelectric ZnO:Sb Thin Films for the Efficient Degradation of Rhodamine-β Dye Pollutant. *ACS Appl. Mater. Interfaces* 2020, *12* (23), 25798–25808. https://doi.org/10.1021/acsami.0c03787.
- (13) Singh, G.; Sharma, M.; Vaish, R. Flexible Ag@LiNbO3/PVDF Composite Film for Piezocatalytic Dye/Pharmaceutical Degradation and Bacterial Disinfection. ACS Appl. Mater. Interfaces 2021, 13 (19), 22914–22925. https://doi.org/10.1021/acsami.1c01314.
- Lei, H.; Zhang, H.; Zou, Y.; Dong, X.; Jia, Y.; Wang, F. Synergetic Photocatalysis/Piezocatalysis of Bismuth Oxybromide for Degradation of Organic Pollutants. J. Alloys Compd. 2019, 809, 151840. https://doi.org/https://doi.org/10.1016/j.jallcom.2019.151840.
- (15) Li, S.; Chen, L.; Liu, Z.; Zhang, M.; Li, B.; Lai, C. Grafting Fe(III) Species on Oxygen-Vacancy Abundant BiOIO3 with Promoted Interfacial Charge Transfer for Photocatalytic Ciprofloxacin Degradation. *Appl. Surf. Sci.* **2021**, *566*, 150658. https://doi.org/https://doi.org/10.1016/j.apsusc.2021.150658.

CHAPTER 4.2.

Conclusions & future outlook of parts 3 and 4,

Conclusions of Parts 3 and 4:

Solar energy is undoubtedly a valuable source of renewable power, but its intermittent and diurnal nature underlines the need to diversify our energy resources. Part 3 of our research is dedicated to addressing this challenge by exploring the harnessing of mechanical energy through emerging piezocatalytic processes, as well as investigating the piezocatalytic properties of novel Sillen-Aurivillius phases. Both photocatalysis and piezocatalysis come with specific challenges that affect their efficiency. Photocatalysis is hampered by rapid charge recombination, leading to a decrease in quantum efficiency. On the other hand, piezocatalysis necessitates a high built-in electric field, resulting in lower efficiency. Part 4 of our research confronts this challenge by integrating piezocatalysis and photocatalysis into a concept known as piezo-photocatalysis, which offers a promising solution to overcome the limitations of standalone photocatalysis and piezocatalysis. This approach not only complements the utilization of solar energy but also enhances the reliability of our renewable energy portfolio. The key findings from Part 3 are summarized below.

Chapter 3.1 focuses on the piezocatalytic properties of various structurally diverse Sillen-Aurivillius phases, emphasizing efficient hydrogen generation without the need for co-catalysts or scavengers. Bi4TaO8Cl nanoplates are highlighted as a prime example, with their exceptional hydrogen production rate of 1.5 mmol/g/h, further improved with hole-trapping agents. A significant milestone is achieved as this work marks the first successful demonstration of piezocatalytic seawater splitting, yielding a hydrogen production rate of 854 μ mol/g/h, surpassing many oxide-based photocatalysts and piezocatalysts designed for pure water. These results pave the way for versatile, highly efficient piezocatalysts with promising prospects for sustainable hydrogen production.

Chapter 3.2 delves into the exploration of piezoelectric properties within centrosymmetric materials (BiOBr) by introducing oxygen vacancies, effectively overcoming the century-old challenge of requiring non-centrosymmetric crystal structures for piezoelectricity. Furthermore, it highlights the exceptional utility of centrosymmetric BiOBr as a bifunctional piezocatalysts for complete water splitting, simultaneously yielding H₂ and H₂O₂, all achieved without the need for co-catalysts or scavengers. The influence of high pressure under

247

piezocatalytic conditions was thoroughly examined through high-pressure synchrotron X-ray diffraction and theoretical investigations, conducted within a pressure range of 0.048 to 42.48 GPa. Remarkably, BiOBr underwent a unique isostructural phase transition under high pressure, accompanied by a reduction in carrier effective masses, resulting in heightened electron mobility while retaining crystallographic symmetry. These groundbreaking findings open doors to the design of piezoelectric materials that transcend the limitations of centrosymmetric structures.

Chapter 4.1 elucidates that as the world is grappling with a pressing issue of water pollution, particularly from organic pollutants and pharmaceuticals, driven by rapid industrialization. The convergence of piezoelectric and photoelectric properties within the Sillen-Aurivillus phases demonstrates exceptional efficiency for environmental decontamination under real-world pollutant conditions through piezo-photocatalysis. This efficiency is attributed to the synergistic effect resulting from the combination of photocatalysis and piezocatalysis. It offers a promising solution to the global challenge of water pollution. To facilitate the rational design of highly synergistic piezo-photocatalysts, the study introduces a gear-interlock framework encompassing seven parameters that describe the degree of synergy in piezo-photocatalysis.

Future outlook

Piezocatalysis and piezo-photocatalysis have rapidly advanced due to their significant advantages in catalytic efficiency and ease of implementation. However, several unresolved issues persist in current research.

The piezocatalysts and piezo-photocatalysts currently developed are still a considerable distance away from practical applications due to issues such as inefficient mechanical energy collection and inadequate recycling. To harness more energy effectively, it is crucial to enhance the responsiveness of piezocatalysts and piezo-photocatalysts to mechanical force. This necessitates exploring novel materials that are also resilient to fatigue. In this context, the Sillen Aurivillius phases emerge as promising candidates for tuning their piezoelectric properties, thanks to their structural flexibility.

On a mechanistic level, there is a lack of clarity regarding the relationship between semiconductor properties and piezoelectricity. For example, the connection between the concentration of free charge carriers and the redox thermodynamics in piezocatalysts or integrated piezo-photocatalysts remains elusive. Furthermore, the extent to which the piezopotential can influence the photocatalytic properties of semiconductor photocatalysts has not been fully elucidated. To gain a more comprehensive understanding of the mechanisms at play, it is imperative to channel increased efforts into theoretical calculations concerning the electronic structure, charge transfer kinetics, and catalytic reaction kinetics of piezocatalysts or piezo-photocatalysts under stress or simultaneous light and stress conditions. Additionally, the development of in-situ characterization techniques under both stress and simultaneous stress and light illumination is of paramount importance.

Currently, piezocatalysts and piezo-photocatalysts are predominantly utilized for pollutant degradation and water splitting. There is a strong need to expand their applications to other areas such as nitrogen fixation, CO_2 reduction, selective organic synthesis, and medical treatments.