RATIONAL DESIGN OF DIFFERENT COMPONENTS AND INVESTIGATION OF CORE PARAMETERS FOR ELECTROCATALYTIC REDUCTION OF DINITROGEN TO AMMONIA

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





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Dedicated to my parents and supervisor

Declaration

The work presented in this thesis has been carried out by me under the guidance of Dr. Ramendra Sundar Dey at the Institute of Nano Science and Technology, Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bona fide record of original work done by me and all sources listed within have been detailed in the bibliography.

Ashmita Biswas

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

Dr. Ramendra Sundar Dey Scientist-D INST Mohali *"Every work has got to pass through hundreds of difficulties before succeeding. Those that persevere will see the light, sooner or later"*

[Swami Vivekananda]

As I embark on this academic journey, I revere to **The Almighty** for all His blessings he poured on me in making me strong enough to persevere, accept failures and succeed. My deep faith in Him has always helped me to overcome difficulties, be at good mental and physical health and move forward to accomplish my thesis work to achieve my ever-desired "**Doctor of Philosophy**" degree.

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List of Abbreviations

Abbreviations	Descriptions
AFM	Atomic force microscopy
ATR-FTIR	Attenuated total reflectance- Fourier transform infrared
	spectroscopy
CA	Chronoamperometry
CC	Carbon cloth
C_{dl}	Double-layer capacitance
C_{sp}	Specific capacitance
CV	Cyclic voltammetry
DFT	Density functional theory
DI	De-ionized
ΔG	Gibbs' free energy change
DMSO	Dimethyl sulfoxide
DOS	Density of states
ECSA	Electrochemical active surface area
EDX	Energy dispersive X-ray spectroscopy
E_g	Optical band gap
EIS	Electrochemical impedance spectroscopy
ESR	Electron spin resonance
EXAFS	X-ray absorption fine structure
FAC	Face angle crystal
FE	Faradaic efficiency
FePc	Iron phthalocyanine
FESEM	Field-emission scanning electron microscopy
FFT	Fast Fourier transformation
FTO	Fluorine-doped tin oxide
GC	Gas chromatography
GCE	Glassy carbon electrode
GGA	Generalized gradient approximation
HER	Hydrogen evolution reaction
НОМО	Highest occupied molecular orbital
HRTEM	High resolution transmission electron microscopy
IC	Ion chromatography
ICP-MS	Inductively coupled plasma-mass spectroscopy
IFFT	Inverse fast Fourier transform
IPA	Isopropyl alcohol

JCPDS	Joint committee on powder diffraction standards
K-L plot	Koutecky–Levich plot
KPFM	Kelvin probe force microscopy
LSV	Linear sweep voltammetry
LUMO	Lowest unoccupied molecular orbital
NEXAFS	Near-edge X-ray absorption fine structure spectroscopy
NHE	Normal hydrogen electrode
NMR	Nuclear magnetic resonance
NPG	Nanoporous gold
NRR	Nitrogen reduction reaction
ОСР	Open circuit potential
OER	Oxygen evolution reaction
PALS	Positron annihilation lifetime study
PAW	Projected augmented wave
PBE	Perdew–Burke–Ernzerhof
PDS	Potential determining step
ppb	Parts per billion
ррт	Parts per million
RHE	Reversible hydrogen electrode
rpm	Rotation per minute
RRCAT	Raja Ramanujan Centre for Advanced Technology
RRDE	Rotating ring disk electrode
SAED	Selected area electron diffraction
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TS	Entropic term
UPS	Ultraviolet photoelectron spectroscopy
UV-vis-NIR	Ultraviolet-visible-near infrared
VASP	Vienna ab initio simulation package
VBS	Valence band spectra
V _{CPD}	Contact potential difference
V_{fb}	Flat band potential
XANES	X-ray near edge absorption spectra
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZPE	Zero-point energy

Abstract

"Ammonia: From past to present to future."

The over-consumption of the non-renewable energy sources tend the world-wide research to rely on green hydrogen/green ammonia as a safe and sustainable fuel for an electrified future. Ammonia, once known as the "friend to farmer" can be synthesized via electrochemical NRR in a carbon-neutral approach, surpassing the century-old energy-intensive Haber Bosch process. However, with the conventional electrocatalyst-electrolyte systems it can only attain a 'niche' status in terms of commercialization. Thus, a rapid improvisation in the cell components is utmost required that manoeuvre the NRR kinetics, thermodynamics as well as energetics to achieve the desired industrial level. However, the rate limiting parameters of NRR are stated as follows:

- (a) Poor N₂ solubility in aqueous electrolyte: low yield rate of NH₃.
- (b) Material selectivity on N₂ adsorption: HER>NRR.
- (c) The sluggish kinetics of OER retard the NRR process: High overpotential and low energy efficiency.

So, in this thesis works our major aim was to improve the yield rate and FE of NH₃ synthesis and to realize the chemistry of active sites that intuitively manipulate the mechanisms and kinetics of the elementary steps of NRR. Primarily, we worked upon a new aqueous electrolyte NaBF₄ that could act as a "co-catalyst", capable of forming N₂-BF₃ adduct. This helped to bring a significant concentration of N₂ in the medium. Moreover, BF₃ helped to modulate the d-band center of Mn-N/C catalyst provoking N₂ adsorption and activation on the catalyst surface by a "push-pull" electronic effect. This multitudinous role of BF₃ resulted into 2.45×10^{-9} mol s⁻¹ cm⁻² production rate of ammonia, approaching the industrial scale periphery at 0.0 V vs RHE.

Eventually we concentrated on adopting different strategies of catalyst synthesis, majorly keeping in mind few important factors like (a) to ensure better orbital overlap with N₂ improving the rate limiting potential, (b) N₂ adsorption over proton adsorption, (c) suppressed HER. Boron having orbital symmetry with N is expected to be more selective for NRR. Thus, firstly we chose boron-carbonitride material and functionalized the edges with O-atom (BNCO). This induced a charging effect on B that consequently improved its binding tendency and charge transfer phenomenon with N₂. Realizing the importance of charge cloud density, we then focussed to engineer NPG@SnS₂ heterostructure material that caused a band-bending at the metal semiconductor interface to equilibrate the Fermi levels. A charge accumulation occurred on the SnS₂ side lowering the work function of the material with four-fold enhancement in conductivity. This strategy also deviated proton adsorption more favourably on the S atoms resulting into 49.3 % FE for NRR. Then we moved to Ag₃PO₄ since both the cationic and anionic parts are already proved to suppress HER. We intended to improve the active site density and thus we improvised the material with group-VIB metal doping. This doping assisted vacancy engineering strategy created additional dopant-Ag active sites and altered the electronic properties of the catalysts facilitating N2 adsorption in a side-on manner via dp orbital mixing, resulting in 54.8 % FE. But this vacancy engineering itself holds significant potential to impact the NRR performance of a material and thus to gain an indepth understanding of this concept we developed oxygen-vacancy enriched SnO₂, where the bridge-type vacancy was found to be more electroactive and stable than the inplane type vacancy. This enabled an end-on followed by side-on N₂ adsorption of the two Sn atoms adjacent to the bridge vacancy site. The proton adsorption being more favoured on the electronegative O-atom, HER got suppressed benefitting NRR with 48.5 % FE. With both M/Ag₃PO₄ and SnO₂-O_v, a detailed kinetic and mechanistic investigations were carried out with RRDE technique and in-situ ATR-FTIR studies respectively together with theoretical support.

After attaining an appreciable NRR performance with several electrolyte-catalyst modifications, our intention deviated to a broader goal of improving the energy efficiency of this process. The several bottlenecks of NRR and on top of that the sluggish OER kinetics intakes about 90 % of the electricity input and raises the overall energy and power demand of the NRR process. So, we explored the inter-dependency of the NRR and OER processes and how the kinetics of one impacts the other. Upon replacing the conventional Pt counter electrode for OER, RuO₂ was found to not only improve the OER kinetics in 0.1 M KOH, but also enhanced the FE for NRR at a lower overpotential and current consumption. As a proof of concept, the FePc||RuO₂ electrolyzer was constructed that displayed a high electricity-to-chemical energy conversion efficiency of 46.7%. The electrolyzer also forecasted a full cell voltage of 2.04 V, which demanded only 603 mV overpotential to attain 0.5 mA current to drive forward the chemical equilibrium of the overall NRR-coupled-OER process.

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different NH4⁺ concentrations, appeared after 2 h of incubation; (f) UV-vis spectra at 460 nm, representing different known concentrations of N₂H₄ after 15 min incubation at room temperature; (g) corresponding absorbance calibration plot used in this study, inset represents the colour of the solutions having different N₂H₄ concentrations, after 15 min of incubation.......81 Figure 3.6. Comparison of yield of NH_3 and corresponding FE for MnN_4 catalyst in different electrolytes at different potentials. The trend for all the activity descriptors follows $NaBF_4 > HCl$ > LiClO₄ > KOH> Na₂SO₄. The error bars represent standard deviation between identical Figure 3.7. UV-vis spectra of electrolyte solutions, representing different known concentrations of NH₄⁺ stained with indophenol blue indicator solutions after 2 h incubation at room temperature and corresponding absorbance calibration plot used in this study; (a, b) for 0.1 M HCl, (c, d) 0.1 M Na₂SO₄, (e, f) 0.5 M LiClO₄ and (g, h) 0.1 M KOH......83 Figure 3.8. (a) CA response of N-C catalyst in 0.5 M NaBF₄ for 2 h run at 0.0 V vs RHE. (b) comparative UV-vis absorption spectra of the electrolyte for N-C and Mn/N-C stained with indophenol blue indicator after 2 h of incubation from the CA run. (c) comparative bar plot representing the NH₃ yield and Faradaic efficiency for Mn/N-C and N-C catalysts at 0.0 V....84 Figure 3.9. (a) EIS of MnN₄ catalyst in different electrolyte conditions (inset denotes the magnified data at higher frequency region); (b) Equivalent circuit diagram and comparison of the Ohmic and charge-transfer resistances at the electrode-electrolyte interface; (c) ¹H-NMR spectra of the working electrolyte in DMSO-d⁶ after different time span of the potential-dependent experiment at 0 V vs RHE; (d) Yield of NH₃ and FE of MnN₄ with NaBF₄ after cycling experiments at 0 V; (e) Comparative bar plot of concentration and yield of NH_3 in N_2 and Ar, at 0 V and in N₂ at OCP for MnN₄; (f) ¹H NMR spectra obtained after electrolysis in 0.5 M NaBF₄ with ¹⁵N₂, ¹⁴N₂ and Ar as the feeding gases; (g) Comparison of ammonia yield and massnormalized production rate quantified by both colorimetric test and NMR measurement with ¹⁴N₂ and ¹⁵N₂ feeding gases; (h) NRR performance map based on area-normalized production rate and mass-normalized yield of NH₃ in traditional aqueous, aqueous/organic, IL electrolytes and Li-Figure 3.10. The model structures of (a) pristine MnN₄ (b) MnN₄ (BF₃) (c) MnN₄/BF₃ (d) MnN₄/BF₃ (BF₃) of the catalyst considered for the theoretical studies. The Mn, N, C, F, B, H atoms are denoted with pink, dark blue, gray, light blue, big green sphere and small green colour Figure 3.11. Thermodynamic studies of NH₃ formation through BF₃ induced NRR on MnN₄ catalyst and electronic properties. (a) the full free energy path of NRR on the model system MnN_4/BF_3 (BF₃); (b) free energy profile of N₂ and NNH adsorption for the four catalyst models namely pristine MnN₄, MnN₄ (BF₃), MnN₄/BF₃ and MnN₄/BF₃ (BF₃). The Mn, N, C, F, B, H

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sphere respectively; the d orbital density of states of Mn site in (c) pristine MnN₄ (d) MnN₄/BF₃ (e) N_2 adsorbed MnN₄ (f) N_2 adsorbed MnN₄/BF₃. The d band centre value is given in the respective subfigure. Dotted line at zero in the x axis represents the Fermi energy level; (g-o) demonstrate the optimized model structure, charge density difference with side view and top view of (g-i) N₂ adsorbed MnN₄ (j-l) MnN₄/BF₃ (m-o) N₂ adsorbed MnN₄ with BF₃ attachment. The yellow and blue colour lobes represent the charge accumulation and depletion with isosurface value of 0.0032 e/Å³; (p) represents the free energy diagram of HER for these four Figure 3.12. (a) Yield of NH_3 with the reported catalyst and our catalyst with $NaBF_4$ in the potential range of -0.5 V to 0.2 V vs RHE; (b) Area and mass-normalized production rate of NH₃. The respective symbols adjacent to (a) and (b) denote the corresponding working electrolytes. Area-normalized production rate of NH₃ with MnN₄ in 0.5 M NaBF₄ (this chapter) was calculated to be 2.45×10^{-9} mol s⁻¹ cm⁻², approaching the predicted industrial scale periphery. All the data Figure 4.1. Optimised model structures of (a) BN, (b) BNC, and (c) BNCO systems. The N, C, O, B atoms are denoted with blue, wine, red, green colour spheres, respectively; Plot of DOS for (d) BN, (e) BNC, (f) BNCO systems. The vertical dotted line at zero represents the Fermi Level. Figure 4.2. Schematic representation of the probable mechanism of BNCO catalyst synthesis by pyrolysis method......105 Figure 4.3. (a) FESEM image of BNCO₍₁₀₀₀₎ catalyst (scale-bar: 100 nm); (b) HRTEM image of BNCO₍₁₀₀₀₎ catalyst (scale bar: 10 nm); (c) Elemental mapping of BNCO₍₁₀₀₀₎ catalyst showing the distinct elements B, C, N and O; (d) XRD of all the synthesized catalysts; (e) FTIR spectra Figure 4.4. Comparative narrow XPS spectra of all the catalysts at (a, b) B 1s, (c, d) N 1s, (e, f) Figure 4.5. NEXAFS spectra of BNCO₍₁₀₀₀₎ catalyst at (a) B K-edge, (b) N K-edge, (c) C K-edge Figure 4.6. (a) Comparative LSV curves of BNCO₍₁₀₀₀₎ catalyst in N₂ purged electrolytes at 10 mV s⁻¹ scan rate; (b) NRR performance of $BNCO_{(1000)}$ catalyst in different electrolyte conditions (0.1 M HCl, 0.1 M H₂SO₄ and 0.1 M H₃PO₄); (c) Comparative plot showing yield and FE of NH₃ synthesis over the wide-ranging potential window for BNCO₍₁₀₀₀₎ catalyst in 0.1 M HCl; (d) Free energy diagram of adsorption of Cl, SO₄ and PO₄ on edge B site of BNCO₍₁₀₀₀₎ system; inset shows the optimised model structures of Cl, SO₄, and PO₄ adsorbed BNCO models; charge density difference analysis of (e) Cl-adsorbed, (f) SO₄-adsorbed and (g) PO₄-adsorbed BNCO system. Yellow and blue lobes indicate electron accumulation and depletion, respectively (Iso-

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Chapter 1

Introduction
Overview: The over-consumption of non-renewable energy sources tends the world-wide research to incline towards the development of sustainable approaches to with-stand the global energy demand. In this scenario, green hydrogen/green ammonia serves as a safe and reliable alternative for an electrified future. Although to meet the practical demands of ammonia, the century-old Haber Bosch process is the sole option, but it deviates from the goal of a "net-zero" society. This chapter thus summarizes the importance of ammonia from past to present and its growing needs for the future economy. The electrochemical method of nitrogen reduction to ammonia has been elaborated with the prospects, consequences, and guidelines to overcome the related challenges. Thereafter, the strategies adopted for the catalyst development in the field have been discussed and the motivation of the thesis with a detailed perspective about the field is elaborated. The rationale behind the selectivity of aqueous electrolyte and catalyst development in this thesis work is focused on justifying the zero-carbon intention of this electrochemical approach and attaining NH₃ production approaching industrial limits in an energy efficient manner.



1.1 Motivation of the thesis

"Nature is our kindest friend and best critic in experimental science if we only allow her intimations to fall unbiased on our minds"

[Michael Faraday]

The dire consequences of the exhaustion of non-renewable energy sources compel the scientific community to explore renewable alternatives to thrive the toilsome situation. In this quest, while the whole world is looking forward to green hydrogen as a potent future fuel, ammonia is surfaced with better features to be looked upon for a green and circular economy. In earlier centuries, this ammonia was widely utilized in agricultural sectors and was known as *"friend to farmer*," but digging deep into that era reveals that ammonia in the 19th century was used for export purposes as well. So, connecting the knots and to overcome the difficulties with liquid hydrogen, ammonia has been realized as the liquid energy for the future and it is believed that it has potential to run the economy all by itself (Figure 1.1). There is an untiring effort all over the world to set-up renewable plants for the green ammonia production and the broad objective is to put a bar on the carbon inclusion or emission during the process or to attain *"carbon-neutrality."* This is an attempt to fulfil the sustainable development goals (SDG) introduced by the United Nations, particularly SDG-7 (*affordable and clean energy*) and SDG-13 (*climate action*).

This thesis is an endeavour to contribute towards the noble cause of protecting the "green" with electrochemical dinitrogen reduction, adopting viable approaches to target an industrial scale of ammonia production in a renewable manner.



Figure 1.1. Schematic representation explaining the green ammonia synthesis and its extensive utility.

1.2 Brief history about the importance of ammonia

"Ammonia: one name many solutions." In the early 1900s, the imbalance between the growing population and the demand for food and crops necessitated the flourishment of fertilizer industries based on ammonia and its derivatives. In this scenario, it was easy to think of the most abundant resource (N_2) to enable large-scale ammonia production. However, the chemically inert nature of this non-polar gas imposed a real challenge on the chemists globally and here when the industrial Haber Bosch process embarked on the advent of ammonia in early 1913 with the development of the first ever ammonia plant in Germany.¹ About 85 % of this artificially fixed nitrogen (to produce ammonia) was utilized to feed about half of the world's total population. The remaining 15 % had significance in industrial applications like synthetic chemical production, refrigerant fuel, and NO_x emission control. So, on the one hand, it was accessed as a blessing, but on the other hand, this ammonia had a dark contribution during the First World War. The Nazis used this ammonia to neutralize the toxic gases and manufactured explosives out of ammonium nitrate that caused several deaths across the world. Nevertheless, considering the transportation sector, the importance of ammonia was realized way back in the early 1800s as an alternative fuel in the internal combustion engines, which spiked during World War-II.² Although until 2010, the improvisation of these engines was less noted, but since 2007, the marine industries started aggressive research on using ammonia as an alternative fuel.³ However, the major challenge associated with this was



Figure 1.2. Schematic representation of the utilization of the Haber-Bosch ammonia (H-B NH_3) in different sectors.

the NO_x emission, that required rapid technological development for a full-fledged use of this fuel. This reveals the importance of ammonia in agriculture, industrial sectors, arms manufacturing to transportation fuel as schematically displayed in Figure 1.2, ever since its discovery and how we live in the world transformed by this one technology by Haber and Bosch.⁴

1.3 Ammonia: The future economy?

Ammonia was a savior once, so can it save the world again? The current global scenario in terms of energy consumption leading to rapid decay of non-renewable energy sources and climate change left the world with no alternative but to get a carbon-neutral society. In the battle to reach net-zero by 2050 as pledged by different nations world-wide, the only way is to fast-track low or no-carbon technologies and fuels. In this perspective, like green hydrogen is much in demand, green ammonia was so far hiding in plain sight. This green hydrogen can be rendered as a fuel to drive electric cars, giving off water as a by-product. However, the significant challenges associated with the use of this fuel are that, H₂ is stored in liquid form that requires extreme cryogenic conditions (-235 °C) and high pressure. In fact, it is highly flammable in direct contact with air, which necessitates a sophisticated storage condition of this liquid H_2 , thereby increasing the overall cost of maintenance and transportation. On the other hand, ammonia also burns CO₂-free. So, besides benefitting the fertilizer industry, it can be of great use as a fuel in the transportation sector.⁵ The ammonia exhibits a higher energy density and when liquified it contains 48 % more H₂ than H₂ itself.⁶ Moreover, it has a safe storage condition, hence economically viable to transport over long distances. Ammonia, besides holding its own as a fuel, can also act as a reservoir/carrier of H₂. So, it can enable a circular economy where after a successful ammonia synthesis, it can be safely shipped to the destination followed by a dehydrogenation step that would get us back its constituent parts like nitrogen and H_2 . Although it is true that it is not that simple to activate the chemically inert N_2 to NH_3 and again revert it back, but more years of research and technological developments would ascertain this process in an energy-efficient way, reach the industrial heights and facilitate the utmost-desired the sustainable society for one and all.

1.4 Production of ammonia: From past to present

Among the four most important worldwide used industrial chemicals, namely hydrogen, ammonia, methanol, and carbon monoxide that are indebted to the syngas processes,

ammonia involves the most complicated catalytic steps with multiple elementary reactions.⁷ The technology of the Haber Bosch process of ammonia synthesis introduced by Fritz Haber and Carl Bosch, along with the remarkable Fe-catalyst discovered by Alwin Mittasch⁸ started a full-fledged operation of the world's first ever ammonia plant in Germany. This process initiates with steam reforming of natural gas to produce hydrogen, which then reacts with N₂ to produce ammonia (NH₃) following the equation 1.1

 $N_2 + 3H_2 = 2NH_3, \Delta H_0 = -45.9 \text{ kJ/mol}$ (1.1)

Over the time, this process has been heavily improvised in terms of technology as well as catalyst development to achieve a remarkable scale of ammonia production. However, one constant problem associated with this process is the emission of enormous carbon monoxide as well as carbon dioxide that extends to about 3 % of the global carbon



Figure 1.3. Schematic representation to understand the different colour codes for ammonia synthesis and its relation with C input/output.

emissions and about 1.4 % of the total CO₂ emissions of the world (approximating 235 million tons).⁹ More importantly, the steam reforming step is highly energy intensive, which increases the energy consumption of the process many-fold, about 1.8 % of the world's total energy production.^{10,11} So, while ammonia still holds significant importance in the global frontiers, the problems associated with this age-old process like (a) excessive intake of natural gas (non-renewable source), (b) an imbalance of the nitrogen cycle, (c) emission of green-house gases like CO₂, NO_x causing fatal environmental

issues, (d) consumption of more energy than production, draw severe attention and need to be thoroughly judged.

Thus, keeping in mind the current climate change conditions and surge for renewability, an alternative way-out is utmost desired that would offer a sustainable and ambient approach to ammonia production fulfilling the "NET-ZERO" vow of the society. With the onset of the generation of brown ammonia (produced in the Haber Bosch process), lately, the emitted carbon was intended to be captured and converted/stored to put a bar on its direct emission and the ammonia thus produced was termed as the blue ammonia. However, the dire desire of the research community then turned into an even better alternative that would absolutely negate the carbon traces from feedstock to product. This calls for the electrochemical method of nitrogen fixation that exploits the electric grid power to electrochemically convert N₂ to green ammonia (NRR). The energy to power these electric grids and generate electricity could be derived from renewable sources like wind, solar, geothermal, hydropower or biomass, thereby taking our zero-carbon agenda a step ahead.¹² The respective colour codes for ammonia synthesis in relation to the consumption/emission of carbon is summarized in Figure 1.3.

1.5 Electrochemical nitrogen reduction reaction (NRR)

Realizing the importance of ammonia (NH₃),¹³ a lot of progress is ongoing in the frontiers of research adopting the greener electrochemical approach of NRR.¹⁴ Although this ammonia synthesis had been demonstrated way back in the 1800s, this became a reality with the development of the first ammonia plant by Haber and Bosch in 1913. However, in the late 1960's, the first electrochemical NRR study was initiated with Pt electrode. Till 2000, the NRR was mostly carried out at high temperatures in solid electrolytes. Beyond this time a new renaissance began for the ambient NRR process that gradually confronted a rapid development after 2015 till date, so it is quite recent (Figure 1.4).^{15,16} With increasing demands for green ammonia, research attempts are made for industrial-scale NH₃ production. This eventually helped to flourish many research directions in NRR, starting from catalyst designing to electrolyte improvisations, membrane study and exploration of reaction kinetics, with enough room for further investigation and developments.¹⁷



Figure 1.4. Time-line of the first inventions contributing towards the growth and development of the NRR field.

1.5.1 Reaction thermodynamics

Dinitrogen (N₂) molecules are often regarded as chemically inert, which is entirely justified by the molecular orbital diagram shown in Figure 1.5. The σ -orbital (HOMO is

bonding in nature while the π^* -orbital (LUMO) is anti-bonding in nature. So, for bond activation electrons should fill the high energy LUMO and it should be removed from the energetically stabilized HOMO, which is not favoured both ways. Naturally, N2 has a negative electron affinity of -1.90 eV and it requires an activation energy as high as 410 kJ mol⁻¹ to break the first N \equiv N bond. Moreover, the wide energy gap (10.82 eV) between HOMO and LUMO of N2 discourages electron transport reactions. In addition, N₂ reduction requires the activated N₂ to pass through several protonation steps to produce NH₃. However, the proton affinity of N_2 being energy-intensive (493.8 kJ mol⁻¹), the first protonation step becomes endothermic in



Figure 1.5. Molecular orbital diagram of N_2 .

nature (+37.6 kJ mol⁻¹), requiring -3.2 V vs RHE potential to accomplish.^{18,19} Thus, from every perspective starting from activation to protonation, NRR is a thermodynamically

challenging process. Since, the redox potential to produce N₂H being quite negative, this makes N₂ to N₂H formation the potential determining step for NRR on most of the catalysts and offers more favourable energy for the adsorption of protons directly on the catalyst surface rather than N₂. It is extremely challenging to find an ideal electrocatalyst with thermodynamically neutral reaction steps. However, several theoretical estimations reveal potential ways to minimize the overpotential for NRR and make it favourable over the competitive HER.²⁰

1.5.2 Mechanisms followed by different catalysts for NRR

The electrochemical NRR is a bio-inspired process where the nitrogenase enzyme has Fe-Mo cofactors that can fix the environmental N₂ and reduce the same following the enzymatic pathway.^{21–23} The enzymatic pathway allows the N₂ molecules to adsorb on the catalyst's active site in a side-on manner. The charge re-distribution between the active site and N₂ reinforces the polarizability of N \equiv N followed by the protonation steps,



Figure 1.6. Different mechanistic pathways for NRR. (a) Associative alternating pathway; (b) Associative distal pathway; (c) Dissociative pathway; (d) Enzymatic pathway; (e) mars-van Krevelen pathway and (f) Surface hydrogenation driven NRR. Reproduced with permission from American Chemical Society.³¹, Copyright (2019).

subsequently on either of the N atoms. This results in the formation and desorption of two moles of NH₃ from the catalyst surface. However, understanding and analyzing the exact NRR mechanism remains challenging due to complicated reaction steps and unidentified reaction intermediates.

Nevertheless, after the advent of electrochemical ammonia synthesis from NRR, three major mechanisms are acknowledged, such as dissociative, associative, and enzymatic pathways (Figure 1.6a-d).^{24,25} Unlike the enzymatic pathway that enables a side-on N₂ adsorption, the dissociative and associative pathways allow end-on adsorption of the N₂ molecules onto the catalyst surface. More elaborately, the dissociative mechanism directly cleaves the N \equiv N and each N atom results in one mole of NH₃. It can be perceived how difficult this process is and it requires extreme temperature and pressure conditions along with a strong catalyst to make it happen. This pathway is followed in the artificial nitrogen-fixing Haber-Bosch industrial process²⁶ to meet the demands of the manufacturing sector. This is because, in the Haber Bosch technique the kinetic parameters can provide enough power to aid the N \equiv N bond breaking.²¹

Contrary to this, the associative mechanism is further classified into alternating and distal pathways where the steps involved in the former is like the enzymatic pathway except for the pattern of N_2 adsorption (Figure 1.6a and 1.6d).²⁷ On the other hand, in the distal pathway, the distal N atom is protonated first and only after the release of one mole of NH₃, the proximal N gets protonated and reduced. These mechanisms are completely catalyst-dependent and there is no generalized rule to categorize the catalysts based on their reaction pathway towards NRR. However, the associative mechanism is most common among a wide genre of catalysts. This end-on adsorption is possible when the catalysts have free unsaturated sites (axially) for N₂ adsorption, otherwise, the side-on adsorption predominates.

Besides these, a particular class of metal nitride catalysts follows the Mars-van Krevelen mechanism of nitrogen reduction (Figure 1.6e).²⁸ Here, the N atom constituting the active catalyst initially takes part in the NH₃ synthesis. The N-vacancy so formed is replenished by the N₂ molecules from the feed gas during the electrochemical process. Thereafter, the NRR on the metal nitrides follows the distal associative mechanism.²⁹ However, a recent report suggests that, even O-vacant V₂O₅ and CeO₂ are interpreted to fall in this mechanistic category of NRR towards ammonia synthesis.³⁰

Recently, an exciting out-of-the-box concept has been highlighted by Ling et al., where the authors have revealed a surface hydrogenation driven NRR process (Figure 1.6f). Here, primarily the catalyst surface gets covered with protons that consequently drive N₂ molecules for activation and reduction to form $*N_2H_2$ by the surface adsorbed protons. Unlike all other cases, here the reduction of N₂ to $*N_2H_2$ is the rate-determining step for NRR.³¹

1.5.3 Rate-limiting factors in NRR

The NRR is conventionally carried out in an H-cell, as shown in Figure 1.7. There, the cathodic and anodic chambers are separated by a proton-exchange Nafion membrane



Figure 1.7. Electrochemical H-cell for NRR in a three-electrode configuration showing two compartments for the reduction and oxidation reactions, separated with Nafion membrane.

enabling an easy proton exchange across the two compartments during electrocatalysis. The NRR process is a reductive phenomenon occurring on the cathode side where the N₂ reduction occurs on the working electrode and the N₂ gas inlet is positioned in a close vicinity of the working electrode. The potential of the working electrode is calibrated with respect to the reference electrode (Ag/AgCl) positioned in the same cathode chamber. The anodic counterpart comprises the Pt wire as the counter electrode where the oxygen evolution reaction takes place conventionally. As NRR is a proton-coupled-electron transfer (PCET) reaction, the source of the proton is the electrolyte itself and the electron is conducted through an external circuit between the counter and working electrodes. However, several challenges are associated with each electrolyzer component that impede the reaction rate and pulls down the reaction kinetics. These have a direct

impact on the yield rate, faradaic efficiency and overpotential for the NRR process.³² A detailed observation about the rate-limiting parameters is summarized below.

1.5.3.1 N_2 solubility. A recent report from Choi et *al.* has concluded that the low yield and production rate of NH₃ is non-convincing of actual N₂ reduction in the medium.³³ The origin of this benefit of doubt is primarily due to the poor N₂ solubility in the aqueous electrolytes. Rationally, if the medium has insufficient N₂ concentration in the proximity of the electrode surface, then naturally the three-phase reaction kinetics slows down affecting the production rate of NH₃. Thus, a major focus needs to be devoted in improving this rate-limiting parameter to bring about a reliable and scalable electrochemical NH₃ synthesis.

In this respect, ionic liquids have turned up as a convenient medium to solvate N₂ gases. Gomes and co-workers worked with room temperature ionic liquids like 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF4],³⁴ 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF6]³⁵ and 1-alkyl-3-methylimidazolium (C_nmim, n = 2,4,6) tris(pentafluoroethyl)- trifluorophosphate (eFAP)³⁶ ionic liquids and calculated the solubility of N₂ in terms of mole fractions of solute and Henry's law constants given by equations 1.2 and 1.3, respectively.

$$x_2 = n_2^{liq} / (n_1^{liq} + n_2^{liq})$$
(1.2)

where, n_2^{liq} is the amount of solute dissolved in the ionic liquid and n_1^{liq} is the total amount of ionic liquid.

$$K_{H} = \lim_{x_{2} \to 0} \frac{f_{2}(p,T,x_{2})}{x_{2}} \cong \phi_{2}(p_{eq},T_{eq})p_{eq}/x_{2}$$
(1.3)

where K_H is the Henry's law constant, f_2 is the fugacity of the solute and ϕ_2 its fugacity coefficient, p, T are the pressure and temperature of gaseous solute present in the gas bulb and p_{eq} and T_{eq} are the equilibrium pressure and temperature respectively.

Fluorinated ionic liquids were found to solvate a greater proportion of the gaseous molecules than the hydrogenated counterions.³⁷ This is because, N₂ is likely to interact with the F-atoms and a charge delocalization over the fluorinated part of the ionic liquids ensure better extent of N₂ solubility. An increase in the fluorinated entities cost a loss of molecular flexibility and lowering of bond polarity, thus showing further enhancement in N₂ solubility.³⁸ Similarly, polar nitrile moieties were found to decrease N₂ solubility for the cationic counterpart of ionic liquids.³⁹ These strategies have been widely implemented on NRR by Simonov, MacFarlane and group.⁴⁰ They not only inferred that,

a low viscous ionic liquid is able to support higher mass transport, resulting in a better yield rate of NH₃ production, but also synthesized a series of fluorine-rich phosphoniumbased ILs, which displayed high N₂ solubilities and all were found promising towards NRR.⁴¹ There are further reports where authors have rendered alcohol medium to improve N₂ solubility instead of the all-aqueous counterpart.⁴² However, if one intends to operate NRR ambiently and in a no-carbon approach, ionic liquid or organic electrolytes are no alternatives because of the sophisticated maintenance and carbon-inclusion, respectively.

1.5.3.2 Competitive hydrogen evolution reaction. One of the major concerns of this electrochemical NRR is the competitive HER having similar thermodynamic potentials for their reduction, as shown in equations 1.4 and 1.5.

$N_{2} + 6H^{+} + 6e^{-} \leftrightarrow 2NH_{3}; 0.092 V vs RHE$ (1.4) $2H^{+} + 2e^{-} \leftrightarrow H_{2}; 0.00 V vs RHE$ (1.5)

This poses a challenge to the material selectivity as most of the metals favor the energetically viable H₂ adsorption rather than N₂.⁴³ This affects the cathodic current density and hence the FE of NH₃ synthesis.^{44,45} To reduce one mole of N₂, producing two moles of NH3, a total of six electrons and six protons are required. It is quite understandable that, such a complicated process would eventually involve several obscured intermediates on the catalyst surface, difficult to arrest and detect. More importantly, even if the proton and electron supply is abundant, the chemically inert nature of the N₂ molecule fails to negotiate in terms of energy to break the first bond of $N \equiv N$, making N₂ activation really trouble-some. So, if the catalyst encounters any low energy intensive and facile alternative like proton adsorption and reduction (HER) in a similar voltage window, then it would any way take that path challenging the selectivity towards NRR or incurring a huge overpotential for NRR.⁴⁶ It is noteworthy that a higher overpotential implies a more negative potential range where, although the current density increases significantly, but the FE for NRR is drastically hampered owing to the rapid H₂ evolution and the rapid bubbling on the catalyst surface leads to material instability.^{13,47–49} So, one can understand how much perturbation this HER causes and it requires to be bypassed for a fruitful NRR process on the catalyst active site. In the quest of ideas to do away with HER, Nørskov and co-workers came up with a finding that HER is dependent on the proton and electron concentration by first-order, while NRR is independent, as shown in equations 1.6 and 1.7.⁵⁰

$HER \propto [H^+]^1 [e^-]^1$	(1.6)
$NRR \propto [H^+]^0 [e^-]^0$	(1.7)

Thus, one acceptable alternative could be a restricted source of protons or electrons from the electrolyte or catalyst to dominate NRR over HER. In these perspectives, the following improvisations have already been done.

A) Use of aqueous-organic electrolytes to limit the proton source,^{42,51}

B) Choice of electrolyte pH as acidic electrolytes are more abundant with protons favoring HER while alkaline electrolytes with less proton source would hamper the protonation steps during NRR,⁵²

C) Choice of alkali metal cations in electrolyte capable of forming hydration shells,⁵³

D) Modulating a hydrophobic envelope over the catalyst surface to form a three-phase interface and prevent HER,^{54,55}

E) Use of semi-metal electrodes like Bi, Sn having limited electron accessibility,⁵⁶

F) Covering the catalyst surface with non-conducting coatings or conductive polymers like polyaniline, polyimide, polypyrrole, etc.⁵⁷

1.5.3.3 Sluggish rate kinetics of counter OER. The electrochemical NRR is always accompanied by a counter-oxidation reaction at the anode compartment, which is imperatively the oxygen evolution reaction. One major aspect of why researchers seek a substitute for the Haber Bosch process is its energy intensiveness and drastic operating conditions.⁵⁸ However, the electrochemical NRR process, owing to several bottlenecks such as the competitive HER, inferior N₂ solubility in aqueous electrolytes, and the poor selectivity of material toward N₂ adsorption, utilizes sufficiently high energy inputs to produce ammonia, moreover at a much lower production rate.⁵⁹ When these issues persist, the sluggish kinetics of the counter OER on the conventional Pt anode surface in the aqueous electrolyte consumes about 90% of the electricity input, which makes the overall NRR coupled OER process energetically and thermodynamically unfavorable.⁶⁰ This could be resolved in a number of ways as follows:

A) Choosing suitable catalysts and electrolytes favoring OER at a low overpotential.

B) Combining NRR with other oxidation reactions like alcohol oxidation, glycerol oxidation, uric acid oxidation etc that could occur facilely improving the NRR kinetics. However, it is to be noted that the potential required for the full cell reaction ($\Delta E_{NRR-oxidation reaction}$) must not exceed $\Delta E_{NRR-OER}$. It should also be noted that, based on the motive of the work, if one desires to develop a bifunctional catalyst, then the other thermodynamic parameters and reaction overpotential will be irrelevant to consider.

1.5.3.4 False positives. An erroneous NH_3 quantification is often encountered during NRR resulting from a nitrogenous impurity source in the electrolyte/catalyst other than the feeding gas.⁶¹ In fact, sometimes the feed gas may also contain nitrogenous contaminants other than N_2 . This has mandated several precautionary measures that include:

(A) Purity checking of feed gas to negate the possibility of any adventitious NH₃ or NO_X interfering during NRR.

(B) Several control experiments in Argon atmosphere as well as at OCP.

(C) Rigorous qualitative and quantitative isotope labelling experiment with $^{15}N_2$ feed gas to ensure the source of the produced NH₃.

1.5.4 Catalyst development for NRR

A review on NRR by Ren et al⁵⁰. classified that about 91 % of the research works in the field accounted for catalyst designing (Figure 1.8).⁵⁰ Any catalysis process proceeds through the adsorption step, which relies on the nature of the catalyst surface, providing active sites for adsorption. Some general features usually attract the N₂ adsorption steps,



Figure 1.8. Histogram of the number of papers against the publication year in NRR field. The bar below the histogram denotes the percentage of papers classified by mechanism, catalysts, electrolytes, and reactors. Reproduced with permission from Royal Society of Chemistry,⁵⁰ Copyright (2021).

like the orbital energy symmetry between N₂ and the adsorbing element, such that the electron donation and π -back donation steps are favored.⁶² Additionally, the material

should have Lewis acidic centers that can provoke N2 adsorption. Actually, Lewis acid sites have a strong tendency to form adduct when it is in the vicinity of a Lewis base. The weak Lewis basicity of the N₂ molecules is rendered by the Lewis acidic entities within the catalyst and helps to attract N₂ adsorption over proton adsorption.⁶³ However, besides regulating the chemical adsorption factors, the electronic properties of the materials also embark a remarkable influence on the rate-limiting steps of NRR. The intrinsic activity of an electrocatalyst towards any reaction depends on the local electronic structure and charge density of the active site. Regulation of the co-ordination environment around the active metal site, proper positioning of d band structure and alteration of density of state and spin state lead to modification of the local electronic structure of a material, resulting in charge accumulation around the active site. All these combined factors can lead to specific adsorption of N₂ and control the binding strength between intermediates and electroactive moieties, thereby resulting in NH₃ production with high selectivity. Thus, the catalysts should be selective to adsorb N₂ adsorption rather than H⁺ and preferably the protonation should occur on the adsorbed N₂ rather than on the active site itself, thereby blocking it for NRR. Alternatively, the HER active sites in a catalyst could be blocked or the proton adsorption could be deviated from the NRR active site by adopting several material engineering approaches as elaborated in the later sections.64-71

Besides this active site manipulation, different synthesis strategies result into shape-specific nanostructures with variable exposed facets that influence the NRR activity of the material. Usually, the low-index facets display stable flat surfaces, while the high-index facets exhibit more unsaturation of d-orbitals and, therefore, more electrocatalytically stable. It has been reported that the high-index facets of low-coordinated atoms can provide high-active sites for electrochemical reactions.⁷² However, these high index facets often bind the intermediates strongly, thereby hampering the NRR kinetics.

1.5.4.1 Single-atom catalysts. Single atom catalysts (SACs) have got significant attention in NRR owing to their maximum atom utilization and unsaturated coordination capable of adsorbing reactant molecules on the active site.^{73,74} The early transition metal catalysts are usually more prone to binding N₂ as compared to protons, but lack popularity owing to their intrinsically poor NRR activity. Whereas, the first-row transition metals like Fe, Co, Mn, Cr as well as Mo, Ru, Ag show high activity towards

NRR, though they can also facilitate proton adsorption in aqueous electrolytes. Comparatively, V, Cr, Mo, and W are better in terms of their energetics towards NRR.⁷⁵



Figure 1.9. Schematic representation of N_2 binding interactions with transition metal (TM) dorbitals as well as sp^2 hybridized orbitals of B(non-metal) or Al.

However, upon manipulating the electronic behaviour of all these metals, their activities towards NRR can also be tuned. Besides metals, semi-metals like Bi, Sn and non-metals like B, Al, preferably in sp² hybridization are also fascinating as these have energy symmetric orbitals as that of N₂ with which these can initiate N₂ adsorption and activation by σ -donation π -back donation interactions, like that with transition metals (Figure 1.9).⁷⁶

1.5.4.2 Doping and functionalization of hetero-atoms. The term "doping" symbolizes the incorporation of heteroatom into a host material with an effort to tune the electronic state and spin state resulting in charge redistribution which can be beneficial for the increase in active site-selective adsorption of reactants⁷⁷, surface polarization⁷⁸ and feasible interfacial charge transfer⁷⁹. Doping of electron-rich or deficient heteroatoms into catalyst system can also manipulate the Fermi level position⁸⁰ of an electrocatalyst. Until now, various p-block and d-block elements have been incorporated as dopants into carbonaceous as well as metal/ non-metal-based catalysts for NRR. Generally, transition metals with lower valency are highly beneficial toward nitrogen adsorption and activation as they contain fully or partially vacant d orbital capable of accepting electrons from bonding orbital of N₂ via σ bonding and simultaneously form π back bonding through donation of electrons from transition metal to the π^* antibonding bonding orbital

of N₂ as observed in nitrogen coordinated with metal complexes.⁸¹ Due to the unavailability of lone pairs of electrons in the N₂ molecule, the σ bonding interaction between metal and N₂ is weak. But, π back bonding between the filled d orbital of transition metal and N₂ results in easy delocalization of d-electrons towards antibonding



Figure 1.10. Schematic representation of metal doping strategies, impact on structural and electronic properties and corresponding N_2 adsorption mechanisms benefiting NRR.

orbital of N₂, resulting in triple bond polarization and bond length elongation, thereby making it easier for further reduction process via minimizing the potential energy barrier. So, transition metals with filled shell d-orbital will be highly active towards electrocatalytic NRR and dopants may replace either the host metal or get positioned at the interstitial lattice spaces differentially affecting N₂ adsorption mechanism as shown in Figure 1.10.⁸² However, the major obstacle with late transition metals in NRR activity lies in their affinity towards proton adsorption over nitrogen,⁸³ leading to lower Faradaic efficiency. Whereas, the p-block elements catalyze the nitrogen activation via electron delocalization from N₂ to vacant or partially filled p orbital and back donation from pblock element to N₂.⁸⁴ But, the non-availability of sufficient π orbitals and poor conductivity of p-block elements result in slightly inferior activity as well. Therefore, doping engineering or edge-functionalization processes have attracted researchers to develop new electrocatalyst, where introducing p-block hetero-atoms have shown to be a promising approach as it effectively regulates electronic as well as physicochemical properties of materials vulnerable towards electrocatalytic activation and reduction of nitrogen (Figure 1.11).



Figure 1.11. Non-metal heteroatom doping in carbon framework and its efficiency towards N₂ adsorption.

1.5.4.3 Interface engineering strategy. Interface engineering is one of the most promising strategies for the development of electrocatalyst, which require manipulation of local charge concentration, numerous active sites, accessible specific surface area and, proper functionality to obtain optimum catalytic activity. In general, interface engineering is defined as the coupling of distinct materials to form one heterostructure in order to manipulate the physical and chemical properties.⁸⁵ The coupling of metal and semiconductor in heterostructure will result in a difference in the contact potential at the junction, eventually altering the band position of semiconductor affecting the Fermi level.⁸⁶ However, the choice of metal and semi-conductor decides the work function of the same and accordingly, band bending occurs at the interface with localized holes or electrons as shown in Figure 1.12, which impact the NRR performance of the material.⁸⁷ This has been proven to be effective to suppress the HER by deviating its adsorption site, making way for an efficient NRR process on the catalyst surface.



Figure 1.12. Interface engineering between metal and semi-conductor influencing the electronic states of the heterostructure at the interface.

1.5.4.4 Vacancy engineering. Tuning surface defects and electronic structure via generating vacancies at the surface has been a promising approach adopted by researchers for multiple electron-proton involving electrocatalytic reactions.⁸⁸ Artificial incorporation of vacancies of heteroatoms, such as N, O and S in host material generally form defects with enriched electrons considered to be highly useful for NRR. In comparison to N and S vacancy, oxygen vacancy proved to gather many more electrons into the site owing to its greater electronegativity, thereby accumulating electron density on to the site, facilitating N₂ adsorption and weakening the triple bond (Figure 1.13).⁸⁹ In one of the reports, it has also been observed that the S-vacant site in Ru/MoS₂ not only



Figure 1.13. Schematic representation of impact of vacancy engineering on NRR (N_2 adsorption and activation).

scavenges the protons but also helps in the subsequent protonation steps of NRR.⁹⁰ In addition to this, the vacancy or defect engineering approach increases the activity of the basal plane besides the electro-active edges in several 2-dimensional electrocatalysts for NRR. Thus, this material synthesis strategy has emerged as a promising research field in NRR.

1.6 Brief outlook of the thesis

The electrochemical ammonia synthesis from dinitrogen reduction has been an emerging hotspot in academia as well as industries owing to the ever-growing demands of green ammonia in fertilizer and transportation sectors. With a pledge of the "Net-Zero" society, different nations have set up ammonia plants with a target of few million tons of ammonia production in the coming two to three years. Realizing the gravity of the matter, it is highly crucial to develop NRR electrolyzers capable of producing industrial-scale ammonia, that too in an energy-efficient manner. However, with the conventional electrocatalyst-electrolyte systems, it can only attain a 'niche' status in terms of

commercialization. Thus, a rapid improvisation in the cell components is utmost required realising the key factors that manoeuvre the NRR kinetics, thermodynamics as well as energetics to achieve the desired goal.

Chapter 2 discusses the detailed experimental procedures and electrochemical characterizations carried out to determine the respective physical and electronic properties of the materials and their electrochemical NRR performance. A summary of the colorimetric methods and a rigorous method optimization for a reliable detection of ammonia by the Indophenol blue method have been elaborated, which is followed in the later chapters of the thesis.

Since, the electrolyte medium is one of the primary cell components, the first and foremost focus is to improve the condition of the aqueous electrolytes and render a detailed investigation about how an aqueous electrolyte can help improve N_2 solubility and affect the catalyst performance over a prolonged duration.

- Chapter 3 explores NaBF4 as a novel aqueous electrolyte capable of forming a Lewis acid-base adduct with N2. The BF3 counter-anion significantly interfered in changing the d-band center of the metal (Mn) constituting the active center of the catalyst and by a push-pull electronic interaction initiated a high yield rate of ammonia production, approaching the industrial scale periphery.
- Chapter 4, on the other hand, discusses how the conventional acidic aqueous electrolytes like HCl, H₂SO₄ and H₃PO₄ with different counter anions cause poisoning effect variably on the catalyst active site and perturb the long-term material performance.

These chapters explain how the electrolyte ions function majorly in determining a material's NRR performance. Besides this, the most noteworthy component is the electrocatalyst, which is pivotal in NRR. In this thesis, several strategies have been implemented for the catalyst designing and an insightful study has been accomplished to understand the NRR activity and mechanism on the electroactive site and how the altered physico-chemical and electronic properties of the catalysts influence NH₃ yield rate and Faradaic efficiency.

Chapter 4 explains how hetero-atom (oxygen) edge-functionalization reinforces the charging effect on the boron center of the boron carbonitride system due to electronegativity difference. This phenomenon is likely to enhance the activity of the B center towards an accelerated orbital overlap with the N₂ molecules, increasing the yield rate of ammonia synthesis.

- Chapter 5 introduces the NPG@SnS₂ catalyst formed by interfacing nanoporous gold (NPG) and SnS₂. The hetero-junction so formed enabled a band-bending to equilibrate the metal/semi-conductor Fermi levels. The free carrier accumulation at the interface and favoured H-adsorption on the S site increased the Faradaic efficiency for NH₃ synthesis on Sn active site to 49.3 %.
- Chapter 6 focusses on a doping-assisted vacancy engineering strategy to synthesize group VI-B metal doped Ag₃PO₄ for NRR. The improvised electronic structure in the doped samples initiated side-on adsorption of N₂ over the dopant-Ag active site in a side-on manner and favored a maximum NRR performance on Mo/Ag₃PO₄-10.
- Chapter 7 concerns a thorough investigation of the type of oxygen vacancy (bridging/in-plane) in SnO₂ responsible for the actual activity increment of the catalyst. The active site determination and its influence on the rate kinetics and mechanistic pathway of NRR have been studied in deep with rigorous experimental, theoretical, and in-situ studies.

Now, after a series of experimental works on electrolyte and catalyst development, it is crucial to develop a full NRR electrolyzer that will consume a low full-cell overpotential and hence improve the electrical to chemical energy conversion efficiency of the NRR-coupled OER process.

- Chapter 8 thus talks about both cathodic and anodic component modifications with FePc in NaBF₄ as cathode and catholyte and RuO₂ in KOH as anode and anolyte. This system was able to favor the thermodynamics of NRR at the cost of low overpotential than the FePc(NaBF₄)||Pt(KOH) system with a two-fold increase in the energy efficiency of the NRR-OER process.
- Chapter 9 summarizes the conclusions of the thesis work and a glimpse of the future perspectives by which this thesis work could be extended further.

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Chapler 2

Material synthesis procedures, analytical techniques, and method optimizations

Overview: The thesis work involves the development of various materials with versatile synthesis techniques, used for electrocatalytic nitrogen reduction reaction. The morphological, structural as well as electronic properties of the materials are widely explored by means of several cutting-edge techniques that benefit the electrochemical performance of the catalysts, essential in the frontier of research domains. Therefore, the following chapter provides a detailed overview of the synthesis procedures, different instrumentations and calculations used for the material characterization and electrochemical performance evaluation with adequate details. Furthermore, the colorimetric method for the detection of electrochemically synthesized ammonia is rigorously refined and optimized that is followed in all the works summarized in the thesis.



Reference: Biswas et al., Langmuir, 2023, 39, 3810-3820.

Part - A

2.1 Introduction

This chapter gives the detailed qualitative information of (a) the chemicals/reagents used for all the projects, (b) the instrumentation details with model number and experimental conditions, (c) experimental procedures and (d) the associated formulae for various material characterization techniques and NRR activity description of the materials used in this thesis work. While several characterization tools provide information about the physical properties of the materials like conductivity, thickness etc, few other techniques manifest the chemical and electronic properties like oxidation state, coordination environment, band gap, flat-band potential and so on. In addition to this, the electrochemical methods provide information about the electrochemically active surface area and the electrochemical redox reactions and charge transfer phenomena ongoing on the catalyst surface. All these analytical and electrochemical details are provided in brief in this chapter.

Chemicals **Purity** Source Ammonium chloride (NH₄Cl) 99.5 % Sigma Aldrich 99 % Sodium tetrafluoroborate (NaBF₄) Sigma Aldrich 99 % Sodium sulphate (Anhydrous) (Na₂SO₄) Sigma Aldrich Potassium hydroxide (pellets) (KOH) 95 % Merck 85 % Hydrazine monohydrate (N₂H₄. H₂O) Sigma Aldrich 97 % Sodium hydroxide (NaOH) Sigma Aldrich 99 % Trisodium citrate dihydrate ($C_6H_9Na_3O_9$) Sigma Aldrich Sodium hypochlorite (NaClO) Sigma Aldrich para-(dimethylamino)benzaldehyde (C₉H₁₁NO) 99 % Sigma Aldrich Sodium nitroferricyanide dihydrate 99 % Sigma Aldrich $(Na_2[Fe(CN)_5NO)]$ Lithium perchlorate (LiClO₄) 99.9 % Sigma Aldrich Maleic acid $(C_4H_4O_4)$ 99 % **TCI** Chemicals 99 % **TCI** Chemicals Sulfanilic acid (C₆H₇NO₃S) dihydrochloride 99.9 % Sigma Aldrich N-(1-naphthyl)-ethylenediamine $(C_{14}H_{14}N_2. 2HCl)$

2.2 Reagents and materials

Sodium nitrite (NaNO ₂)	99 %	Sigma Aldrich
Hydrochloric acid (HCl)	37 %	Sigma Aldrich
Ethanol (C ₂ H ₅ OH)	99.5 %	Sigma Aldrich
Melamine (C ₃ H ₆ N ₆)	99 %	Sigma Aldrich
Dimethylsulfoxide-D ⁶ (DMSO-D ⁶)	99.8 %	Sigma Aldrich
Sn granules (Sn)	-	Sigma Aldrich
Sulphur powder (S)	99.9 %	Sigma Aldrich
Salicylic acid (C ₆ H ₄ (OH)CO ₂ H)	99 %	Sigma Aldrich
Phenol (C_6H_5OH)	99 %	Sigma Aldrich
Sodium citrate monobasic (C ₆ H ₇ NaO ₇)	99.5 %	Sigma Aldrich
Silver nitrate (AgNO ₃)	99 %	Sigma Aldrich
Silver/gold alloy foil (Ag:Au 1:1)	12 ct	Goodfellow, USA
Acetone (C ₃ H ₆ O)	99 %	Merck
Boric acid (H ₃ BO ₃)	95 %	Merck
Sulphuric acid (H ₂ SO ₄)	99 %	Merck
Gold chloride trihydrate (HAuCl ₄ . 3H ₂ O)	99.9 %	Sigma Aldrich
Cobalt chloride hexahydrate (CoCl ₂ . 6H ₂ O)	99 %	Sigma Aldrich
Chromium chloride hexahydrate (CrCl ₃ . 6H ₂ O)	99 %	Sigma Aldrich
Ferrous chloride tetrahydrate (FeCl ₂ . 4H ₂ O)	99 %	Sigma Aldrich
Ferric chloride pentahydrate (FeCl ₃ . 5H ₂ O)	99 %	Sigma Aldrich
Manganese chloride tetrahydrate (MnSO ₄ . 4H ₂ O)	99 %	Sigma Aldrich
Sodium molybdate dihydrate (Na2MoO4. 2H2O)	99.5 %	Sigma Aldrich
Sodium orthovanadate (Na ₃ VO ₄)	99.9 %	Sigma Aldrich
Nickel chloride hexahydrate (NiCl ₂ . 6H ₂ O)	99.9 %	Merck
Bismuth nitrate pentahydrate (Bi(NO ₃) ₃ . 5H ₂ O)	99 %	Sigma Aldrich
Zinc chloride (ZnCl ₂)	99.9 %	Sigma Aldrich
Tungsten chloride (WCl ₄)	99 %	Sigma Aldrich
Perchloric acid (HClO ₄)	98.5 %	Merck
Potassium chloride (KCl)	99.5 %	Merck
Sodium chloride (NaCl)	99 %	Sigma Aldrich
Lithium chloride (LiCl)	99 %	Sigma Aldrich
Potassium sulphate (K ₂ SO ₄)	99 %	Merck

Disodium hydrogen phosphate anhydrous (NaH ₂ PO ₄)	99 %	Merck
Sodium tungstate dihydrate (Na2WO4. 2H2O)	99 %	Merck
Tin chloride pentahydrate (SnCl ₄ . 5H ₂ O)	99.9 %	Sigma Aldrich
Ruthenium oxide (RuO ₂)	90 %	Sigma Aldrich
Iron phthalocyanine (FePc)	90 %	Sigma Aldrich
Graphite strips (10 cm ×1 cm)		Excel instruments
Ni foam	-	Merck
Carbon Cloth (CC)	-	Kanopy Tech
		Solutions.
Copper sulphate (pentahydrate)	≥99.9%	Sigma Aldrich
Hydrogen peroxide (H ₂ O ₂) 30 %	-	Sigma Aldrich
Holey carbon coated Cu grid, Carbon film on Cu mesh	-	Agar Scientific Ltd
grid for TEM analysis		(UK)
Isopropyl alcohol (IPA)	97%	Merck
Nitric acid (HNO ₃)	90 %	Sigma Aldrich
Orthophosphoric acid (H ₃ PO ₄)	85%	Merck chemicals
Perchloric acid (HClO ₄)	70%	Merck chemicals
Sodium dihydrogen phosphate (NaH2PO4·H2O)	99 %	Sigma Aldrich
Sulphuric acid (H ₂ SO ₄)	≥99%	Merck chemicals
FTO-coated glass	-	Tech-Instro
¹⁴ N ₂ gas cylinder	99.9 %	Sigma gases
¹⁵ N ₂ gas cylinder	98 %	Sigma Aldrich

2.3 Material synthesis techniques and other experimental procedures

2.3.1 Hydrothermal/Solvothermal method

The hydrothermal method of catalyst synthesis is a chemical method where a heterogenous reaction is carried out in an aqueous medium in a closed autoclave under high pressure and temperature beyond the critical point. Solvothermal method is a similar approach where a non-aqueous solvent is taken and the temperature should be ideally above the boiling temperature of the solvent. These methods produce precipitate of the product after a successful completion of the reaction. Depending upon the condition of chemical reactions like temperature and duration (time), the morphology of the

nanostructured materials greatly varies. A schematic representation of this method is displayed in Figure 2.1a

2.3.2 Electron-beam evaporation method

Electron beam evaporation (e-beam evaporation) is a physical vapor deposition (PVD) process by which a uniform thin layer coating of the metal of interest is formed over a substrate. This technique is operated under high-vacuum condition where a target anode is bombarded with a high-power electron beam given off from a tungsten filament, which then strikes the target with a certain orientation in the presence of magnets. Thereafter, the targeted material melts and sublimates into the gaseous phase and gets deposited on the substrate held directly above the target. The thickness of this deposition method can be controlled manually. A schematic illustration of this method is shown in Figure 2.1b.

2.3.3 Pyrolysis/high temperature annealing method

Pyrolysis or high-temperature annealing is usually done in an inert atmosphere (Argon) at a high temperature. This method can be variably used to design different class of materials like single atom doped carbon, heteroatom doped materials, sulfurization or selenization to form metal dichalcogenides, vacancy engineered materials etc. A schematic representation of the experimental set-up is shown in Figure 2.1c.



Figure 2.1. Schematic representation of (a) hydrothermal/solvothermal, (b) e-beam deposition and (c) pyrolysis or high temperature annealing methods of nano-material synthesis.

2.3.4 Mechanical stirring method

This is a very simple, one-pot synthesis approach where the reactants are made to react in a suitable solvent medium under a specific temperature, slightly beyond room temperature but below the boiling point of the solvent with continuous stirring. Over the reaction time, it produces precipitate of the final product formed, which can be collected by ultracentrifugation.

2.3.5 Nafion (115) membrane cleaning

All the electrochemical experiments were carried out in an H-type electrolysis cell where the cathodic and anodic compartments were separated by the Nafion (115) membrane. This membrane allows the permeability of protons from one chamber to the other and is non-selective to any other ions. The membrane was pre-treated by heating it in 5 wt% H_2O_2 aqueous solution at 80 °C for 1 h and then in ultrapure water at 80 °C for another 1 h.

2.4 Instrumentation for material characterization

2.4.1 X-ray diffraction

XRD study of materials provides information about the crystallinity and its crystal structure. It works on the principle of Bragg's Law introduced by W. L. Bragg in 1912 and the corresponding equation 2.1 is stated as follows:¹

$n\lambda = 2dSin\theta \tag{2.1}$

where, θ and λ are the incident angle and wavelength of the radiation (1.5418 Å for Cu K α) respectively, *d* is the perpendicular distance between adjacent planes and *n* is the order of reflection. It is a non-destructive technique where; a monochromatic X-ray beam is incident on the sample surface and it gets diffracted from the unique crystal planes. The detected scattered X-ray beam identifies the different planes constituting a material. It is instrumental to identify the phase change of a sample depending upon the experimental conditions and the presence of different planes corresponding to a heterostructure material. It also gives sufficient information about the crystallite size and the type of strain (compressive or tensile) generated in the crystal lattice owing to heteroatom doping or vacancy engineering. So, for any nanostructured material, the primary identification for the formation of the desired material is obtained from XRD data analysis.

The XRD study was performed on a Bruker D8 advances instrument using Cu-K α ($\lambda = 1.5406$ Å) radiation in the 2 θ range from 10° to 80° with an acceleration voltage of 40 kV.

2.4.2 Scanning electron microscopy, energy-dispersive X-ray spectroscopy and mapping

The SEM gives the morphological or topological information about a sample. When a focussed beam of high energy electrons scans the surface of a sample in a raster pattern under a high vacuum condition, it interacts with the atoms in the sample producing secondary electrons (SE), back scattered electrons (BSE) and characteristics X-rays.² These signals are detected to produce the images of the sample with high magnification and resolution. It also detects the atomic % of different elements present in the sample by the EDX and the elemental distribution in atomic level by means of elemental mapping. However, it is to be noted that, EDX can trace the elements having atomic number greater than or equal to that of boron (B).

Surface morphology was investigated using SEM Jeol JSMIT300 at an acceleration voltage of 10-15 kV equipped with a Bruker XFlash 6130 EDX.

2.4.3 Field-emission scanning electron microscopy

FESEM works on a similar principle as that of SEM, but it takes advantage of providing an ultra-high-resolution of the surface image of a sample. The major difference between FESEM and SEM is its emission source, while the SEM utilizes thermionic emitter, FE-SEM uses field-emitter.³

The FESEM analysis was performed using JEOL JSM-7600F (FESEM) model.

2.4.4 Transmission electron microscopy

TEM provides similar information about the sample morphology as FESEM. However, the major different between the two is that, while FESEM or SEM utilizes the knocked-off electrons, TEM uses the electrons transmitted through the sample of <100 nm thickness. This technique utilizes a high acerating voltage upto 300 kV and resultantly provides a better-resolved image as compared to FESEM. Therefore, TEM is more informative not only with respect to the morphology and crystal structure of the material, but and it also helps to detect any defect states within the lattice, that could be identified by a disruption in the regular lattice fringe corresponding to a particular plane.⁴

TEM analysis was investigated out on a JEM2100 instrument suitable for HRTEM studies. The instrument was armed with digital micrograph software for investigating SAED pattern of the sample surface and equipped with EDX and elemental mapping facilities. Holey carbon-coated copper grids and carbon film on copper mesh grids (Agar Scientific Ltd.) were used for the sample preparation for TEM measurements.
2.4.5 Raman spectroscopic technique

Raman spectroscopy gives detailed information about the stretching vibration of the chemical bonds present in a material arising from the possible phonon interactions. It is a non-destructive technique and is applicable for a wide range of polar as well as non-polar entities like C-C, C=C, C-N, C=O etc. It works on the principle that when a sample is excited with a high-intensity laser beam, a light scattering occurs, which can be elastic and inelastic in nature. The former is referred to as Rayleigh scattering while the latter is the Raman scattering. The energy difference between the incident light and the scattered light is known as the Raman-shift. Usually, different molecules are associated with different vibrational energies that shift the energy of the incident light. When it is red-shifted (to higher wavelength and lower wavenumber), it is termed as anti-stokes scattering.⁵

The Raman spectroscopy was performed on a WITEC Focus Innovations Alpha-300 Raman confocal microscope at a laser wavelength of 532 nm (green laser) and the signal that we obtained in the positive wavenumber region corresponds to the anti-stokes scattering.

2.4.6 Attenuated total reflectance- Fourier transform infrared spectroscopy and In situ FTIR

Unlike Raman spectroscopy, ATR-FTIR is also a vibrational spectroscopy but based on the absorption of light corresponding to the vibrational energy of different molecules. It is applied to the hetero-nuclear molecules that are infrared active such as O-H, NH₂, C-H and gives information about the different modes of vibration of the chemical bonds between atoms like stretching, bending and so on.⁶

FTIR spectroscopy was carried out on Thermo Scientific-NICOLET *iS20* FTIR instrument at room temperature. For the analysis, powder samples were mixed with KBr (as a reference) and then finely ground to make a pellet. Otherwise, it was also carried out on ATR spectral mode, recorded with the same instrument as well as Bruker FTIR-ATR spectrometer (VERTEX-70). Zinc selenide (ZnSe) and Au coated quartz crystals were used for the respective instruments as substrate for the ATR measurements, sensitive to pH below 5 and beyond 9.

Thermo Scientific-NICOLET *iS20* FTIR instrument in ATR mode was also used for the in-situ FTIR characterizations. Here, a Jackfish-J2 spectro-electrochemical cell set-up was assembled on a Si- FAC as shown in Figure 2.2. Hence, the electrochemical work-station (CHI-760E potentiostat) was interfaced with the FTIR instrument, where during the electrochemical reactions, the FTIR scans were recorded in absorbance mode for 128 scans and resolution 4 (for each scan).



Figure 2.2. In-situ FTIR cell set-up assembling the Jackfish J-2 spectro-electrochemical cell with the FTIR instrument and interfacing with the electrochemical work-station.

2.4.7 Ultraviolet-visible-near infrared spectroscopy

UV-vis-NIR spectroscopy works in a way that when light is incident on a sample with a significant energy, it causes electronic transitions between the different vibrational and rotational energy states present in the sample. When the excited electrons revert to the ground state, they emit an energy that is arrested in the detector giving rise to the UV-vis-NIR spectrum. It works on the principle of Lambert-Beer's law following equation 2.2 as stated below:

$$\boldsymbol{A} = \boldsymbol{\varepsilon} \times \boldsymbol{l} \times \boldsymbol{c} \tag{2.2}$$

where, A is the absorbance, ε is the molar absorption coefficient, 1 is the optical pathlength and c is the concentration of the attenuating species. This spectrum can be acquired in absorbance (A), transmittance (T) as well as % reflectance (%R) modes. These can be inter-related as shown in equations 2.3 and 2.4:

$$A = -logT \tag{2.3}$$

$$A = \log\left(\frac{1}{R}\right) \tag{2.4}$$

This technique not only gives information about the different σ , π and soret bands for the electronic transitions within the chromophore units but also determines the band gap of the materials obtained from diffused-reflectance UV-visible spectroscopy.

UV-vis-NIR characterizations were performed in UV-vis-NIR (Cary 5000 UVvis-NIR, Model: G9825A CARY) spectrophotometer that can measure 300-2800 nm by a Pb Smart NIR detector.

2.4.8 X-Ray photoelectron spectroscopy and Ultraviolet photoelectron spectroscopy

XPS is a surface-sensitive technique which gives information about the chemical bonds, oxidation states and valence energy levels of the material. This instrument works under an ultra-high vacuum condition, it is highly surface sensitive and works on the principle of photoelectric effect for both electrically conducting as well as non-conducting material surfaces. When a monochromatic X-ray (Al K α or Mg K α) is irradiated over the sample surface, owing to the high penetration depth of the X-ray photon, it hits the core level electrons present in the material, transfers its energy to the electron, which then ejects from its initial ground state with certain kinetic energy associated with it.^{7,8} The photoemitted core electron is analyzed as a function of binding energy that give the detailed information about its chemical environment and states within the sample. While XPS works up to 10 nm thickness of the sample surface, UPS is even more surface sensitive and could analyze only up to 2-3 nm. Beyond 10 nm, XPS complemented with sputtered profiling is required to obtain information about the sub-surfaces of the sample. From UPS, the work function, Fermi level and valence edge of the sample can be deduced and thus it gives more information about the electronic properties of the sample.

XPS spectroscopy was executed on a K-Alpha plus XPS system of ThermoFisher Scientific instruments in an ultrahigh vacuum chamber $(7X10^{-9} \text{ torr})$ using Al-K radiation (1486.6 eV). The same instrument with He-I and He-II sources are used for UPS studies with the respective photon energies 21.22 eV and 40.8 eV.

2.4.9 X-ray absorption spectroscopy

XAS works with the help of photon energy where like XPS, the core level electrons of the material are excited with an energy 0.1-100 keV using a crystalline monochromator Based on the nature of the core electron, the edges are named such that excitation of 1s electron occurs at K-edge, while 2s or 2p occurs at L-edge. The XAS spectra consist of two parts:⁹

(a) The pre-edge and rising edge constituting the XANES dominated by the core electron transition to the quasi-bound states of the photoelectrons with a relatively lower kinetic energy. This region gives information about the oxidation state and a rough idea about the coordination environment (tetrahedral/octahedral) of the central metal atom.

(b) EXAFS includes the high kinetic energy region of the photoelectrons. Along with the central atom, the scattering of photoelectrons from the neighboring atoms appears as a single scattering event. Thus, EXAFS gives more reliable information about the exact coordination number of the neighbouring atoms present in the first shell and second shell.

The EXAFS were carried out with the dispersive EXAFS beam line (BL-9) at Indus-2 synchrotron radiation source at the RRCAT, Indore, India. The beam source was operated at 2.5 GeV (300 mA). In this beamline a bent crystal Si (111) polychromator is used to select a band of energy, the data was collected in transmission mode for reference samples and in fluorescence excitation mode for the synthesized catalyst. All the spectra were measured under ambient conditions. Data analysis was carried out using DEMETER programs. Athena and Artemis software was utilised to extract the measured data and fit the profiles. All the information about the local atomic environments around the central absorbing atom of the metal, coordination numbers (N), the nearest neighbour distances (σ) as of the absorbing and scattering atoms were obtained from the Fourier transform $|\chi(R)|$ of the EXAFS oscillation curves.

2.4.10 Kelvin probe force microscopy

KPFM is a non-contact variant of atomic force microscopy (AFM) that measures the surface potential of the sample. The surface potential is associated with the localized surface charges and the work function of the material. The contact potential difference is determined due to the electrostatic interaction between the conducting AFM tip and the sample surface at the nanoscale level.

The KPFM measurements are performed using a conducting tip (Model: SCM-PIT) to probe the position of the Fermi level and surface potential of our catalyst.

2.4.11 Electron spin resonance

ESR can detect the presence of unpaired electrons in a system such as free radicals or odd-electron molecules trapped in a sample. Basically, these unpaired electrons are considered to behave like tiny magnets having a spin moment around their axes. So, when these are exposed to a strong magnetic field, the electrons absorb the microwave radiation and produce the ESR signals. This is usually a room temperature technique but

can also be accomplished at low temperatures and it can greatly help to detect the trapped charges in vacancy engineered samples.

The electron spin resonance (ESR) spectra were recorded at low temperature (77 K) using an X-band spectrometer (Bruker EMX series spectrometer; EMM 1843) with modulation frequency of 100 kHz and 1 G amplitude using DPPH as the reference. The g-value is calculated using the equation 2.5:

$$h\nu = gbH \tag{2.5}$$

where h is the Planck's constant, v is the frequency in GHz, g is the g-factor, b is the Bohr magneton and H is the magnetic field in mT.

2.4.12 Positron annihilation lifetime study

The PALS provides information about the free charge carriers in a system susceptible to recombination or annihilation. The lifetime of this annihilation determines the density and nature of vacancies generated in the material.

PALS was acquired on a powder sample with sample covering the Na-22 radioactive source. The positron lifetime spectrometer is constructed from two identical BaF₂ scintillation detectors with fast timing electronics and the overall time resolution of the spectrometer was 250 ps. The spectrum was analyzed using *PALSFit*software¹⁰ to extract positron lifetimes.

2.4.13 Surface profilometry

The surface profilometer usually measures the surface roughness of a sample. A microscopic tip is moved along the x-axis and the vertical movement of the tip over the surface gives information about the curvature or flatness. Generally, this technique is used for the determination of the thickness of multi-layered heterostructure samples.

The surface profilometry was carried out on a Bruker Dektak XT stylus profiler instrument.

2.4.14 Inductively coupled plasma-mass spectroscopy

ICP-MS is an analytical technique that determines the isotopic concentration of multiple elements present in a sample in ppb level. The sample is ionized with an inductively coupled plasma, which then then atomized to create atomic and small polyatomic ions that are thus detected.

The Agilent 7900 ICP-MS instrument had been used to carry out the ICP-MS analysis.

2.4.15 Gas chromatography

GC gives an idea about the number of gaseous elements present in a mixture with a different retention time corresponding to gases. The height intensity of the peaks reveals the concentration of each of the elements present in the mixture. It is generally equipped with thermal conductivity detector (TCD) for detecting the inorganic gases (N_2 , H_2) and components and the flame ionization detector (FID) for the organic gases respectively.

Gas chromatography experiment was performed with the help of PerkinElmer, Arnel Engineered Solutions and, Clarus 680 GC.

2.4.16 Ion chromatography

Ion chromatography is a separation method for different ions and polar molecules depending on their affinity for the ion exchangers. The effluent is made to pass through a pressurized chromatographic column where the respective ions are absorbed by the suitable ion exchange resin used for the process.

Ion chromatography (IC) was performed for the detection of NO₃⁻ with Eco IC Metrohm, where the anionic column consisted of Metrosep A Supp 17 – 250/4.0 and the eluent consisted of 5 mmol/L Na₂CO₃ and 0.2 mmol/L Na₂HCO₃ with a flow rate of 0.6 mL/min. Another project included in the thesis used this technique for the determination of NH₄⁺. The accessories used were: 930 Compact IC Flex Oven/ChS/PP, IC Conductivity Detector and 858 Professional Sample Processor; Metrosep C 6 – 250/4.0 column is used with nitric acid and 18-crown-6-ether as eluent. The sample solution was filtered through 0.22 μ syringe filter and then injected into the ion chromatograph. Samples were injected using the 858 Professional sample processor with PP for analyses and automatic integration with MagIC Net 3.3 software using peak area for all analytes.

2.4.17 Electrical conductivity measurements

This instrument is used for the measurement of the electrical conductivity of the material *via* two-probe and the four-probe techniques. In the two-probe method, the two connections correspond to the input and output sources, whereas the four-probe method involves two connections for input voltage source and two connections for the output current source.

A Keithley Source meter 2400 is used as a power supply source to analyze the electrical conduction in the material.

2.4.18 Nuclear magnetic resonance

NMR is a widely used tool for the structure determination of organic molecules. The basic principle of NMR involves three steps: 1.) The aligned polarization of the nuclear spin under the application of magnetic field B_0 , 2.) The perturbation of these nuclear spin polarization by a weak oscillating magnetic field (known as radio-frequency pulse), 3.) The emitted electromagnetic waves detection and analysis in terms of chemical shift values in ppm. The position of NMR peak, shifting from the ideal peak position, the nature of the peak splitting and the coupling constant value give the detailed information about the functional groups and inter/intramolecular interactions present in a compound.

The ¹H, ¹¹B and ¹⁹F NMR spectra used in the thesis projects were taken from 400MHz Bruker Advance II400 NMR spectrometer.

2.4.19 Electrochemical measurements

All the electrochemical measurements done in the thesis projects were performed in CHI 760E electrochemical workstation (CH Instruments, USA), Metrohm Autolab (M204 multichannel potentiostat galvanostat) equipped with FRA 32M module and RRDE setup, and BioLogic VSP and SP 50e potentiostats. The techniques used involve CV, LSV, CA, EIS, Mott-Schottky analysis etc. in order to understand the electrochemical reactions and charge transfer phenomena occurring on the surface of the electrode material. The analysis is basically done using two processes, the Faradic as well as the non-Faradic process, which involves the transfer of the electron/charge through the electrode/electrolyte interface following the Faraday law. This faradaic process includes surface redox reactions (oxidation and reduction) owing to the charge transfer through the interfaces. It is to be noted that for all the nitrogen reduction reaction experiments, 10 mL min⁻¹ gas flow rate was maintained in 40 mL of electrolyte (chapter 3 to chapter 5) and 20 mL of electrolyte (chapter 6 to chapter 8) in each compartment of the H-cell.

2.4.19.1 Three-electrode cell configuration. The electrochemical studies were done in a standard three/two-electrode system electrochemical cell. The as prepared electrode material worked as working electrode, Ag/AgCl (3.0 M KCl) as the reference electrode and platinum (Pt) wire as the counter electrode under ambient atmospheric conditions. The reference electrode was calibrated with respect to the RHE and their potentials can be related by equation 2.6:

 $E_{RHE} = E_{Ag/AgCl} + 0.0591 \times pH + 0.210 (E^{\circ} at Ag/AgCl, 3 M KCl)$ (2.6)

2.4.19.2 Two-electrode cell configuration. In order to investigate the full-cell reactions (cathodic as well as anodic) and the associated electrochemical overpotential for the

processes, a two-electrode configuration was adopted. Here, activated carbon cloth modified with catalyst served as the cathode in one compartment of the H-shaped electrolyzer used for the purpose. On the other hand, Ni foam modified with the anode catalyst was taken as the counter electrode in another compartment of the H-cell. Here, the full cell potential was determined with respect to the counter electrode only. Both the cell compartments were separated by the Nafion-115 membrane in order to separately undertake the cathodic and anodic reactions, with a proton flux/permeability across the membrane.

2.4.19.3 Type of working electrodes used and their cleaning procedures. Ideally, a GCE is used for some of the studies that are cleaned with 1, 0.3, and 0.05 μ m alumina (Al₂O₃) powder followed by CV cycling in 0.5 M H₂SO₄. In another project, glass, and FTO-coated glass substrates (1×1 cm²) were cleaned successively with IPA, water and acetone and hot air dried to make it clean from any kind of aerial impurity. In other projects activated carbon cloth and graphite strips (1×1 cm²) were taken, where the carbon cloth was cleaned with acid and then heat-treated to activate it and graphite strips were cleaned via ultrasonication in DI water followed by IPA.

2.4.19.4 Cyclic and linear sweep voltammetry. The forward and backward sweeping of potential with respect to current within a fixed potential window, recorded at different scan rates is termed as CV, which includes both the redox reactions during the forward and backward sweeping. The half reaction in any of the directions is referred to as the LSV.

2.4.19.5 Chronoamperometry. The potential-dependent current scan over a definite time span is termed as CA. The fixed potential values for the CA studies were variant for the different projects based on the performance of the respective catalysts.

2.4.19.6 Impedance measurements. EIS measurements for three-electrode system was conducted at a particular potential in a frequency range of 10^5-10^{-2} Hz. It offers kinetic information about an electrochemical system and identifies the different resistance factors like solution resistance and, charge-transfer resistance at the electrode/electrolyte interface.

2.4.19.7 Mott-Schottky. Mott-Schottky measurements give information about the flatband potential of a material. When an electrode is dipped into the electrolyte solution, at the interface, the Fermi levels of the catalyst and the electrolyte tend to equilibrate that associate a band-bending of the electronic levels of the material. So, at an applied potential range, this band reverts to its original electronic state, giving information about the Fermi-level or the flat band potential of the material. This plays a vital role in the determination of the electronic property of the material and its behavior towards an electrochemical reaction. The obtained spectra display a negative or a positive slope that talks about the conducting nature of the sample.

2.5 Calculations and formulae for evaluating material properties

The experimental techniques discussed above can be implemented to explore the physical, chemical, electronic as well as electrochemical properties of the different samples prepared for the projects included in the thesis. These are listed as follows:

2.5.1 Electrochemically active surface area

The electrochemical C_{dl} of an electroactive material is measured to access their ECSA obtained by CV scans. The CV scans at different scan rates were taken in the non-Faradaic region in the working electrolyte condition. At a constant potential, the difference in the anodic and cathodic current densities were linearly correlated with the applied scan rates and the slope of the fitting curves revealed the C_{dl} of the active materials. The double-layer charging current " i_c " is equal to the product of the scan rate "v" and the electrochemical double-layer capacitance, " C_{dl} " as given by equation 2.7:

$$i_c = v C_{dl} \tag{2.7}$$

The difference in the fitted slopes of charging and discharging CV scans was used to determine the C_{dl} ,¹¹ ECSA is then calculated by dividing the C_{dl} by the specific surface capacitance (C_{sp}) of electrode surface as depicted in equation 2.8:

$$A_{ECSA} = \frac{c_{dl}}{c_{sn}} \times (geometric \, area) \, cm^2$$
(2.8)

2.5.2 Crystallite size (*L*_c) from XRD

The crystallite size L_c (in nm) with respect to the grain boundaries of the material can be evaluated by means of XRD following the Debye–Scherrer equation (2.9).¹²

$$L_{c=}\frac{0.89 \times \lambda}{D \times \cos \theta} \tag{2.9}$$

where λ is the wavelength of the X-ray of Cu K α used in this study (1.54 Å), and *D* is the full width at half-maxima of the peak obtained for the corresponding planes of the catalysts.

2.5.3 Estimation of band gap from UV-visible spectroscopy

The E_g between the band edge minimum of the conduction band and the band edge maximum of the valence band was estimated by fitting the absorption coefficient (α) and photon energy (E_{ph}) in the Tauc's relation given by equations 2.10 and 2.11:¹³

$$\mathbf{E}_{\mathbf{ph}} = \mathbf{h}\mathbf{v} = \frac{\mathbf{h}\mathbf{C}}{\lambda} \left[\mathbf{where}, \mathbf{v} = \frac{\mathbf{C}}{\lambda}\right] = \frac{1240 \text{ eV}}{\lambda}$$
(2.10)

$$\alpha h \upsilon = \mathbf{A} (h \upsilon - \mathbf{E}_{g})^{n}$$
(2.11)

where, hv is the photon energy of the incident photon in eV, h is the plank's constant, C is the speed of light, λ is the wavelength of the incident light, A is a constant and n depends on the transition probability (n = $\frac{1}{2}$ or 2 for the indirect and direct band transition).

 $(\alpha hv)^2$ or $(\alpha hv)^{1/2}$ were plotted against hv and the straight-line interception to the curve on x-axis gives the value of the optical band gap (Eg).

2.5.4 Flat-band potential from Mott-Schottky analysis

The V_{fb} of our catalysts was investigated from Mott-Schottky analysis. The measurements were carried out at the frequency ranging from 0.01 Hz to 100 kHz and the voltage window was maintained from -1.0 to 0.0 V *vs.* Ag/AgCl.

The V_{fb} was calculated from the Mott-Schottky¹⁴ equation 2.12 given by-¹⁵

$$C^{-2} = \frac{2}{e_0 \varepsilon_0 \varepsilon_0 N_d} \left(V - V_{fb} - \frac{kT}{e_0} \right)$$
(2.12)

where C is the capacitance of the space charge layer at the electrode surface (in F), e_0 is the electronic charge, ε_0 is the vacuum permittivity, ε_r is the dielectric constant, N_d is the number of donor sites, V is the applied electrode potential, k is the Boltzmann constant, and T is the absolute temperature. A positive slope in the plot between C⁻² vs. V (vs. RHE) indicates an *n*-type semiconducting behaviour of the material. An extrapolation of the x-intercept in the Mott-Schottky plot provided the V_{fb} of the respective material.

2.5.5 Work function from UPS analysis

UPS can be exploited to calculate the work-function of a material using equation 2.13. The work function value gives the exact position of the Fermi level from the vacuum level. Now, having known the band gap of the material, the Fermi edge gives information about the valence band maximum from which the conduction band minimum can be derived. Hence, the entire electronic band structure of the material can be determined.

$\phi = h\vartheta - (Secondary \, cut \, off \, energy - E_F) \tag{2.13}$

where, hv represents the photon energy of He-I (21.22 eV) and E_F is the Fermi edge energy.

2.5.6 Surface potential from Kelvin Probe Force Microscopy

The KPFM measurements were carried out using a conducting tip in tapping mode in order to probe the work function and, hence, the position of the Fermi level of the investigating material. The work function (Φ in eV) is determined from the V_{CPD} in mV between the tip and the investigated sample using the following equation 2.14:¹⁶

$$V_{CPD}(mV) = \frac{[\varphi_{sample}(eV) - \varphi_{tip}(eV)]}{e}$$
(2.14)

where e is the electronic charge having a value of 1.623×10^{19} C.

2.5.7 I-V measurements using Sourcemeter

The conductivity of the catalysts was estimated by means of I-V measurements with the help of a two-probe technique, where the separation between the two probes (s) was maintained as 0.1 cm for all the cases. The following equations 2.15 and 2.16 were considered to obtain the resistivity (ρ in Ω -cm) and hence the conductivity (σ in S-cm⁻¹) of all the materials under study.

$$\rho = \frac{V \times a \times h}{I \times s} \tag{2.15}$$

$$\boldsymbol{\sigma} = \frac{1}{\rho} \tag{2.16}$$

where V is the potential difference measured between the two voltage probes, I is the uniform current being passed through the sample, a is the sample width and h is the sample height or thickness, obtained from the surface profilometer measurements.

2.5.8 d-band center from valence photoelectron spectroscopy

The position of the d-band center (E_d) is calculated from the VBS measured by XPS. All the VB spectra were normalized in the same region (-0.49–10 eV) Because the energy of the excited electron is low in the binding energy range of the VBS, it can correspond to the outermost electron of the sample element. The Shirley background is subtracted from the measured spectra, with the background energy to be 0.5 eV. The position of the center of the valence band (d-band center) is given by following equation 2.17: ^{17,18}

$$E_d = \int \frac{N(\varepsilon)\varepsilon d\varepsilon}{N(\varepsilon)d\varepsilon}$$
(2.17)

where ε is the binding energy (eV) N(ε) is the DOS or, in our case, the XPS-intensity after background subtraction.

2.6 Activity descriptors for electrochemical nitrogen reduction reaction performance of materials

The electrochemical NRR produces ammonia that can be quantitatively determined by several evaluation determining parameters. Generally, (i) the more accessible N_2 molecules around the catalyst and a kinetically faster NRR process having low-intense energy steps ensure a better yield and production rate for NH₃ synthesis and (ii) the better tendency of N_2 adsorption on the catalyst surface surpassing its affinity for proton adsorption produces more current for NRR and accelerates the FE by suppressing the competitive HER. The overall enhanced reaction kinetics and rate help to diminish the overpotential for the NRR process and make it more thermodynamically feasible with an improved electrical to chemical energy conversion efficiency. All these parameters can be derived using the following equations.

2.6.1 Yield-rate of NH₃

The NH₃ yield rate (R_{NH3}), normalized to mass, given by $\mu g h^{-1} mg_{cat}^{-1}$ can be calculated using equation 2.18, where C is the measured NH₃ concentration ($\mu g mL^{-1}$), V is the volume of the catholyte (mL), t is the electrolysis time (h), and mg_{cat} is the mass of the catalyst loaded on the electrode surface.

$$R = \frac{C \times V}{t \times mg_{cat}}$$
(2.18)

2.6.2 Faradaic efficiency

The FE is calculated using equation 2.19, where 3 is the number of electrons necessary to produce one mole of NH_3 molecule, F is the Faraday constant (96485 C mol⁻¹), M is the relative molar mass of NH_3 (M = 17 g mol⁻¹), and the Q is the total charge passed through the electrodes (C).

$$FE = \left(\frac{3 \times F \times C \times V}{M \times Q}\right) \times 100\%$$
(2.19)

2.6.3 Production rate of NH₃

The surface-area-normalized production rate of NH₃ (mol s⁻¹ cm⁻²) was calculated as below:

$$Production \ rate_{area} = \frac{C \times V}{M \times t \times A}$$
(2.20)

The mass-normalized production rate of NH_3 (mmol h⁻¹ g_{cat}⁻¹) was calculated as below:

$$Production \ rate_{mass} = \frac{C \times V}{M \times t \times g_{cat}^{-1}}$$
(2.21)

2.6.4 Tafel plot and exchange current density (j_0)

The kinetic experiment was accomplished with RRDE set-up in Metrohm Autolab in a conventional three-electrode system. This working electrode contains a glassy carbon disc and a Pt ring. The Tafel plot that gives information about the NRR overpotential is extracted from the linear sweep voltammetry curve obtained at a given rpm at 2 mV s⁻¹. Hence, the exchange current density was derived from the intercept of the equation 2.22.

$$E = \frac{-2.3RT}{\alpha F} \left[logj - logj_0 \right]$$
(2.22)

where, E is the potential expressed in V vs RHE, R is the universal gas constant, T is the experimental temperature (K), α is the transfer coefficient, F is the Faraday constant, *j* is the experimental current density and *j*₀ is the exchange current density. Current densities are expressed in mA cm⁻².

2.6.5 Diffusion current density (j_D)

The diffusion current density was calculated from the difference of residual and limiting current densities (at the onset and the plateau regions respectively) from the LSV plots taken with RRDE at 2 mV s⁻¹.

2.6.6 Thermodynamic equilibrium potential

The standard potential for the NRR in acidic or neutral medium at 298.15 K is considered as^{19,20}:

$$2 NH_4^+ = N_2 + 8 H^+ + 6 e^-; E^0 = 0.275 V$$
(2.23)

The thermodynamic equilibrium potential for NRR under the reaction condition was calculated according to the Nernst equation, assuming 1 atm of N_2 in the solution.²¹

$$E = E^{0} + \frac{RT}{nF} \ln \frac{p_{N_{2}}[H^{+}]^{8}}{[NH_{4}^{+}]^{2}}$$
(2.24)

where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T is the temperature in Kelvin (298.15 K), n is the number of transferred electrons (6), F is the Faraday constant (96,485 C mol⁻¹), [H⁺] is the proton concentration and taking the pH of the working electrolyte. Assuming [NH₄⁺] to be 10^{-7} M in the solution, the corresponding thermodynamic equilibrium potential is determined using equation 2.24.

2.6.7 Full cell potential and reaction overpotential

NRR is a cathodic reaction and is conventionally accompanied with the counter oxidation reaction that is the oxygen evolution reaction (OER) as shown in equation 2.25:

$$\frac{1}{2}N_2 + \frac{3}{2}H_2O \to NH_3 + \frac{3}{4}O_2$$
(2.25)

The overall thermodynamic full cell potential at the experimental reaction conditions is calculated using the following equation 2.26:

$$\boldsymbol{E_{cell}} = \boldsymbol{E_{ox}} - \boldsymbol{E_{red}} \tag{2.26}$$

Considering the thermodynamic potential for the water oxidation reaction to be 1.23 V, the E_{cell} for the full cell reaction can be calculated using equation 2.23 and 2.25.

Based on this value, the overpotential for the full cell reaction at different experimental conditions were calculated from equation 2.27:

$$\boldsymbol{E}_{overpotential} = \boldsymbol{E}_{cell,expt} - \boldsymbol{E}_{cell} \tag{2.27}$$

2.6.8 Thermodynamic Gibbs' energy change

The thermodynamic Gibbs' energy change (ΔG_{Th}) for the full cell reaction involving NRR and OER can be calculated using equation 2.28, expressed in kJ mol⁻¹ and the equilibrium constant (k), representing the rate of forward reaction is calculated using equation 2.29.²²:

$$\Delta G_{Th} = -nFE_{cell} \tag{2.28}$$

$$\Delta G_{Th} = -RTlnk \tag{2.29}$$

2.6.9 Energy efficiency of electrolyzer

The ammonia production energy efficiency (η_{EE}) of the system was calculated according to the following equation 2.30²³:

$$\eta_{EE}(\%) = \frac{\Delta G \text{ for ammonia production } (J \text{ mol}^{-1}) \times ammonia \text{ produced } (mol)}{\int IV dt(J)}$$
(2.30)

where, ΔG is the free energy for NH₃ generation, V(V) is the full cell potential for a two-electrode system and $\int IVdt (J)$ is the electricity consumed in the process (energy input).

2.6.10 ¹H-NMR studies

NMR measurements were carried out for the quantitative detection of the produced ammonia with DMSO-d⁶ as solvent and maleic acid as internal standard sample. Prior to NMR sample preparation, the electrolyte solution was concentrated to 1 mL and a quantitative amount of the sample was added to DMSO-d⁶ and subjected to 6000 scans for getting a proper triplet signal (with coupling constant j=52 Hz) for ¹⁴NH₄⁺ and doublet for ¹⁵NH₄⁺ (coupling constant j=72 Hz). It is to be noted that, the coupling constant values are calculated as a product of the chemical shift value (δ in ppm) and 400 MHz (spectrometer frequency) using equation 2.31.

$$\delta(ppm) = \frac{j(Hz)}{spectrometer\,frequency\,(MHz)}$$
(2.31)

The catholyte solution was concentrated to 1 mL and 400 μ L was taken out of it for NMR analysis. This was subsequently added with 50 μ L of 0.01 M maleic acid solution followed by DMSO-d⁶ and subjected to ¹H-NMR study. The obtained peaks were integrated and by using the following equation 2.32, the concentration of NH₃ was quantified and matched with that obtained from UV–visible spectroscopic method.

$$\frac{I_{sample}}{I_{standard}} = \frac{H_{sample} \times C_{sample}}{H_{standard} \times C_{standard}}$$
(2.32)

where *I* stands for the integral values, H stands for the number of protons (4 in case of sample NH_4^+ and 2 in case of the vinylic protons of maleic acid) and *C* stands for the concentrations of the sample and standard (0.01 M for maleic acid).

Part - B

2.7 Introduction

The electrochemical NRR has emerged in the recent past, and much progress is evidenced in this field, pivoting versatile catalyst development, electrolyte modifications, and kinetics study with non-conventional approaches in order to achieve the industrial targets of ammonia production.^{24–27} However, the synthesis of ammonia with a high production rate and Faradaic efficiency makes sense when it is properly and accurately quantified, negating the possibilities of false results from other nitrogenous contaminants as well as side-product formation. Usually, the primary detection and quantification of ammonia is done using the UV-visible spectroscopic technique derived from a century-old Berthelot reaction of formation of indophenol dye or (i.e., produced by salicylate method).²⁸ This is further validated with alternative NMR) or IC techniques, where to-date NMR is considered to be the most reliable.²⁹ However, the use of expensive apparatus and standard reagents limit the extensive use of NMR as a preliminary detection technique. Thus, in order to have a valid guidance at the first hand, the UV-visible spectroscopic methods like the Nessler's reagent method, salicylate method, and indophenol method are widely followed and need proper optimization with a full-fledged knowledge of all the prospects and consequences of the methods.³⁰ A background study suggests that till 2019, most of the research works were concerned with the versatile catalyst development and identification of the false positive responses giving erroneous results for the ammonia production. Several protocols were set up providing a proper guidance toward obtaining a reliable data, and the necessity of the isotope labelling experiment ($^{15}N_2$) was realized.³¹ In the mid of 2020, few review reports came up emphasizing the importance of detection techniques but not in much details³² and till that most of the researchers were not aware of the proper protocols to be followed for ammonia detection. Gradually, research interests started to incline and focus on the detection methods and the fallacies related to the techniques came to the fore suggesting a need for the proper roadmap toward spectroscopic ammonia detection.

2.8 Colorimetric detection methods used and optimization of electrochemically produced NH₃

In order to have a valid guidance about the production of NH_3 during NRR of our synthesized catalyst, at the first place, the UV-visible spectroscopic methods like the Nessler's reagent method, salicylate method, and indophenol method are widely followed. The Nessler's method has been avoided in this thesis work as it included toxic chemicals. Besides the detection of NH_3 , it is also mandatory to check the side product formation (N_2H_4) and if there is any nitrogenous contaminants (NO_x) present in the feed gas or electrolyte that can falsify the experimental results. The following colorimetric detection methods, described in details are widely used in this thesis work.

2.8.1 Watt and Chrisp method for side-product (N₂H₄) detection

The production of hydrazine is spectrophotometrically determined using Watt and Chrisp method.³³ A mixture of para-(dimethylamino) benzaldehyde (5.99 g), HCl (concentrated, 30 mL), and ethanol (300 mL) is used as the color reagent. 2 mL of the electrolyte solution was added with 2 mL of the above color reagent and kept in incubation for 15 min at room temperature. The amount of hydrazine formed during the electrolysis is determined based on the absorbance intensity at 450 nm. The concentration of the produced hydrazine was then estimated from the concentration-absorbance calibration curve obtained with standard hydrazine solutions, and estimated using the linear regression plot.

2.8.2 Griess' method for determination of NO_x contamination in feeding gas and the working electrolyte

 NO_x contamination was determined using the N-(-1-naphthyl)- ethylenediamine dihydrochloride spectrophotometric method.³⁴ The chromogenic agent was obtained by dissolving sulfanilic acid (0.5 g) in deionized water (90 ml) and acetic acid (5 ml), followed by adding N-(1-naphthyl)-ethylenediamine dihydrochloride (5 mg) and bringing the solution to 100 ml. The prepared solution was covered and protected from light. The chromogenic agent (4 mL) was mixed with 1 mL of the investigating solutions. After an incubation period of 15 min, the absorption spectrum was measured using an ultraviolet-visible spectrophotometer at ~ 540 nm.

2.8.3 Salicylate method for NH₃ detection

This method was adopted to estimate the concentration of ammonia in the Na₂SO₄ electrolyte after electrolysis followed by incubation for 2 h. The coloring agents were prepared as follows- solution A: 1 M NaOH solution containing 5 wt% of each salicylic acid and sodium citrate; solution B: 0.05 M NaClO; solution C: 1 wt% C₅FeN₆Na₂O (sodium nitroferricyanide) aqueous solution. The concentration-absorbance curves were calibrated using a series of standard ammonia solutions. First, 2 mL of the aliquot solution was taken from the cathode chamber, followed by the sequential addition of 2 mL of solution A, 1 mL solution B and 0.2 mL solution C. After keeping for 2 h at room temperature, the UV-vis absorption spectrum was measured at 655 nm and the concentration of NH₃ was estimated from the calibration equation obtained from the known concentrations of NH₄⁺ plotted with respect to the corresponding absorbance values.

However, both the salicylate method and Indophenol blue method follow the century-old Berthelot reaction. If one looks closely into each step of the Berthelot reaction (Figure 2.2), it would be perceived how each step drives the next one and demand proper conditions of incubation time and medium pH.²⁸ Simultaneously, volume correction of the investigating solution is another important factor, which influences the absorbance and concentration of ammonia obtained by the UV–visible spectroscopic method. Although in one of the reports, the salicylate method is considered more reliable among the other UV–visible spectroscopic methods,³⁵ we believe that upon maintaining the proper pH and all other conditions both salicylate and indophenol methods could be effectively used and are equal contenders in the UV–visible spectroscopic quantification of ammonia. In fact, it has been observed that, the salicylate method is sensitive to foreign metal ions and can often give

erroneous results and falsify the ammonia quantification.³⁶ So, keeping reference of the Berthelot reaction, we focussed on optimizing the Indophenol blue method of ammonia detection and quantification shedding light on the protocols to be followed to achieve the maximum absorbance corresponding to the ammonia production. More emphatically, we aimed to provide an insightful guideline on the indophenol method regarding the pH of the medium while preparing the coloring solutions, order of mixing of reagents, importance of volume correction, stability of the dye, condition of incubation and interference from foreign elements to attain the above-mentioned goal.

2.8.4 Indophenol-blue method for NH₃ detection

At the very first stage of the reaction, ammonia molecules react with sodium hypochlorite (NaClO) and form monochloramine. Further, the monochloramine reacts with phenol (PhOH) and form benzoquinol chloramine or its resonating form benzoquinone chlorimine, which show coupling reaction with another phenol molecule and form the Indophenol dye. Therefore, elaborately, the basic mechanistic steps and role of each component used in this method can be summarized as follows: (i) sodium hypochlorite (NaClO): it acts as oxidizing agent and forms the



Figure 2.3. Schematic representation of the mechanistic steps of the Berthelot reaction followed in the Indophenol blue method of ammonia detection.

monochloramine upon reacting with the NH₃ present in the analyte; (ii) phenol: it reacts with the monochloramine and forms benzoquinone chlorimine; (iii) sodium hydroxide: this is used to achieve the desirable pH; (iv) trisodium citrate: it is used to chelate the undesired metal ions which can cause interference in the detection method;^{37,38} and (v) sodium nitroferricyanide (II) dehydrate: this is a coupling reagent that increases the kinetics of step (ii) of Figure 2.3.³⁹

2.8.4.1 Optimization of pH for the formation and stability of Indophenol dye. While the order of mixing of reagents, incubation time, volume correction and temperature are elaborated in Figure 2.4a-d, it was observed that pH had a very significant role in the dye formation and its stability. The very first step of monochloramine (NH₂Cl) formation depends on the NH₃ present in the medium and NaClO, behaving as an oxidizing agent. Precisely, it should be taken care of that all NH₄⁺ in the electrolyte should be converted to NH₃ and thus, before NaClO is added, the pH of the solution should be \geq 9.25. This is because NH₄⁺ has a pKa value of 9.25,



A. Phenol + NaOH (till pH=9.25) + NaClO + nitroferricyanide **B.** Phenol + nitroferricyanide + NaOH (till pH=9.25) + NaClO

C. Phenol + NaOH (till pH=9.25) + nitroferricyanide + NaClO

Figure 2.4. Initial optimizations of the Indophenol method of ammonia detection in a table form based on (a) sequence of mixing of coloring agents, (b) incubation time for the appearance of maximum color corresponding to the indophenol dye, (c) dilution effect upon addition of excess volume of coloring agents, and (d) different environmental temperature conditions. It is to be noted that 0.5 μ g mL⁻¹ NH₄Cl in water was considered as the investigating aliquot, and the incubation was carried out in dark as widely followed in literature.

and it could be expected that beyond this pH, all the NH_4^+ in the medium would be converted to NH_3 to react with NaClO forming NH_2Cl instantaneously, which has a pH stability in the range of 7.5–11.5. The second most crucial role of pH is realized with the phenol. It is to be noted that the pKa value of Ph-OH is 9.98 beyond which it exists as the phenate ion (Ph-O⁻). The formation of Ph-O⁻ hinders the coupling reaction with the so formed NH₂Cl, and therefore, the second cross-coupling step leading to the formation of indophenol dye also gets hampered even though the medium contains the catalyst $[Fe(CN)_5(NO)]^{2-}$. Thus, it is better to add NaClO after pH = 9.25 is reached, and then, the pH should be gradually raised for appearance of the maximum color. In order to verify our claims, 0.1 M HCl was taken with 0.5 µg mL⁻¹ NH₄Cl and different pH were maintained from pH = 4 to pH = 12. A varied UV–visible spectra was observed over the range of different pHs, as shown in Figure 2.5a. At an acidic pH (as explained in Figure 2.5b), there was no signature peak corresponding to the indophenol blue complex at 630 nm because at a lower pH, NH₃ would exist as NH₄⁺ leading to an unsuccessful monochloramine formation (as shown



Figure 2.5. (a) UV-visible spectra obtained at different final pH of the colored solution incubated in dark for 2 h prior to analysis. 0.1 M HCl mixed with 0.5 µg mL⁻¹ NH₄Cl in water was taken into consideration for the tests; inset shows broadly the apparent change in the peak position (redshift) and intensity with varying pHs of the medium; (b) schematic representation of the drawbacks in acidic pH condition inhibiting the dye formation; inset shows the unusual color of the solution; (c) reaction mechanisms of each step of the indophenol method in the pH range from 8 to 11 forming the indophenol complex successfully as can be seen from the blue color of the solution in the inset; (d) prospects and consequences of a higher medium pH on the color and intensity of the dye; inset shows the apparent color change from blue to greenish at a much basic condition (pH = 12).

in the images of the vials in the inset of Figure 2.5b). However, two broad humps appeared in the UV-visible spectra, out of which the one at 390 nm represented the $[Fe(CN)_5(NO)]^{2-}$ and the one between 400 and 500 nm resembled the free indophenol in the aqueous medium that could have formed very insignificantly. From the reactions steps in Figure 2.5c, it can be ascertained that the peak for the dye at 630 nm corresponding to the indophenolate ion gradually started appearing as the solution overcame the neutral pH condition, where some of the converted NH₃ present in the medium resulted into the dye formation. With further increase in the pH value to 10, the peak at 630 nm intensified with the maximum absorbance value declaring the complete conversion of NH4⁺ to NH3 and formation of the indophenol complex (appearance of blue colored solution in the vials, shown in the inset of Figure 2.5c). When the pH was further raised to 11, the peak intensity at 630 nm retained with a little redshift (inset of Figure 2.5a). Beyond this, at pH 12, the peak intensity at 630 nm dropped as the monochloramine degraded beyond pH = 11.5. Moreover, the high pH deprotonated the phenol groups partially owing to which the efficacy of Ph-O⁻ to undergo reaction with NH₂Cl disfavored the formation of the dye to some extent, as explained schematically in Figure 2.5d. However, at $pH \ge 11$, the peak appeared to be redshifted as in the basic condition of the medium, the chromophore complex exhibited a better conjugation and enhanced intra-molecular charge mobility.⁴⁰ It is noteworthy to mention that the appearance and intensification of the peak at 390 nm at a high pH could be attributed to the fact that a higher medium basicity provokes the back conversion of $[Fe(CN)_5(H_2O)]^{2-}$ to $[Fe(CN)_5(ONO_2)]^{4-}$ at a faster rate. However, due to the lowered rate of dye formation, the blue color of the dye gets interfered with the yellow color of the unreacted nitroferricyanide and the solution appeared as greenish; inset at the bottom of Figure 2.5d. Thus, the pH range of the coloring solution could be maintained between 9.5 and 11 in order to achieve the maximum absorbance for the electrochemically produced ammonia.

2.8.4.2 Interference of alkali metal salts, Nafion solution, and transition metal ions in the formation of Indophenol dye. The alkali metal salts are widely implemented as supporting electrolytes for the electrochemical reduction of nitrogen. But interference of these salts in the detection methods adds to the uncertainties in the quantification of ammonia. Here we intended to investigate the effect of alkali metal ions (Li⁺, Na⁺, and K⁺) and the anion counterparts like (OH⁻, Cl⁻, ClO₄⁻, SO₄²⁻, and

 PO_4^{3-}) on the indophenol method of ammonia detection. For checking the role of cations, we had stuck to Cl^- as the anion and for the effect of anions, H^+ was considered as the constant cation and all the concentrations were maintained as 0.1 M as conventionally used in literature.⁴¹ It was interesting to show that the indophenol method does not encounter much interference from the alkali metal ions or the relevant anions and the difference in the absorbance value for the indophenol dye was within the error limit of the detection method, as shown in Figures 2.6a,b. Additionally, for the mixed cation/anion systems commonly used for the NRR studies or even for nitrate reduction to ammonia, we have explored several electrolytes conventionally used in literature like 0.1 M K₂SO₄, 0.1 M Na₂SO₄, 0.5 M LiClO₄, 0.1 M NaOH, and 0.1 M KOH. Figure 2.6c represent the bar plot for the absorbance values obtained from



Figure 2.6. Sensitivity tests of the indophenol blue method toward interferants like (a) alkali metal cations like Li^+ , Na^+ , and K^+ including H^+ with Cl^- being the constant anion and (b) electrolyte anions like OH^- , Cl^- , ClO_4^- , SO_4^{2-} , and PO_4^{3-} with H^+ as the constant cation and (c) mixed cation/anion like 0.1 M K₂SO₄, 0.1 M Na₂SO₄, 0.5 M LiClO₄, 0.1 M NaOH, and 0.1 M KOH. All solutions are prepared in water added with 0.5 µg mL⁻¹ NH₄Cl; (d) bar plot representing the % deviation of the absorbance value for the dye with increasing concentration of Nafion solution, ranging from 0.5 to 5000 ppb with respect to 5 mL electrolyte solution. All the solutions were incubated in dark for 2 h prior to spectroscopic studies. The error bars are derived from the standard deviation values from three sets of experimental data.

UV-visible spectra of the blank electrolytes and electrolytes containing 0.5 μ g mL⁻¹ NH₄Cl. In all cases, with respect to the blank electrolyte, the one containing NH₄Cl displayed an absorbance value near like that obtained with water (~0.144) suggesting

that even the mixed ions do not impose negative effects on the ammonia detection and color formation. Another very important aspect mostly overseen is the 5 wt % Nafion solution used as an additive in the catalyst ink preparation and thus to study its interfering effect in the Indophenol blue method, we have taken 0.5 to 5000 ppb of 5 wt % Nafion in 5 mL of water containing 0.5 µg mL⁻¹ NH₄Cl as interferants that are expected in ppb to ppm level only. Interestingly, as shown in Figures 2.6d, beyond 50 ppb of 5 wt % Nafion, a noticeable enhancement in the absorbance value could be evident that implies an excess of Nafion interferes in the dye formation and adds to false negative results. We next investigated the effect of other transition metals used widely for NRR on the detection of ammonia. This study is important because either sometimes some metal contamination remains in the electrolyte (although mostly we use high purity analytical grade reagents $\geq 99\%$ from reputed companies; mostly Sigma-Aldrich/Merck/TCI) or during the prolonged exposure of the catalyst into the electrolyte under potential, there crops up possibilities of metal leaching from the catalyst surface. So, we have considered a series of 14 such transition metals like Ag(I), Au(III), Bi(III), Co(II), Cr(III), Cu(II), Fe(II), Fe(III), Mn(II), Mo(VI), Ni(II), V(III), W(VI), and Zn(II). Since the interference from these metals are expected to be in parts per billion (ppb) or at the most parts per million (ppm) level, we considered $10 \,\mu\text{M}$ of each of these salts for investigation. Our observation revealed that while all other transition metals remained inert toward the detection of ammonia via indophenol method, Au(III) exceptionally showed quite a high absorbance value (Figure 2.7a and it was reproducible as many times as the experiment was performed). The unanticipated behaviour of Au(III) was further investigated in deep. It was found from the UV-visible spectrum in Figure 2.7b that in the presence of a base, Au(III) shows a slow reduction to Au(0), which is confirmed from the small hump at 530 $\text{nm}^{42,43}$ and it is already reported that Au nanoparticles in the 0 oxidation state is good enough toward reduction of nitrite and nitrate into ammonia. It was fascinating to look into the detailed reaction steps where we uncovered that Au(0) actually participated in the step where there was a reversible transition between $[Fe(CN)_5(ONO)]^{4-}$ to ([Fe- $(CN)_5(H2O)^{2-} + NO_2^{-})$. Au (0) participated in the conversion of this NO_2^{-} to NH_3 , which thereafter took part in the subsequent reaction steps to form the indophenol dye, as shown in the schematic as Figure 2.7c. As shown in Figure 2.7d, e, even in the absence on NH4⁺, the solution containing Au salt produced a deep blue color and displayed a sharp peak at 630 nm, which gradually reduced when the volume of the



Figure 2.7. (a) Interference of transition metal ions that could be possibly found as trace contaminants in water or mostly used as catalysts in NRR, 10 μ M of each of these salts was taken in water along with 0.5 μ g mL⁻¹ NH₄Cl; (b) UV-visible spectra of 10 μ M Au(III) salt in basic solution; (c) schematic representation of the interference of Au(0) in the intermediate steps of the indophenol dye formation; (d) color of the solution containing 10 μ M HauCl₄ added with the coloring agents in absence of NH₄Cl, color code represents the varying volume of sodium nitroferricyanide added to the solution like pink: 12.5 μ L, yellow: 5 μ L, blue: 0 μ L; (e) corresponding UV-visible spectra showing intense peak at 630 nm. All the solutions were incubated in dark for 2 h prior to spectroscopic studies. The error bars are derived from the standard deviation values from three sets of experimental data.

nitroferricyanide was lowered from 12.5 to 5 μ L and absolutely disappeared and the solution turned colorless in its absence.

2.8.4.3 Optimized method. 5 mL of the aliquot solution was taken and added to 2 mL of 10mg/mL phenol solution in ethanol, followed by 0.2 mL of 0.5 wt% of $C_5FeN_6Na_2O$ (sodium nitroferricyanide) in water. The resulting solution was added to NaOH solution containing trisodium citrate as a buffer, till the pH reached above 9. Finally, 0.1 mL of NaClO was added and the final pH of the solution was raised to 9.9. Then, the resultant solution mixture was incubated for 2 h before UV-vis analysis at an absorbance of 630 nm. The concentration of ammonia evolved in the reduction

process was determined by a calibration plot (concentration vs absorbance) obtained from a set of solutions containing a known concentration of NH₄Cl in the working electrolyte. To each of these solutions, the above-mentioned reagents were added and their absorbance was measured after a 2 h incubation time.

2.9 Conclusion

This chapter mainly consists of two parts where part-A provides an overview of the standard synthesis procedures used in this thesis work for the development of highly efficient electrode materials for electrochemical NRR application. The instruments used for the material characterizations are briefed along with the associated formulae considered for deriving the physical, chemical as well as electronic properties of the materials. Also, the electrochemical techniques used like cyclic voltammetry, linear sweep voltammetry, chronoamperometry etc. are introduced along with the cell configuration details. This is followed by a discussion on the NRR activity descriptors that evaluate the electrochemical performance of the materials, our ultimate purpose. Eventually, part-B of this chapter consists of all the colorimetric techniques used for the quantitative detection of NH₃, N₂H₄ and NO_x in all the studies. Detailed information about the optimization of the Indophenol blue method of NH₃ detection is provided, which is followed in all the later chapters of the thesis.

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Chapler 3

A Lewis acid-base chemistry induce high production rate of ammonia by overcoming N_2 activation issues in aqueous electrolyte **Overview**: Aqueous electrolytes although offer ambient electrochemical conditions for NRR but impede the reaction kinetics due to inferior N₂ solubility. Herein we introduce a new aqueous electrolyte (NaBF₄), which not only acts as an N₂-carrier in the medium but also works as a full-fledged "co-catalyst" along with our active material MnN₄ to deliver high yield of NH₃ (328.59 μ g h⁻¹ mg_{cat}⁻¹) at 0.0 V vs RHE. The Lewis acidity of the free BF₃ molecules alter the metal d-band center and help to polarize the N≡N bond of the adsorbed N₂ and its first protonation by a "push-pull" kind of electronic interaction. This turned out to be effective enough to lower the energy barrier of the potential determining steps of NRR. Resultantly, a high production rate of NH₃ (2.45 × 10⁻⁹ mol s⁻¹ cm⁻²) was achieved, approaching the industrial scale periphery.



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Reference: Biswas et al., PNAS, 2022, 119 (33), e2204638119.

3.1 Motivation of the chapter

While a majority of research on NRR is focused on electrocatalyst development, it is often overseen that the sufficiency of N_2 molecules is required at the electrode-electrolyte interface to initiate the NRR. This is mostly impeded due to the poor N_2 solubility in the aqueous electrolytes. So, if there is less N_2 available to the catalyst, then however efficient it is, the production rate of NH₃ would be severely hampered and HER would eventually dominate, lowering the FE for NRR as well. Serious attention to the electrolyte is the hour's call as it plays a more important role rather than just serving as a medium for the reaction. In fact, from the practical point of view, the net-zero goal and ambiance of the electrochemical process limit the excursion of electrolytes to aqueous conditions only, which made us exploring a new aqueous electrolyte, NaBF₄ for NRR.

3.2 Introduction

A very recent study by Ren et. al. has elaborated that about 90.7 % of the research works related to NRR have focused on the suitable catalyst development, while only 4.7 % have been devoted to work on the electrolytes, which is indeed a very crucial factor for NRR, but is mostly overseen and in infancy.¹ In order to do away with the competitive HER, several researchers have sought help of organic based or molten hydroxide electrolytes that would lower the proton content in the electrolyte medium. Nonetheless, most organic electrolytes become unstable in the reducing environment of the catholyte and the requirement of large amounts of organic solvents deviate from the goal of green NH₃ synthesis.^{2–4} Tsuneto et. al. tried to further increase the NH₃ formation efficiency by incorporating Li⁺ into the organic electrolyte.⁵ But that is not an universal approach as, few metals have tendency to form alloy with Li, thereby passivating it.⁶ Contrary 0.0to this, a special candidature has been given to the ionic liquids (ILs) that serve as excellent non-aqueous electrolytes.⁷⁻¹⁰ Although several works have demonstrated the importance of fluorinated ionic liquids in solvating $N_2^{11,12}$ but none of them offer a mechanistic investigation of the actual interaction role of ionic liquid. Moreover, it has been observed that ionic liquids help to elevate the FE of NRR, but have very little impact on the yield and production rate of NH₃.¹³ In fact, one of the serious limitations to the use of ionic liquids is its high cost that is not worthwhile to be used in commercial scale.

However, this does not anyway disregard the advantages of aqueous electrolytes because of their simplicity, economical-friendliness and providing proton exposure and transfer efficiency, which is again essential for the protonation steps of NRR. N_2

solubility is one of the major concerns of the aqueous electrolytes, where the electrolytes only serve as a platform for the NRR process to occur. In this chapter, we postulate a strategy in which NaBF₄ in water was taken as working electrolyte such that the electrolyte itself can act as a "co-catalyst" along with the active material to bring about a negotiable N₂ solubility and activation during NRR in ambient condition. We have thoroughly demonstrated the "bi-catalytic" activity of our electrode-electrolyte system reinforcing high production rate for NH₃ synthesis. NMR studies reveal the existence of both BF₄⁻ and BF₃ in the medium. BF₃, having moderate Lewis acidity forms an adduct with N₂ promoting its solubility in aqueous electrolyte. In this study, Mn-N/C with MnN₄ active unit has been chosen as a model catalyst as N2 is known to chemisorb on the transition metal by transferring electron from its bonding orbital and accepting electron in its π^* antibonding orbital, which is requisite for the N=N bond activation.^{14–17} More interestingly, free BF₃ has been found to interact with both the catalyst active site (MnN₄) as well as to the adsorbed N_2 molecules, where in the former it helps in bond re-location by shifting the metal d-band center and help the later in its activation, bond polarizability and first protonation at a detrimentally faster rate by a "push-pull" mechanism.^{14,18,19} This many-fold influence of BF₃ on the electrode-N₂ system stood out to be promising for the high yield of ammonia with a very good production rate, approaching the industrial scale periphery.⁶

3.3 Experimental Section

3.3.1 Sample preparation

Literature studies have shown that the transition metal doped nanocarbons are very much efficient for the electrocatalytic NRR due to the dual role of the active metal center and the conductive carbon support. In this chapter, a conventional one-step pyrolysis method at 800 °C (3 °C min⁻¹) for 2 h in Ar atmosphere was implemented with the transition metal precursor, MnCl₂. 4 H₂O and melamine (source of N and C) to obtain our desired catalyst MnN₄. The obtained black powder was treated with 6 M HCl to do away with any unreacted metals in the product. This was followed by washing with deionized water several times, till the pH turned neutral and then with ethanol. The final powered catalyst was therefore obtained by drying the washed material in hot air oven at 70 °C overnight.

The N-C catalyst was prepared with only melamine precursor at 800 °C for 2 h in Ar atmosphere but at a very slow ramp rate of 1 °C min⁻¹. The obtained black powder was water washed and dried in hot air oven at 70 °C overnight.

3.3.2 Electrode fabrication

A quantitative amount of the MnN₄ catalyst (8 mg) was dispersed in a 1:1 (v/v) mixture of water and isopropyl alcohol (1 mL) and ultrasonicated for 30 min. Before modifying the GCE with the as-prepared ink, these were properly cleaned with 1, 0.3, and 0.05 μ m alumina (Al₂O₃) powder followed by CV cycling in 0.5 M H₂SO₄. The glassy carbon part of the electrode was then drop-casted with 0.45 mg cm⁻² of the catalyst ink. This mass loading was maintained throughout the study.

3.3.3 Computational modeling

DFT based calculations are performed using the VASP²⁰. The electron exchangecorrelation was represented by the PBE functional within the GGA²¹. The PAW²² pseudopotential is employed to describe ion-electron interaction using the plane-wave basis set with a cutoff energy of 450 eV. For the electronic self-consistent loop and ionic relaxation loop, the energy convergence criteria are set to be 10^{-6} eV and 10^{-4} eV, respectively. The Brillouin zone is sampled at the gamma point for the MnN₄ flake system. The vacuum of 20 Å is used in all directions to avoid the interaction between repeating images.

Free energy profile is an effective method to estimate the catalytic performance and thermodynamic overpotential for the electrochemical NRR. We used the following equation to calculate Gibbs free energies (G), G = E+ZPE-TS-neU, where E is the energy calculated using DFT, n is the number of electrons and U is the applied potential at the electrode^{23,24}. The ZPE and TS of adsorbed atoms/ions are negligible to that of the gaseous phase at room temperature and ambient pressure. Whereas the ZPE and TS values for the free molecules were considered from a chemical database. The charge density difference analysis is performed using the PWscf package of Quantum ESPRESSO distribution.²⁵

3.4 Results and discussion

3.4.1 Conventional electrolytes vs NaBF4

The existing hurdle of N_2 activation in aqueous electrolytes was our prime focus to resolve in this study. Mostly, with the conventional aqueous electrolytes, research focus orients on the discussion of pH effect and size of cations in suppressing HER, promoting NRR kinetics. While investigating a series of aqueous electrolytes, we derived at a point that the anionic counterparts like Cl⁻, OH⁻, SO₄²⁻, ClO₄⁻ can somewhat influence the

catalyst active site for N₂ adsorption but typically, these electrolytes have no interaction with N₂. Therefore, these do not serve as the role of "carrier" of N₂ into the medium, in vicinity of the catalyst unlike NaBF₄.^{26,27} NaBF₄ in aqueous medium is easily hydrolysed to form fluoroboric acid (HBF₄), which is considered as superacid with Hammett acidity function (H₀) of -16.6.²⁸ The superacid HBF₄ exists in equilibrium between H_3O^+ + $[BF_4]^- \leftrightarrow H_2O.BF_3$ in aqueous medium. BF₃, being the limelight of this chapter has a multitudinous effect not only on the catalyst (MnN₄) surface but also with N₂ as follows:

- (a) Majorly, the tendency of interaction between the BF₃ and N₂ to form N₂→BF₃ adduct enables N₂ sufficiency in the three-phase interface (gas-liquid-solid) and in the proximity of the catalyst, which was so far a missing link for all other aqueous electrolytes.
- (b) BF₃, on the other hand imparts negative charge density from its non-bonding orbitals to the LUMO of MnN₄ (D_{4h} point group symmetry), as confirmed from the low negative metal d-band center value, close to fermi level in presence of BF₃.
- (c) The charge polarized Mn-center triggers the adsorption of N_2 molecules, and through σ -bonding and π -back bonding interactions help in protonation of N_2 .
- (d) This N₂ activation and protonation step is further provoked by the Lewis acidic effect, served by free BF₃ (unlike all other anions) on the adsorbed N₂ molecules. The boron center of BF₃ pulls the electron density from the adsorbed N₂ and delocalizes the charge over terminal F atoms. The symbiotic electronic push-pull effect of BF₃-induced-MnN₄→N₂ and N₂→free BF₃ leads to significantly improved N₂ activation, polarization as well as first protonation on the catalyst surface in NaBF₄ rich aqueous electrolyte.¹⁸
- (e) Finally, the easy desorption of the final product NH₃, because of its increased solubility and interaction with BF₃, forms a frustrated Lewis acid-base pair (H₃N→BF₃).

The superiority of BF₃ as compared to all other conventional aqueous electrolytes has been schematically demonstrated in Figure 3.1a-c.


Figure 3.1. (a) Role of BF_3 on free N_2 forming $BF_3.N_2$ adduct; N_2 solubility in aqueous medium; (b) BF_3 as a "co-catalyst" along with Mn- N_4 active site towards enhanced $N \equiv N$ bond activation, polarization and first protonation; (c) Advantages of BF_3 as an anion, as compared to the other conventional electrolytes (anions like Cl^- , ClO_4^- , OH^- , SO_4^{2-}).

3.4.2 Promoting N_2 solubility by the Lewis acidic effect of BF₃ in aqueous electrolyte

Our choice of electrolyte was such that (a) it would be a cheap, abundant, and watersoluble inorganic salt and (b) it would deliver BF₃ in the medium for the plausible interaction with the purged N₂ gas. The existence of BF₃ in the aqueous solution of NaBF₄ was rightly confirmed from the NMR spectra of ¹¹B and ¹⁹F.^{29,30} In the ¹¹B-NMR spectrum in Figure 3.2a (black line), for the symmetrical environment around boron for BF₃.H₂O, a quartet signal (1:3:3:1) at 0.036 ppm could be observed owing to the B-F coupling interactions, which was found to collapse in the signal at -1.49 ppm due to the rapid quadrupolar relaxation of boron at the sufficiently unsymmetrical boron site for BF_4^- . The 1.52 ppm high field shift (red line) of the quartet for BF₃.H₂O could be attributed to the acid-base interaction between the oxygen atom and boron center. This is in pretty much congruence with the ¹⁹F-NMR spectrum in Figure 3.2b (black line), where the two main peaks (singlets) at -151.14 and -151.09 were due to the F-with¹⁰B and F-with¹¹B BF₃.DMSO-d⁶ complex. The peak intensity corresponding to F-with¹¹B is reasonably lower due to the low extent of isotopic impurity in the NaBF₄ salt. Besides this, a skewed quartet could be observed between -146.17 to -146.0 ppm, denoting the coupling between three symmetrical F atoms and two protons in the $BF_3.H_2O$, as also evidenced in the ¹¹B-NMR spectrum. This denaturing of the quartet could be due to the overlap between the 1:2:1 triplet of F-with ¹⁰B and F-with ¹¹B. No separate signals could be found for BF_4^- as for the ¹⁹F-NMR, B-F could be not observable.^{29,30} A high field shift of 0.01 ppm and 0.08 ppm could be seen in the ¹⁹F and ¹¹B NMR for the respective $BF_3.H_2O$ signals, which indicates a considerable gain of electronic charge on BF_3 that is delocalized from boron to fluorine. Unlikely, in the ¹⁹F NMR, a greater high field shift of 0.12 ppm was seen for the peaks corresponding to $BF_3.DMSO-d^6$ presumably because



Figure 3.2. (a) ¹¹B-NMR spectra of NaBF₄ in DMSO-d⁶ in ambient and N₂ purged conditions. Inset represents the quartet and skewed multiplet peaks for B-F coupling; (b) ¹⁹F-NMR spectra of NaBF₄ in DMSO-d⁶ in ambient and N₂ purged conditions. Inset represents the skewed quartet signal coming from ¹⁰BF₃.H₂O and ¹¹BF₃.H₂O due to F-H coupling and singlet peaks for F representing BF₃.DMSO-d⁶ in the medium; (c) UV-spectra for the electrolyte at Ar purged condition and under N₂ purging for different time span; (d) Hirshfeld surface analysis for N₂-BF₃ adduct formation; (e) Schematic representation of the interaction between BF₃ and N₂ forming N₂→BF₃ adduct.

 N_2 serves as a better base and can replace $\ensuremath{\text{DMSO-d}^6}$ in the adduct. The signal corresponding to BF_4^- in the ¹¹B NMR displayed no change as it is coordinatively and electronically already saturated. This interaction between N2 and BF3 could be supported by the rising UV peak at 265 nm when NaBF₄ solution was made to interact with N₂ for increasing feeding time (Figure 3.2c). Simultaneously, by performing Hirshfeld surface analysis (Figure 3.2d), the small effect of BF₃ on free N₂ molecules is clarified, which induces N₂ solubility in the electrolyte through weak Van der Waals interactive forces. BF₃ is known to have moderate Lewis acidity as compared to other boron halides, because of the $p\pi$ - $p\pi$ back bonding between the symmetry matched 2p orbitals of F and B due to which a partial positive charge dominates over F, while the B center remains somewhat electronically sound. In the advent of any Lewis base, BF_4^- will tend to exist as BF₃ and capture electron density to neutralize the partial positive charge over F. As an opportunity to this, in presence of N₂, not only BF_4^- will form N₂ \rightarrow BF₃ adduct but the N₂ may partly replace H₂O molecules from the BF₃.H₂O to form BF₃.N₂. This interaction induces N_2 solubility in the aqueous medium, where BF₃ typically acts as a "sink" for N_2 as schematically shown in Figure 3.2e and enhances N2 accessibility in the vicinity of the active material, which was so far a distant dream with any of the conventional electrolytes in practice.

3.4.3 Structural evidence and characterization of the catalyst

Due to the proper energy and symmetry of the metal 3d orbital enabling N₂ activation, Mn embedded in an N-doped carbon matrix is considered as a model system for our investigating catalyst.³¹ The catalyst synthesis involves simple mechanical grinding followed by carbonization at 800 °C with a slow reaction rate of 3 °C min⁻¹ to obtain our final material MnN₄. A sheet-like morphology could be observed in the HRTEM image (Figure 3.3a) and the corresponding SAED pattern displays the dominant (002), (101) and (004) surfaces of carbon (inset of Figure 3.3a). XRD analysis suggests that the catalyst is crystalized in the hexagonal carbon phase (space group- P63/mmc) and the planes obtained from SAED are quite consistent with those obtained from XRD data in Figure 3.3b. The sp² hybridized carbon plane with defects caused by N and Mn dopants was verified from the RAMAN spectra with an I_D/I_G ratio of 0.94 with precise 2D peak indicating the formation of few-layered Mn and N co-doped all planar-graphene sheet (Figure 3.3c). The formation of Mn-N bond was confirmed from the Mn-N stretching vibration at ~ 614 cm⁻¹ in the FTIR spectrum (Figure 3.3d).³² The XPS analysis of MnN₄ catalyst evidenced the presence of all the four elements like Mn, N, C, O as shown in Figure 3.3e and the corresponding atomic weight % are tabulated in Table 3.1. The

Table 3.1. Peak position and atomic % of all the elements comprising the MnN_4 catalyst from XPS analysis.

Elements	Peak position (eV)	Atomic %
Carbon (C)	285.03	89.64
Nitrogen (N)	399.49	3.55
Oxygen (O)	532.32	6.4
Manganese (Mn)	642.18	0.41

valency of the Mn atom was shown from the high-resolution deconvoluted Mn spectra that displayed distinct spin-orbit coupled Mn 2p peaks with a doublet separation of 11.67 eV (Figure 3.3f).³³ The deconvoluted N 1s spectra displayed peaks corresponding to pyridinic N, pyrrolic N, quaternary N, N-oxides and Mn-N_x peaks with 30.8, 19.72, 13.51, 8.59 and 27.38 % respectively (Figure 3.3g). The XANES profile demonstrated that the active species Mn exhibited an oxidation state in between 0 and +3 (Figure 3.3h). The Fourier transform (FT) k^3 -weighted EXAFS spectra in Figure 3.3i showed that, for MnN₄, only a primary peak at 1.76 Å can be observed, without the signal of the Mn–Mn shell (compared with Mn foil), which further proves that there was no agglomeration of Mn atoms in the form of nanoparticles, in agreement with XRD. EXAFS shell fitting analysis in Table 3.2 indicated four N-coordinate Mn centres (MnN₄) in MnN₄ catalyst.³⁴

Table 3.2. Structural parameters of the MnN₄ catalyst obtained from the EXAFS fitting.

Sample	Bond type	R (Å)	σ²	CN	<i>E</i> _θ shift (eV)	R-factor
Mn,N/C	Mn-N ₁	1.89±0.12	0.005	4.0	-8.739	0.029

Note: R, the distance between absorber and backscatter atoms; CN, coordination number; σ^2 , Debye–Waller factor; E₀, edge-energy shifts; S₀², amplitude reduction factor, which is fixed as 1.0 during the fitting. The pretreatment of data was performed using Athena and the oscillation of the Mn *k*-edge was selected for further EXAFS fitting using Artemis software.



Figure 3.3. (a) HRTEM image for the as-obtained MnN_4 , inset shows the exposed surfaces of {002}, {101} and {004}. Scale bar: 20 nm (A) and 10 1/nm (inset); (b) XRD patterns for MnN_4 denoting the diffraction peak for carbon; (c) RAMAN spectra for MnN_4 catalyst, showing distinct D, 2D and G-bands; (d) FTIR spectra for MnN_4 catalyst; (e) XPS full survey spectra for MnN_4 catalyst, showing all the constituent elements like C 1s, N 1s, O 1s and Mn 2p; (f) Deconvoluted XPS profile for the Mn 2p of MnN_4 catalyst indicating spin-orbit coupled peaks at a 11.67 eV separation; (g) Deconvoluted XPS profile for the N 1s spectra for MnN_4 catalyst; (h) Normalized XANES spectra at the Mn k-edge of Mn foil, MnO, Mn_2O_3 , MnO_2 , and MnN_4 ; (i) FT-EXAFS spectra of Mn foil and MnN_4 , and the curve fitting with the $Mn-N_1$. The inset represents the corresponding atomic model.

3.4.4 Effect of surface adsorbed BF₃ on the *in*-situ electrochemical conversion of N₂ to NH₃

The key factor to improve the production rate of ammonia is by improving the kinetics of the potential determining steps of NRR. In general, the probable rate determining steps are: (a) N₂ adsorption, owing to the poor accessibility and interaction of N₂ onto the catalyst surface; (b) first protonation, because of the polarizability issue of N₂ and high energy intensive proton affinity of N₂ (493.8 kJ mol⁻¹)³⁵ and (c) desorption of the target product (NH₃). Among these, for MnN₄ type of systems, it has been theoretically proved that the first protonation of N₂ is the potential limiting step.³⁶ With the BF₃-dominated aqueous electrolyte, it was possible to effectively overcome all these issues and bring

about a low overpotential for NRR with high production rate. The electrochemical response of NRR activities of the catalyst was primarily obtained from the LSV curves for NaBF₄-N₂ system, which differed in current density from the Ar saturated electrolyte condition (Figure 3.4a). All potential values mentioned in this chapter are calibrated with respect to RHE, following equation 2.6 of chapter 2. Interestingly, the NaBF₄-catalyst system also outperformed all the conventional electrolytes like HCl, Na₂SO₄, LiClO₄ and KOH both in terms of onset potential and current densities (Figure 3.4a). A vivid theoretical study was carried out with the five different types of anions for respective electrolytes, such as BF₃ (NaBF₄), Cl (HCl), ClO₄ (LiClO₄), OH (KOH) and SO₄ (Na₂SO₄) (Figure 3.4b) to gain insight about the solvation effect. By considering each



Figure 3.4. (a) LSV curves comparing NRR performance of MnN_4 in different electrolytes in terms of current density; (b) The optimized structures of MnN_4 , N_2 , and NNH adsorbed MnN_4 by considering BF_3 , Cl, OH, SO₄, ClO₄ anions attached to the Mn site (brown, deep green, green, grey, blue, pink, red, yellow and fluorescent green represent C, H, B, F, N, Mn, O, S and Cl atoms respectively); (c) Demonstration of the free energy profile of N_2 and NNH adsorption on MnN_4 active site of our catalyst by considering five attached anions to the Mn site such as BF_3 , Cl, OH, ClO₄, SO₄. The respective Mn d band center and overpotential (η) values for these anions are given in the figure.

anion attached with the Mn site, we calculated the free energy profile of N₂ and NNH adsorption (Figure 3.4c). We observed ΔG_{N2} in the following order, -0.59 eV (BF₃) <-0.53 eV (Cl) < -0.22 eV (ClO₄) < -0.1 eV (OH) < 0.11 eV (SO₄). The BF₃ anion showed the higher N₂ adsorption for NRR. The corresponding values of overpotential (η) were 0.54 V, 0.75 V, 1.01 V, 0.95 V, 1.08 V respectively. Whereas these electrolytes (except

BF₃ anion) did not play role in the N₂ polarisation, where the structural distortion was observed after attaching these anions to the adsorbed N₂. For more clarity, we computed the d band center values of Mn site attached with different electrolyte anions (BF₃, Cl, ClO₄, OH, SO₄). From this investigation, a linear relationship was observed between d band center shift and the adsorption of N₂ as well as NNH intermediate on Mn site (Figure 3.4c). The Mn site with attached BF₃ shows (-1.55 eV) the highest d band center (lower negative value) that is the origin of its higher NNH adsorption and lower thermodynamic overpotential of NRR. Therefore, the electrolyte with BF₃ anion is the most promising medium for strong N₂ adsorption, low NRR overpotential, and N₂ polarisation to synthesize NH₃ with high yield rate.



Figure 3.5. (a) CA response of MnN_4 catalyst for 2 h run (each) in 0.5 M NaBF₄ electrolyte; (b) UV-vis absorption spectra of the electrolyte (0.5 M NaBF₄ with dissolved NH_{4^+}) stained with indophenol blue indicator after 2 h of incubation from the CA run; (c) UV-vis absorption spectra for the detection of N_2H_4 at different applied potentials for 2 h of NRR measurements in 0.5 M NaBF₄; (d) UV-vis spectra at 630 nm, representing different known concentrations of NH_4^+ stained with indophenol blue indicator solutions after 2 h incubation; (e) corresponding absorbance calibration plot used in this study, inset represents the colour of the solutions having different NH_4^+ concentrations of N_2H_4 after 15 min incubation at room temperature; (g) corresponding absorbance calibration plot used in this study, inset represents the colour of the solutions having different known concentrations of N_2H_4 after 15 min incubation at room temperature; (g) corresponding absorbance calibration plot used in this study, inset represents the colour of the solutions having different known concentrations of N_2H_4 after 15 min incubation at room temperature; (g) corresponding absorbance calibration plot used in this study, inset represents the colour of the solutions having different N_2H_4 concentrations, after 15 min of incubation.

Thus, to experimentally verify the role of different electrolytes, it was essential to carry out the potential-dependent CA study from +0.05 to -0.3 V for the catalyst in 0.5 M NaBF₄ (Figure 3.5a). But, before any electrochemical studies, the purged gas was passed through acid and base traps and colorimetrically examined to detect the trace of any nitrogenous impurity like gaseous NH₃ or NO_x respectively (methods are elaborated in section 2.8 of chapter 2). Thereafter, a quantification of the impurity source in the feed gas was summarized in Table 3.3. After the CA studies for 2 h at each potential, the

Gas	Purity	NO _x	N2O	NH3	Total N-
	(From supplier)	(µmol)	(µmol)	(µmol)	impurities (μmol)
$^{14}N_2$	99.99 % (Sigma Gases)	< 0.001	<0.001	0.009	~ 0.01

Table 3.3. Summary of the ${}^{14}N_2$ gas purity analysis.

resultant electrolyte was subjected to Indophenol-blue method and Watt and Chrisp methods to detect the production of NH₃ and N₂H₄ respectively (Figure 3.5b and 3.5c). The concentration of NH₃ was determined from the standard calibration plots derived from the known concentrations of NH₄⁺ and N₂H₄ as shown in Figures 3.5d, e and Figure 3.5 f, g respectively (inset of Figure 3.5e and Figure 3.5g indicate the colours formed with the solution containing gradually increasing concentration of reactants mixed with colouring agents). Similarly, the same set of CA tests and corresponding UV-visible spectra were performed with the catalyst in all the different electrolytes but the yield rate and FE for NH₃ formation was exceedingly high in case of 0.5 M NaBF₄ than all other electrolytes owing to the minimum free energy requirement of the catalyst in NaBF₄ for the first protonation of adsorbed N₂, as shown in Figure 3.6. The maximum yield for NH₃ in 0.5 M NaBF₄ was obtained at 0 V vs RHE (328.59 μ g h⁻¹ mg_{cat}⁻¹), with a FE of 18.6



Figure 3.6. Comparison of yield of NH_3 and corresponding FE for MnN_4 catalyst in different electrolytes at different potentials. The trend for all the activity descriptors follows $NaBF_4 > HCl > LiClO_4 > KOH > Na_2SO_4$. The error bars represent standard deviation between identical electrolysis experiments.

% (equation 2.18 and 2.19 from chapter 2). The concentration of NH_3 for all other electrolytes was calculation from the standard calibration plots as shown in Figure 3.7ah. To no surprise, extensive potential-dependent studies, and corresponding. This exceedingly high yield of NH_3 could also be attributed to the product specificity of our catalyst during NRR as there was no evidence of the side product (N_2H_4) formation



Figure 3.7. UV-vis spectra of electrolyte solutions, representing different known concentrations of NH_4^+ stained with indophenol blue indicator solutions after 2 h incubation at room temperature and corresponding absorbance calibration plot used in this study; (a, b) for 0.1 M HCl, (c, d) 0.1 M Na₂SO₄, (e, f) 0.5 M LiClO₄ and (g, h) 0.1 M KOH.

(Figure 3.5c). To exaggerate the role of BF_3 on MnN_4 active site, the control sample N-C was also subjected to CA at 0.0 V (Figure 3.8a), only to find the NH₃ yield to be 80.34 μ g h⁻¹ mg_{cat}⁻¹, which is much lower as compared to Mn/N-C material. The FE was also as low as 5.9 % (Figure 3.8b, c). This was expected as BF_3 played a major role to play on the Mn active site in altering the metal d-band center, which in turn helped in facile



Figure 3.8. (a) CA response of N-C catalyst in 0.5 M NaBF₄ for 2 h run at 0.0 V vs RHE. (b) comparative UV-vis absorption spectra of the electrolyte for N-C and Mn/N-C stained with indophenol blue indicator after 2 h of incubation from the CA run. (c) comparative bar plot representing the NH₃ yield and Faradaic efficiency for Mn/N-C and N-C catalysts at 0.0 V.

 N_2 adsorption and its subsequent reduction. The result was absolutely in congruence with the EIS of MnN₄ catalyst in different electrolyte conditions, where the minimum Ohmic and charge-transfer resistance could be evident in the MnN₄-NaBF₄ interface (Figure 3.9a, b). The BF₃-N₂-MnN₄ interaction could be further established from the increasing NH₃ concentration in the catholyte upon increasing the potential-dependent experiment time from 2 h to 4h to 8h, as evident from the from the ¹H-NMR data for ¹⁴NH₃ in Figure 3.9c. Furthermore, for five consecutive NRR cycles at 0 V (2 h each) with the same electrode, the NRR performance remained in harmony with respect to the yield, FE, and area-normalized production rate of NH₃ as evident from Figure 3.9d. The negligible deterioration in performance could be put upon to the insignificant mass loss from the electrode surface, upon prolonged exposure to the reaction conditions.

To verify the reliability of the produced NH₃ from the feeding gas, several blank control experiments were conducted that showed negligible NH₃ formation in (a) Ar purged condition and (b) at OCP under N₂, ensured that there was no participation of the catalyst-N in the high yield of NH₃ (Figure 3.9e). Most importantly, the isotope labelling experiment with ¹⁵N₂ feeding gas was performed in 0.5 M NaBF₄ at 0 V. While the ¹H NMR spectrum corresponding to ¹⁴NH₄⁺ displayed a triplet coupling with a J_{N-H} of 52 Hz, a doublet coupling with non-identical peak positions was observed for the ¹⁵NH₄⁺ with a J_{N-H} of 72 Hz and there was no NMR signal for the Ar purged experiment and under no potential in the ¹⁴N₂-MnN₄-BF₃ system (Figure 3.9f). For reliability of the NH₃ produced, vigorous comparative quantifications are utmost required with both the ¹⁴N₂ and ¹⁵N₂ gases via colorimetric as well as NMR methods (details are provided in section 2.6.10 of chapter 2). According to our observation, the calculated yield of NH₃ and the mass-normalized production rate from ¹⁵N₂ gas accords well with that obtained from ¹⁴N₂ gas (Figure 3.9g), which further confirms that the NH₃ was chiefly produced by electroreduction of N₂ on the Mn-N₄ catalyst surface with the help of BF₃. The error bars denote the standard deviation values of three different data sets. A broad literature survey



Figure 3.9. (a) EIS of MnN_4 catalyst in different electrolyte conditions (inset denotes the magnified data at higher frequency region); (b) Equivalent circuit diagram and comparison of the Ohmic and charge-transfer resistances at the electrode-electrolyte interface; (c) ¹H-NMR spectra of the working electrolyte in DMSO-d⁶ after different time span of the potential-dependent experiment at 0 V vs RHE; (d) Yield of NH_3 and FE of MnN_4 with $NaBF_4$ after cycling experiments at 0 V; (e) Comparative bar plot of concentration and yield of NH_3 in N_2 and Ar, at 0 V and in N_2 at OCP for MnN_4 ; (f) ¹H NMR spectra of the magnified mass-normalized production rate quantified by both colorimetric test and NMR measurement with ¹⁴N₂ and ¹⁵N₂ feeding gases; (h) NRR performance map based on area-normalized production rate and mass-normalized yield of NH_3 in traditional aqueous, aqueous/organic, IL electrolytes and Li-mediated NRR over current state-of-the-art electrocatalysts.

reveals that our electrode-electrolyte system in ambient aqueous condition stands out to be way better than the ionic liquid, conventional aqueous as also aqueous/organic electrolytes and nearly comparable to the Li-mediated approach of NH₃ synthesis in terms of NH₃ yield and area-normalized production rate as summarized in Figure 3.9h.

3.4.5 Thermodynamics of BF₃-induced NRR in terms of d-band center of metal and origin of the activity towards NRR

We performed DFT based calculations to understand the NRR mechanism, effect of electrolyte, and the origin of catalytic performance in MnN₄ catalyst. We considered four energy-optimized model systems like pristine MnN₄, MnN₄ attached to BF₃ (MnN₄/BF₃), MnN₄ in presence of free BF₃ anion (MnN₄ (BF₃)), and the fourth one MnN₄ attached to BF₃ in presence of free BF₃ anion (MnN₄/BF₃ (BF₃)) (Figure 3.10a-d). The NRR



Figure 3.10. The model structures of (a) pristine MnN_4 (b) MnN_4 (BF₃) (c) MnN_4/BF_3 (d) MnN_4/BF_3 (BF₃) of the catalyst considered for the theoretical studies. The Mn, N, C, F, B, H atoms are denoted with pink, dark blue, gray, light blue, big green sphere and small green colour sphere respectively.

mechanism and the full free energy profile for the model-d (given in Figure 3.11a) inferred that the alternating pathway is preferred over the distal pathway due to the lower value of free energy change of NHNH step compare to the NNH₂ step.^{37–39} Whereas the enzymatic or mixed mechanism is not feasible on MnN₄ systems due to the higher value of change in Gibbs free energy of N₂ adsorption (ΔG_{N2}) with end-on configuration (-0.38 eV) than that of side-on configuration (-0.066 eV).

We extrapolated our finding to the free energy profile of N₂ and NNH adsorption to compare the NRR performance vividly (Figure 3.11b). Firstly, we compared the N₂ adsorption energies for the four models. The values of ΔG_{N2} for MnN₄, MnN₄ (BF₃), MnN₄/BF₃ and MnN₄/BF₃ (BF₃) catalysts were -0.38 eV, -0.26 eV, -0.59 eV and -0.49 eV respectively. We found that the nitrogen adsorption was exothermic (negative ΔG_{N2}) for all the four models and particularly MnN₄/BF₃ showed higher N₂ adsorption among them, which could be attributed to the charge redistribution between BF₃ and MnN₄ imparting a local charge density over Mn-active site. From the projected density of states study, the d band center (ϵ_d) values⁴⁰ of Mn site in MnN₄ and MnN₄/BF₃ catalysts were -1.64 eV and -1.55 eV respectively (Figure 3.11c, d). The higher ϵ_d value in MnN₄/BF₃ indicated that the binding of BF₃ anion influenced the chemistry of the Mn site by shifting the ϵ_d towards the Fermi level that led to the strong N₂ and NNH adsorption as compared to pristine MnN₄.⁴¹ Further, the negative shift of ϵ_d (laying at -2.26 eV for MnN₄ and -2.24 eV for MnN₄/BF₃) was observed after N₂ adsorption, which revealed that the charge



Figure 3.11. Thermodynamic studies of NH_3 formation through BF_3 induced NRR on MnN_4 catalyst and electronic properties. (a) the full free energy path of NRR on the model system MnN_4/BF_3 (BF_3); (b) free energy profile of N_2 and NNH adsorption for the four catalyst models namely pristine MnN_4 , MnN_4 (BF_3), MnN_4/BF_3 (BF_3). The Mn, N, C, F, B, H atoms are denoted with pink, dark blue, gray, light blue, big green sphere, and small green color sphere respectively; the d orbital density of states of Mn site in (c) pristine MnN_4 (d) MnN_4/BF_3 (e) N_2 adsorbed MnN_4 (f) N_2 adsorbed MnN_4/BF_3 . The d band centre value is given in the respective subfigure. Dotted line at zero in the x axis represents the Fermi energy level; (g-0) demonstrate the optimized model structure, charge density difference with side view and top view of (g-i) N_2 adsorbed MnN_4/BF_3 (m-o) N_2 adsorbed MnN_4 with BF_3 attachment. The yellow and blue colour lobes represent the charge accumulation and depletion with isosurface value of 0.0032 $e/Å^3$; (p) represents the free energy diagram of HER for these four model systems with the value of ΔG_H .

transfer occurred from the Mn site to N₂ during adsorption (Figure 3.11e, f). To visualize these charge transfers, we performed the charge density difference analysis. The charge redistribution was observed on the Mn site due to the attachment of both N2 and BF3 anion (Figure 3.11g-l) (BF₃ to MnN₄ to N₂). Secondly, the formation of the NNH intermediate during first protonation is the known PDS that defines the overpotential for NRR $(\eta_{NRR})^{42}$. It was observed that the MnN₄ and MnN₄/BF₃ shows the overpotential of 0.93 V and 0.54 V respectively, whereas for systems, (MnN₄ (BF₃) and MnN₄/BF₃ (BF₃) the PDS step is exothermic in nature. Under the N₂-adsorbed-MnN₄ condition, N₂ behaved as a better "base" to attract the free BF3 ions in the medium and pass on the electronic charge to F through B centre via a push-pull mechanism, which eventually helped to polarize N₂. Here, we examined negligible change in the ε_d value of the Mn center (-2.27 eV in NN_MnN4 (BF3) and -2.24 eV in NN_MnN4/BF3 (BF3)) that indicated, there was no charge transfer found on Mn site, while charge redistribution was prevalent on N₂ (push-pull effect), which thereby boosted the first protonation process at the distal N for the initiation of NH₃ synthesis (Figure 3.11m-o). From the full free energy profile, we could find that the last step of NH_3 release for MnN_4/BF_3 (BF₃) system showed an energy barrier of 0.98 eV, but this step was not involved in the NRR mechanism due to high NH3 solubility in the BF3 dominated medium forming a frustrated Lewis pair as $NH_3 \rightarrow BF_3$ ⁴³. We can infer that the overpotential can be exothermic and endothermic within a maximum value of 0.54 V in presence of BF₃ anion under its different binding positions. Overall, we can conclude that the binding or presence of BF₃ anion improves the N₂ adsorption as well as reduces the η_{NRR} .

3.4.6 Dominance of NRR over HER

HER is a well-known competitive pathway that hinders the production efficiency and NH₃ yield of NRR⁴⁴. For our four model systems we estimated that the values of change in Gibbs free energy of hydrogen adsorption (ΔG_H) for pristine MnN₄, MnN₄ (BF₃), MnN₄/BF₃ and MnN₄/BF₃ (BF₃) catalysts were +0.32 eV, +0.26 eV, +0.12 eV and +0.09 eV, respectively (Figure 3.11p). Importantly, we observed the endothermic nature of HER in all these models, which thereby favoured the exothermic nitrogen adsorption (negative value of ΔG_{N2}) more ($\Delta G_{N2} < \Delta G_H$). Especially, the hydrogen poisoning effect⁴⁵ on Mn active site could be avoided due to the positive values of ΔG_H .

3.4.7 Approaching industrial-scale production rate of NH₃

The primary objective of this chapter was to overcome the rate determining steps of NRR with an improvised aqueous electrolyte system (NaBF₄), which served as an ideal "co-catalyst" along with MnN₄. BF₃-induced overall charge polarization triggered the feasible N₂ reduction on the MnN₄ active site at a low overpotential with a successive high yield of NH₃ synthesis (328.59 μ g h⁻¹ mg_{cat}⁻¹), which is so far the highest among all the conventional aqueous electrolyte-induced NRR, irrespective of the catalysts (Figure 3.12a and Table 3.4). Additionally, this chapter turned out to be tremendously beneficial in terms of the area-normalized production rate (equation 2.20 of chapter 2), as high as 2.45×10^{-9} mol s⁻¹ cm⁻², which is almost approachable to the industrial scale periphery.⁶ However, one could be cautious to the catalyst with high area-normalized NH₃ production yet low mass-normalized one. Thus, we also report the mass-normalized NH₃ production following equation 2.21 of chapter 2, which helped to evaluate and compare



Figure 3.12. (a) Yield of NH_3 with the reported catalyst and our catalyst with $NaBF_4$ in the potential range of -0.5 V to 0.2 V vs RHE; (b) Area and mass-normalized production rate of NH_3 . The respective symbols adjacent to (a) and (b) denote the corresponding working electrolytes. Area-normalized production rate of NH_3 with MnN_4 in 0.5 M $NaBF_4$ (this chapter) was calculated to be 2.45×10^{-9} mol s⁻¹ cm⁻², approaching the predicted industrial scale periphery. All the data included in both the figures are analysed at ambient temperature and pressure.

the NH₃ synthesis rate over a wide-ranging approaches, electrolytes, and catalyst systems. In every respect, NaBF₄- MnN₄ catalysed NRR (this chapter) stood way better than all the conventional systems being worked upon so far, as could be seen from the area as well as mass-normalized NH₃ production rate plot in Figure 3.12b and table 3.5.⁴⁶

Table 3.4. Comparison of reported catalysts in terms of high NH_3 yield over a wide-ranging potential from -0.5 V to +0.2 V vs RHE.

Catalysts	Electrolyte	Potential (V vs RHE)	NH ₃ yield (µg h ⁻¹ mg _{cat} ⁻¹)	References
Au ₁ Cu ₁ /GCE	0.05 M H ₂ SO ₄	-0.2	154.91	Nanoscale, 2020, 12, 1811-1816
Mo ₂ C nanorod	0.1 M HCl	-0.3	95.1	ACS Cent. Sci. 2019, 5, 1, 116–121
PdCu	0.5 M LiCl	-0.1	35.7	Angew. Chem. Int. Ed., 2020, 59, 2649- 2653
PdP ₂ /rGO	0.5 M LiClO ₄	-0.1	30.6	J. Mater. Chem. A, 2019, 7, 24760- 24764
RuP ₂ /rGO	0.1 M HCl	-0.05	32.3	J. Mater. Chem. A, 2020, 8, 77-81
Au/TiO ₂	0.01 M HCl	-0.4	64.6	J. Mater. Chem. A, 2020, 8, 6586-6596
Fe ₂ O ₃ /NC/C	0.1 M HCl	-0.1		ACS Sustainable Chem. Eng., 2019, 7, 8853-8859
RhSe nanocrystals	0.1 M HCl	-0.1	175.1	<i>Adv. Mater.</i> 2020, <i>32</i> , 2001267
Fe	Ionic liquid	-0.8	9.605	<i>Energy Environ. Sci.</i> , 2017,10, 2516-2520
Au/o-CFP	0.1 M Na ₂ SO ₄	-0.3	40.6	<i>Adv. Sci</i> .2020,7, 2002630
Mo-SnS ₂	0.05 M LiClO4	-0.5	41.3	J. Mater. Chem. A, 2020, 8, 7117-7124
AuCu/ZIF-8	0.1 M HCl	0.0	64.6	J. Mater. Chem. A, 2020, 8, 8868- 8874
CoS ₂ /NS-G	0.05 M H ₂ SO ₄	-0.2	25	Proc. Natl. Acad. Sci. 2019, 116, 6635– 6640
Ru SAs/N-C	0.05 M H ₂ SO ₄	-0.2	120.9	<i>Adv. Mater.</i> 2018, <i>30</i> , 1803498
Au ₁ Co ₁ @GO	0.5 M K ₂ SO ₄	-0.2	36.82	ACS Sustainable Chem. Eng. 2020, 8, 1, 44–49
Ru/PEI	0.1 M KOH	-0.1	188.7	J. Mater. Chem. A, 2019, 7, 25433- 25440

PdPb/C	0.1 M HCl	0.05	25.68	Applied Catalysis B: Environmental, 2020, 265, 118481			
FeOOH/CNTs	MeOH-water	-1.2 V vs Ag/AgCl	262.5	ACS Energy Lett. 2021, 6, 3844–3850			
MnN ₄	0.5 M NaBF ₄	0	328.59	This chapter			
Note: GCE = gla	Note: GCE = glassy carbon electrode; rGO = reduced graphene oxide; CFP = carbon fiber						
paper; ZIF = zinc-imidazole framework; GO = graphene oxide; PEI = polyethyleneimine;							
CNTs = carbon n	anotubes.						

Table 3.5. State-of-the-art NRR electrocatalysts. Most papers reported either electrode areanormalized or catalyst mass-normalized NH_3 production rates, so some values in the table were calculated from the catalyst loading and geometric area of the electrode that are included in the reports.

Catalysts	Electrolyte	Potential (V vs RHE)	Production rate (mol s ⁻¹ cm ⁻²)	$\begin{array}{c} \textbf{Production} \\ \textbf{rate} \\ (\textbf{mmol} \\ \textbf{h}^{-1}\textbf{g}_{cat}^{-1}) \end{array}$	References
LaCoO ₃	0.1 M Na ₂ SO ₄	-0.7	7.59×10^{-11}	10.7	ACS Catal., 2020, 10, 1077-1085
PEBCD	0.5 M Li ₂ SO ₄	-0.7	3.28 × 10 ⁻¹¹	0.0923	J. Am. Chem. Soc., 2017, 139, 9771- 9774
Pd/C	0.1 M PBS	0.1	2.21×10^{-11}	0.0794	Nat. Commun., 2018, 9, 1795
MXene	0.5 M Li ₂ SO ₄	-0.3	7.71×10^{-11}	0.158	Joule, 2019, 3, 279-289
Cu/PI	0.1 M KOH	-0.3	2.03×10^{-10}	0.146	Nat. Commun., 2019, 10, 4380
Fe ₁ -N-C	0.1 M KOH	0	1.22×10^{-10}	0.440	<i>Nat. Commun.</i> , 2019, <i>10</i> , 341
Au/Ni	0.05 M H ₂ SO ₄	-0.14	2.42×10^{-10}	0.435	J. Am. Chem. Soc., 2019, 141, 14976- 14980
C- Ti _x O _y /C	0.1 M LiClO ₄	-0.4	1.45×10^{-10}	0.871	Angew. Chemie Int. Ed., 2019, 58, 13101-13106
Fe	Ionic liquid	-0.8 vs NHE	2.29×10^{-11}	0.565	<i>Energy Environ.</i> <i>Sci.</i> , 2017, <i>10</i> , 2516-2520
Bi	0.2 M Na ₂ SO ₄	-0.6	4.46 × 10 ⁻¹¹	0.321	Angew. Chemie Int. Ed., 2019, 58, 9464-9469
MoS ₂ /C	0.1 M Li ₂ SO ₄	-0.2	4.38×10^{-10}	0.158	<i>Adv. Energy</i> <i>Mater.</i> , 2019, <i>9</i> , 1803935
Co ₁ /N-C	0.05 M Na ₂ SO ₄	-0.2	2.39×10^{-10}	0.123	J. Mater. Chem. A., 2019, 7, 26358-26363

Fe ₁ -N-C	0.1 M HCl	-0.05	1.56×10^{-11}	0.0468	J. Mater. Chem. A., 2019, 7, 26371-26377
Ru ₁ /N-C	0.05 M H ₂ SO ₄	-0.2	5.04 × 10 ⁻ 10	7.11	<i>Adv. Mater.</i> , 2018, <i>30</i> , 1803498
PdCu/C	0.5 M LiCl	-0.1	5.95×10^{-10}	2.10	Angew. Chemie Int. Ed., 2020, 59, 2649-2653
Fe-N/C-CNT	0.1 M KOH	-0.2	2.85×10^{-10}	2.05	ACS Catal., 2019, 9, 336-344
B/N-CNF	0.1 M KOH	-0.7	5.31 × 10 ⁻	1.91	J. Mater. Chem. A., 2019, 7, 26272-26278
B ₄ C-B-C	0.1 M HCl	-0.45	4.67 × 10 ⁻	1.68	<i>Chem. Commun.,</i> 2019, <i>55</i> , 7406- 7409
Cl-GDY	0.1 M HCl	-0.45	1.75×10^{-10}	1.57	ACS Catal., 2019, 9, 10649-10655
P/MnO ₂	0.1 M Na ₂ SO ₄	-0.5	4.13×10^{-10}	1.49	Small, 2020, 16, 1907091
CoS ₂ /N,S-C	0.05 M H ₂ SO ₄	-0.2	8.17 × 10 ⁻	1.47	Proc. Natl. Acad. Sci., 2019, 116, 6635-6640
N-C	0.005 M H ₂ SO ₄	-0.4	3.64×10^{-10}	1.31	ACS Energy Lett. 2019, 4, 377-383
Au-Fe ₃ O ₄	0.1 M KOH	-0.2	1.75×10^{-10}	1.26	Adv. Funct. Mater., 2019, 1906579
VN	Flow cell	-0.1	1.10 × 10 ⁻ 10	0.792	J. Am. Chem. Soc., 2018, 140, 13387- 13391
Cu	0.1 M KOH	0.0	1.76 × 10 ⁻	0.706	<i>Chem. Commun.</i> , 2019, <i>55</i> , 12801-12804
W ₂ N ₃	0.1 M KOH	-0.2	3.80 × 10 ⁻	0.686	<i>Adv. Mater.</i> , 2019, <i>31</i> , 1902709
Ru/NC	0.1 M HCl	-0.21	3.59×10^{-10}	0.647	<i>Chem</i> , 2019, <i>5</i> , 204-214
Fe-ReS ₂ @N- CNF	0.1 M Na ₂ SO ₄	-0.2	1.31 × 10 ⁻⁹	4.73	Adv. Funct. Mater., 2020, 30, 1907376
P@SnO _{2-x}	0.1 M Na ₂ SO ₄	-0.4	7.97 × 10 ⁻	2.87	Angew. Chemie., 2019, 131, 16591- 16596
Mo ₁ /N-C	0.1 M KOH	-0.3	5.56×10^{-10}	2.00	Angew. Chemie Int. Ed., 2019, 58, 2321-2325
C@CoS@TiO ₂	0.1 M Na ₂ SO ₄	-0.55	8.09 × 10 ⁻	0.787	Angew. Chemie Int. Ed., 2019, 58, 18903-18907

COF/NC	0.1 M KOH	-0.2	2.05×10^{-10}	0.737	<i>Nat. Commun.</i> , 2019, <i>10</i> , 3898
Fe ₃ Mo ₃ C/C	1 M KOH	-0.5	2.14×10^{-10}	0.0770	Angew. Chemie Int. Ed., 2019, 58, 15541-15547
rGO	0.1 M HCl	-0.116	1.28×10^{-10}	0.459	<i>Nano Energy</i> , 2020, 68, 104323
MnN ₄	0.5 M NaBF4	0	2.45 × 10 ⁻⁹	19.32	This chapter

Note: CNF = carbon nanofiber; CNT = carbon nanotube; GDY = graphdiyne; COF = covalent organic framework; rGO = reduced graphene oxide; PEBCD = poly(N-ethylbenzene-1,2,4,5-tetracarboxylic diimide).

3.5 Conclusion

The widely highlighted problem of NRR that is the competitive HER is most likely worked upon with several catalyst development and electrolyte modifications, while the N₂ solubility and activation issues in the aqueous medium are generally neglected. This chapter justifies our aim to contribute towards this trouble-maker by using NaBF₄ as a working electrolyte, which served as a "full-packaged co-catalyst" along with MnN₄, reinforcing the NRR kinetics at the cost of low overpotential. The Lewis-acidic nature of BF3 induced adduct formation with the N2 molecules and acted as a carrier of N2 gas into the medium in vicinity of the electrocatalyst. Simultaneously, the charge polarization over MnN₄ active site due to BF₃ delocalized the metal d-band centre, which triggered N₂ adsorption on the catalyst site. Under this condition, free BF₃ form the medium interacted with the adsorbed N₂ and brought about the facile polarization of the N \equiv N bond and its first protonation at a much lower energy barrier. This push-pull charge transfer effect enormously helped to overcome the potential determining steps and this BF₃ mediated NRR resulted in a huge production rate of NH₃, which could be compared to that of industrial scale, which was not achieved so far with any aqueous or ionic liquid electrolytes.

In short, this kind of user-friendly aqueous electrolyte is being investigated for the first time for NRR. Since BF₃ displayed tremendous potential in triggering the kinetics of NRR, this new finding may encourage researchers to work more on aqueous electrolyte designing towards an even improved NRR performance of the electrocatalysts. Not only that, electrocatalysts could also be functionalized with BF₃ derivatives, which could be one entirely new route of study in the field of NRR.

3.6 References

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Chapler 4

Inducing charging effect on boron via oxygen edge-functionalization in BNCO towards proficient electrochemical ammonia synthesis **Overview**: The electrochemical NRR primarily requires material selectivity for N_2 adsorption over proton adsorption that will enable σ - π interaction between the energetic symmetric orbitals of N and active atom. In this chapter, we report the synthesis of an oxygen-functionalized boron carbonitride matrix via a two-step pyrolysis technique. The conductive BNCO₍₁₀₀₀₎ architecture, the compatibility of B-2p_z orbital with the N-2p_z orbital and the charging effect over B due to the C and O edge-atoms in a pentagon altogether facilitate N₂ adsorption on the B edge-active sites. The optimum electrolyte acidity with 0.1 M HCl and the lowered anion crowding effect aid the protonation steps of NRR via an associative alternating pathway, which gives a sufficiently high yield of ammonia (211.5 µg h⁻¹ mg_{cat}⁻¹) on the optimized BNCO₍₁₀₀₀₎ catalyst with a FE of 34.7 % at -0.1 V vs RHE.



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Reference: Biswas et al., Nano-Micro Lett., 2022, 14, 214.

4.1 Motivation of the chapter

Although the electrolyte NaBF₄ introduced in chapter 3 helped attain an impressive production rate of NH₃, but it did not affect the FE of the process much. Also, NaBF₄ was specified to MN₄ systems (M=transition metals), which would limit the horizon of material improvisation. Thus, in all the following chapters, we concentrated on the conventional aqueous electrolytes and focused more on catalyst development to balance the yield as well as FE for NRR. Initially, we intended to look for non-metallic systems because of a simpler chemistry, and B is the best contender in this case because of its orbital energy symmetry with N₂. In fact, we perceived that besides catalyst, electrolyte ions also play an important role in the long-term NRR performance of the material and they should not have a detrimental effect on the active site. Therefore, a combined attention should be devoted to both the material synthesis strategy as well as the choice of electrolyte.

4.2 Introduction

In majority of the B-compounds, B serves as a Lewis acidic site and its orbital compatibility with N₂, which is on the other hand a weak Lewis base appears to serve the purpose of N₂ adsorption on the B units successfully. However, to obtain a better yield of ammonia, it is crucial to drive the forces that tend to bind N₂ with B active sites that is the σ -bonding and the π -back bonding interactions that weaken the N=N bond on the catalyst surface.¹ One probable way out to this could be doping some foreign elements in the BN architecture that would either serve as a better active site for NRR² or enhance the local charging effect over B to make way for the delocalization of the charges to the adsorbed N₂ for the facile increment of N–N bond length and easy first protonation.³ Cdoping in BN framework is looked upon for this purpose, where some reports suggest that BN acts as a trigger while the edge C provided the active sites for NRR.⁴ Contrary to this, a few reports considered B as the active centre in the BNC or B-doped C catalyst accomplishing facile N₂ adsorption and reduction with a knee-high energy requirement.^{5,6} In particular, the edge B atoms having lone pair of electrons were found to be more effective to draw N₂ for adsorption. However, there is a lagging in parity between theoretical and experimental findings to establish the actual active site and the importance of C in the BN framework, promoting NRR. It is more interesting to observe that to increase the efficiency of metal-free carbon-based catalyst, heteroatoms like oxygen play crucial role to accumulate free charge cloud over the adjacent atoms and help in spin polarization, which in turn lower the potential for the rate determining steps of NRR.^{7,8} Thus, this concept could be rendered in BCN class of catalysts to provoke the NRR efficiency of the B active sites through charging effect, however, has not been explored.

Besides the active site, electrolytes play a parallel importance in NRR. It has been seen in many cases that electrolyte ions (cations or anions) play a major role to provoke NRR,⁹ either by suppressing HER¹⁰ or by enhancing the local concentration of N₂ in the vicinity of the electrode material. However, the fact that electrolyte ions could also have some interaction with the active site is mostly unseen, as (a) This calls for a common practice to perform NRR in all the known electrolytes and (b) This requires rigorous theoretical findings. But along with the development of a suitable catalyst, the choice of electrolyte also needs thorough attention to ensure that the electrolyte ions do not offer poisoning effect on the active site.

In this chapter, we have insightfully focused on the above-mentioned issues of catalyst development and its preservation throughout the NRR process. Keeping in mind, the significant contribution of B towards NRR, our active catalyst BNCO₍₁₀₀₀₎ was developed. It was found that the presence of C dopants and O functionalities formed an electron-rich pentagon at the edges, deviating from the regular B-N-C hexagonal units owing to which the adjacent B site encountered a better charging effect and the material experienced improved conductivity with charge cloud density accumulated near the Fermi level. This helped to improve the charge transfer efficiency from B to the adsorbed N_2 reinforcing the potential determining steps of NRR. More interestingly, a series of experiments with different set of acidic electrolytes like HCl, H₂SO₄ and H₃PO₄ (varying the anionic counterpart) revealed that HCl is a better competent for NRR on B active site yielding 211.5 μ g h⁻¹ mg_{cat}⁻¹ NH₃ and with a FE of 34.7 % at -0.1 V vs RHE. H₂SO₄ and H₃PO₄ caused a crowding effect because of the bulkiness of anions hindering the passage of N₂ and bound with the B site through O end $(SO_4^{2-} and PO_4^{3-} serving as better)$ Lewis bases than N₂), partly poisoning the active site. This study thus brings to the fore the importance of catalyst development as well as selectivity of electrolyte for an unperturbed and high yield of ammonia.

4.3 Experimental Section

4.3.1 Synthesis of BNCO electrocatalyst

This chapter concerns the synthesis of the active material by a two-step pyrolysis method. Primarily, melamine and boric acid were taken as precursors of C, N, O and B in 1:2 weight ratio. After stirring the mixture in ethanol, it was dried overnight and the resultant powder was pyrolyzed at 550 °C followed by 1000 °C (3 °C min⁻¹) for 2 h. Thereafter, the obtained black powder was subsequently washed thoroughly with distilled water and ethanol and dried in hot air oven at 70 °C to obtain oxygen edge-functionalized boron-carbonitride framework (BNCO₍₁₀₀₀₎). The other control samples were obtained at a different pyrolysis temperatures of 800, 900, and 1100 °C named as BNCO₍₈₀₀₎, BNCO₍₉₀₀₎, and BNCO₍₁₁₀₀₎, respectively, while maintaining the ratio of melamine and boric acid as 1:2. In order to establish the importance of B as an active site for NRR, only melamine was pyrolyzed at 1000 °C at 2 °C min⁻¹ to obtain NC. In addition to this, to foreplay the effect of C doping, pristine BN was synthesized using boric acid and urea by pyrolyzing the precursors at 1000 °C for 5 h.¹¹

4.3.2 Electrode modification

10 mg of the BNCO₍₁₀₀₀₎ catalyst was dispersed in a 1:1 (v/v) mixture of water and isopropyl alcohol (1 mL) and ultrasonicated for 30 min. This same ink solution was used for all the electrochemical studies involved in NRR. Before modifying the GCE with the catalyst ink, it was properly cleaned with 1, 0.3 and 0.05 μ m alumina (Al₂O₃) powder and ultrasonicated with deionised water for 3 min. Furthermore, CV was performed for 100 cycles in 0.5 M H₂SO₄ at 100 mV s⁻¹ scan rate to remove all form of impurities from the catalyst surface. The glassy carbon part of the electrodes was then drop-casted with the catalyst ink and dried overnight under vacuum.

4.3.3 Computational modelling

First-principles-based DFT calculations are performed using plane-wave technique implemented in the VASP.¹² PAW pseudopotentials are used to define the core electrons.¹³ The GGA proposed by PBE is employed to describe electron exchange– correlation interactions.¹⁴ An optimised value of cut-of energy of 450 eV through convergence test is used in the plane-wave basis set. The energy convergence criteria are set to be 10–5 eV for electronic self-consistent loop and 10–4 eV for ionic relaxation loop. The Brillouin zone sampling within Monkhorst pack scheme is obtained using the $1\times5\times1$ K-point grid. The vacuum of 20 Å is considered in X and Z directions to avoid the interaction between repeating images. In nitrogen reduction reaction, the electrochemical activity and reaction mechanism on the catalysts can be estimated by

plotting the Free Energy profile. For this, the Gibbs free energies (G) of each reaction steps are calculated by using equation 4.1,

$$G = E + ZPE - TS - neU \tag{4.1}$$

where E is the DFT energy, n is the number of electrons and U is the applied potential at the electrode,¹⁵ which are provided in the table below for the free molecules like H_2 , NH_3 and N_2 (Table 4.1).

Molecule	E (eV)	TS (eV)	ZPE (eV)	G (eV)
H_2	-6.77	0.41	0.27	-6.91
N_2	-16.19	0.59	0.15	-16.63
NH ₃	-19.41	0.58	0.92	-19.07

 Table 4.1. The DFT energies, TS and ZPE for free molecules.

4.4 Results and discussion

4.4.1 Energy optimized structure and electronic states of the catalysts

Boron atom has gained immense popularity in terms of facile adsorption interaction with N_2 atoms, owing to the symmetry in their orbital energy. Besides this, B is also known to impart stability to the key intermediates of NRR via a charge balance mechanism.¹⁶ However, to make NRR more thermodynamically feasible, a driving force is inevitable,



Figure 4.1. Optimised model structures of (a) BN, (b) BNC, and (c) BNCO systems. The N, C, O, B atoms are denoted with blue, wine, red, green colour spheres, respectively; Plot of DOS for (d) BN, (e) BNC, (f) BNCO systems. The vertical dotted line at zero represents the Fermi Level.

which would account for an enhancement in the charge transfer efficiency of the B active centre to the adsorbed N₂. The material is expected to become more electronically active, provided the electronic states near its Fermi level is more populated that in turn reinforces the material conductivity.¹⁷ This could be operative in presence of foreign dopants and not only that a better charge density near the Fermi level helps in enhanced N₂ adsorption and weak binding of the key intermediates of NRR, thereby uplifting the NRR kinetics energetically.¹⁸ In this realm, it was important to realize the correlation between the local charging effect over active B site and its impact on the NRR performance and hence for this chapter, three energy optimized model structures for pristine BN, BNC, and BNCO were formulated as shown in Figure 4.1a-c. Through density of states study, we found that the BNC and BNCO systems became more conductive with large electronic states near Fermi level due to C and O units as compared to BN (Figure 4.1d-f) and accordingly we approached to synthesize our desired active material BNCO₍₁₀₀₀₎ along with all the necessary control samples, required to justify the motive of this chapter.

4.4.2 Structural illustration and formation mechanism of the catalyst

The synthesis of the active material initiated with mechanical stirring of the precursors, melamine, and boric acid at 65 °C in ethanol, where an inevitable H-bonding between the two moieties enable the formation of a single-sourced co-crystal for the synthesis of boron carbonitride framework.¹⁹ Nevertheless, it is important to mention the significance of the two-step pyrolysis process towards NRR activity of the material. At 550 °C, a condensation reaction would eliminate H₂O and NH₃ from the precursor and an irregular architecture of boron nitride and carbon-nitride is expected to form. However, as boric acid is taken in excess, there persists a possibility of further inter-molecular H-bonding at the edges as depicted in Figure 4.2. Beyond 550 °C, the B(OH)₃ units get converted to



Figure 4.2. Schematic representation of the probable mechanism of BNCO catalyst synthesis by pyrolysis method.

 B_2O_3 , which further take part in the high temperature pyrolysis step to deliver our final active catalyst, oxygen edge-functionalized boron-carbonitride (BNCO₍₁₀₀₀₎). So, the structural disintegration followed by elemental re-organization of the precursors led to the formation of boron carbonitride architecture with well-defined boron active sites per hexagon unit and islands of edge pentagons containing O functionality. The synthesis method and the probable mechanism has been schematically elaborated in Figure 4.2.

4.4.3 Morphology and structural characterization

The FESEM image in Figure 4.3a presents that the catalyst resembled a hardened granular morphology, which could be attributed to the crosslinking effect of the intramolecular boronic acid and melem moieties forming the BNCO₍₁₀₀₀₎ active material.²⁰ The irregularly organized lattice fringes in the HRTEM image in Figure 4.3b depicted the crystalline nature of the material. The elemental composition of the BNCO₍₁₀₀₀₎ catalyst was verified by means of FESEM mapping, where Figure 4.3c evidences the presence of B, N, C, and O atoms. The XRD pattern of all the synthesized materials was consistent with that obtained for C-doped BN type of material architecture (Figure 4.3d).²¹ The characteristic peaks located at 20 of 26 and 43° could be ascribed to



Figure 4.3. (a) FESEM image of $BNCO_{(1000)}$ catalyst (scale-bar: 100 nm); (b) HRTEM image of $BNCO_{(1000)}$ catalyst (scale bar: 10 nm); (c) Elemental mapping of $BNCO_{(1000)}$ catalyst showing the distinct elements B, C, N and O; (d) XRD of all the synthesized catalysts; (e) FTIR spectra of all the as-synthesized catalysts.

the (002) and (100) planes of BCN.^{22,23} The slight shifting in the (100) plane to a lower angle from the XRD spectrum of pristine BN originated from the planar strains that could have developed due to the C doping and O edge-functionalization.^{24,25} This necessitated the establishment of the elemental bonds constituting the catalysts, which was verified from FTIR spectroscopy. As demonstrated in several reports, the formation of BN architecture occurs at a temperature of 900 °C and above, the nature of the FTIR spectra for the catalysts BNCO₍₉₀₀₎, BNCO₍₁₀₀₀₎, and BNCO₍₁₁₀₀₎ was consistent with that obtained for BN with the signature vibrations appearing at 1345 and 761 cm⁻¹ for B–N stretching and B–N–B bond, respectively, as shown in Figure 4.3e.^{21,26,27} The other peaks corresponding to B–C, C–N,²⁸ B–O–C, C=O, and C=N bonds could also be seen from the stretches in between 900 and 1400, ~ 1800, and 2100 cm⁻¹, respectively. The chemical bonding environment within the BNCO₍₁₀₀₀₎ catalyst was further determined by XPS. A comparative XPS study of all the catalysts has been provided to have a clear vision of the formation of our active catalyst. The atomic weight % of the elements B, N, C and O obtained from survey spectra of XPS is shown in Table 4.2. The high-

	Boron (B 1s)	Nitrogen (N 1s)	Carbon (C 1s)	Oxygen (O 1s)
NC	-	5.2	92.46	2.34
BN	42.49	29.28	_	28.23
BNCO(800)	9.84	10.66	71.38	8.12
BNCO(900)	45.86	31.74	10.42	11.98
BNCO (1000)	47.71	28.18	15.48	8.6
BNCO (1100)	36.13	19.57	36.9	7.4

Table 4.2. Atomic % of all the elements comprising the BNCO catalyst and all the control samples from XPS analysis.

resolution B 1s spectra in Figure 4.4a evidence the gradual formation of the C-doped BN structure with C–B–N peak at 190.73 eV,²⁹ along with the lowering in the integral peak area of B–O (at 192 eV)^{5,27} with the gradual rise in temperature from 800 to 1000 °C. At 1100 °C, the B–O peak disappeared along with the emergence of a small peak at 188 eV corresponding to B–C bond. The deconvoluted peaks appeared identical for the BNCO₍₁₀₀₀₎ as well as pristine BN samples in Figure 4.4b, where the peak corresponding to B–O could be reasonably from the O edge-functionalization of the B centres. Likewise, in the N 1s narrow spectra in Figure 4.4c, the peak corresponding to N–C at 399.58 eV appeared to be rather broadened in the sample formed at 800 °C along with

the presence of N-B bonding characteristic at 398.15 eV. It could be expected that at this temperature, a disordered structure was formed which eventually got reorganized at a temperature of 900 to 1100 °C, where a gradual increment in the N–B peak intensity could be observed with a simultaneous lowering of the N–C peak intensity. The greater number of B–N pairs manifested greater number of active sites at 1000 °C, beneficial for NRR. However, although it appeared that the N–B peak got even more intense in case of 1100 °C, the relative elemental content of this material BNCO₍₁₁₀₀₎ revealed a lowering



Figure 4.4. Comparative narrow XPS spectra of all the catalysts at (a, b) B 1s, (c, d) N 1s, (e, f) C 1s and (g, h) O 1s edges.

in the B and N atomic percentage with simultaneous rise in the C content of the material. In case of pristine NC, pyridinic N, pyrrolic N and N-oxides could be seen from the peaks at 397.9, 400.3, and 403.9 eV, respectively, in Figure 4.4d,³⁰ while for pristine BN, peaks corresponding to N–B and N–O could be evidenced at 398.8 and 400.2 eV, respectively. The N–B peak in the final material was found to be shifted to a lower binding energy by 0.6 eV, which could be attributed to the disorderness in the structure due to foreign dopants like C and O. In the high-resolution C 1s spectra in Figure 4.4e, a sharp fall in the C–B peak intensity could be seen with rise in pyrolysis temperature from 800 to 1000 °C, which was an indication for the formation of more BN motifs with repetitive C doping per hexagonal unit of BN, consistent with that obtained in N 1s spectrum.²³ But due to rise in the C content with further rise in temperature to 1100 °C, assumingly there occurred a structural disruption from the regular C-doped BN framework and an increase

in the extent of graphitization enhanced the C content in the material with emergence of a broad C–B bond in the C 1s spectrum. In the B 1s spectrum, for 1100 °C material, there was appearance of a new peak corresponding to B–C, besides the conventional C–B–N peak, corroborating our finding from the C 1s spectra. However, the appearance of C–O peak also indicated the presence of O functionalization at the edges of all the synthesized catalysts (Figure 4.4e, f). It is not surprising that the high-resolution O 1s spectra in Figure 4.4g, h disclosed the same conclusion drawn from the B 1s and C 1s spectra regarding the B–O and C–O bonds, though it was found that the O content gradually diminished at higher pyrolysis temperature.

In order to have some insightful idea about the local electronic structures of the BNCO₍₁₀₀₀₎ material, NEXAFS was employed. Basically, in NEXFAS technique, a core level electron is excited to a partially unoccupied higher orbital level and hence the spectra obtained from NEXAFS is directly associated with the nature of the unoccupied orbital states. The B 1s NEXAFS (Figure 4.5a) spectrum showed a characteristic sharp peak at 190.67 eV for the B 1s π^* transition, which could be designated to the sp² hybridized, planar edge B atoms.³¹ The three resonances at 197.02, 198.48, and 203.2 eV (represented as δ_1 , δ_2 , and δ_3) were attributed to the σ^* excitations, where the former two involved antibonding interactions between N 2s and B 2p_{xy} orbitals.³² These



Figure 4.5. NEXAFS spectra of BNCO₍₁₀₀₀₎ catalyst at (a) B K-edge, (b) N K-edge, (c) C K-edge and (d) O K-edge.

stretches resembled that of h-BN.³³ The shoulder peaks at ~ 192.6 eV were attributed to the B–O motifs, possibly originating from the unreacted boron oxides, as complied with the XPS narrow spectrum for B 1s.²⁰ In all of the cases, a negative shift could be observed in the binding energies for our material BNCO₍₁₀₀₀₎ than that reported for pristine h-BN, which was due to some tensile strain due to the C doping effect, that affected the intraplanar local structure. For the N 1s NEXAFS in Figure 4.5b, the peak at 402.8 eV denoted the π^* resonance while the broadened peaks at 409.7 eV (δ_1) and 417.6 eV (δ_2) were attributed to the σ^* features and the formation of C–B–N bond.³⁴ The slight shift in the π^* peak position was due to the fact that N, being more electronegative imposed a more polarization effect on the B-N bond in BNCO(1000) system that likely impacted the binding energies of the participating bonding electrons.^{33,35} The C 1s NEXAFS spectrum in Figure 4.5c evidenced the presence of two distinguishable peaks at 285.2 (π^*) and 292.6 (δ^*) eV for the 1s to π^* and 1s to σ^* resonances of the sp² hybridized C, respectively.³⁶ The traces of B–O units were also evident from the O 1s NEXAFS as shown in Figure 4.5d.³⁷ All of the above-mentioned characterizations provide ample evidence for the formation of distinct C-doped BN moiety with O functionalization at the edges, where BNCO₍₁₀₀₀₎ catalyst serves as a potent candidate for NRR. The electronegativity of O and the charging effect between C–B–N unit combats the potential intensive steps of NRR and bring about facile ammonia production as discussed in the later section.

4.4.4 Electrochemical NRR performance: Role of electrolyte anions and B-active units for improved NRR kinetics

The lone pair of electrons over nitrogen brings about a weak Lewis basicity in the N₂ molecules, while the Lewis acidic nature of the B atom makes it a suitable candidate for N₂ adsorption.⁵ To facilitate the protonation of the adsorbed N₂ molecules, it is necessary to maintain a proton sufficiency in the medium. This makes the use of acidic electrolyte an optimum choice for NRR.³⁸⁻⁴⁰ In fact, acidic electrolyte acts as a proper trap to capture all the converted ammonia in form of NH₄⁺. Thus, for this chapter, primarily three acidic electrolytes were considered for NRR that, is, 0.1 M HCl, 0.1 M H₂SO₄ and 0.1 M H₃PO₄. The comparative LSV curves of the active material BNCO₍₁₀₀₀₎ in N₂ purged condition (Figure 4.6a) displayed a better NRR onset potential for H₃PO₄, though performance-wise HCl stood as a better competent. A fair explanation to this could be the better adsorption and binding probability of N₂ by phosphate radicals (PO₄³⁻-N₂; N-
N bond length 1.26 A°), which increases the N–N bond length to a greater extent as compared to SO_4^{2-} (1.24 A°) and Cl⁻ (1.15 A°). Moreover, from chemistry point of view, P and N being same group elements, their 3p-2p overlap leads to an enhanced interaction which helps to bring N₂ into the solid–liquid-gas interface and initiate NRR at a lower overpotential. The NRR activity was also reasonably good for both H₃PO₄ and H₂SO₄ as obtained from the CA scans (2 h each) over a wide-ranging potential window (0 to -0.4 V) and verified from UV–visible spectra of the colorimetric detection of NH₃ (Indophenol-blue method). But considering the proton donating ability of HCl, a stronger acid than H₂SO₄ and H₃PO₄, the NRR performance exceeded the latter two at -0.1 V as shown in Figure 4.6b, c with NH₃ yield rate 211.5 μ g h⁻¹ mg_{cat}⁻¹, FE of 34.7 % and



Figure 4.6. (a) Comparative LSV curves of $BNCO_{(1000)}$ catalyst in N_2 purged electrolytes at 10 mV s⁻¹ scan rate; (b) NRR performance of $BNCO_{(1000)}$ catalyst in different electrolyte conditions (0.1 M HCl, 0.1 M H_2SO_4 and 0.1 M H_3PO_4); (c) Comparative plot showing yield and FE of NH_3 synthesis over the wide-ranging potential window for $BNCO_{(1000)}$ catalyst in 0.1 M HCl; (d) Free energy diagram of adsorption of Cl, SO₄ and PO₄ on edge B site of $BNCO_{(1000)}$ system; inset shows the optimised model structures of Cl, SO₄, and PO₄ adsorbed BNCO models; charge density difference analysis of (e) Cl-adsorbed, (f) SO₄-adsorbed and (g) PO₄-adsorbed BNCO system. Yellow and blue lobes indicate electron accumulation and depletion, respectively (Iso-surface value = 0.001 e Å⁻³).

12.44 mmol h⁻¹ g_{cat}^{-1} mass-normalized ammonia production rate, calculated from equations 2.18, 2.19 and 2.21 of chapter 2. More importantly, the bulky anions SO₄²⁻ and PO₄³⁻ led to a crowding effect and blocked the B active sites by binding with B through O end (Lewis acid–base interaction). The thermodynamic favourability of this phenomenon as shown in Figure 4.6d hindered the smooth pathway for N₂ adsorption over the B active sites in case of H₂SO₄ and H₃PO₄. The theoretical results revealed that a greater charging interaction was induced from B to PO₄ than SO₄ and is the lowest for Cl anion in Figures 4.6e-g, which accorded with the NRR activity trend found experimentally (Figure 4.6b). However, it is important to secure the B active centres to get an uninterrupted NRR activity. Thus, 0.1 M HCl was considered to have an optimum acidity and anion effect to persuade facile NRR and was taken as the working electrolyte for all the electrochemical studies. In all cases, the concentration of NH₃ was calculated from the UV–visible standardization curves following the Indophenol blue method and

Catalysts	Electrolyte	Potential	NH ₃ yield	References		
		(V vs RHE)	$(\mu g h^{-1} m g_{cat}^{-1})$			
Mo ₂ N- BN	0.1 M Na ₂ SO ₄	-0.3	37	Applied Catalysis B: Environmental, 2021, 287, 119952.		
BCN	0.1 M HCl	-0.3	7.75	Small, 2019, 15, 1805029.		
BNQDs/T i ₃ C ₂ T _x	0.5 M LiClO ₄	-0.4	52.8	<i>Energy & Environmental</i> <i>Materials</i> , 2021, 5, 1303- 1309.		
C-BN	0.1 M HCl	-0.55	36.7	ACS Sustainable Chemistry & Engineering, 2020, 8, 5278.		
h-BNNs	0.1 M HCl	-0.75	22.4	Nano Research, 2019, 12, 919.		
(BNQDs) /graphitic C ₃ N ₄	0.5 M LiClO ₄	-0.3	72.3	Journal of Colloid and Interface Science, 2022, 606, 204.		
B-BCN	0.05 M Na ₂ SO ₄	-0.6	41.9	Applied Catalysis B: Environmental, 2021, 283, 119622.		
BNQDs@ Nb ₂ CT _x	0.5 M LiClO ₄	-0.4	66.3	Small, 2021, 17, 2102363.		
BNFC	0.05 M H ₂ SO ₄	-0.4	41	Journal of Materials Chemistry A, 2020, 8 , 8430.		
BNCO	0.1 M HCl	-0.1	211.5	This chapter		
Note: BN - boron nitride: BNODs - boron nitride quantum dats: h BNNs - beyagonal						

Table 4.3. Comparison of NRR performance of the reported BNC class of electrocatalysts.

Note: BN = boron nitride; BNQDs = boron nitride quantum dots; h-BNNs = hexagonal boron nitride nanosheets.

the corresponding linear regression plots (HCl: y = 0.252x + 0.031; H₂SO₄: y = 0.258x + 0.021; H₃PO₄: y = 0.270x + 0.029). Nevertheless, for an elaborate NRR study of our active material in 0.1 M HCl, the LSV polarization curves were produced at 10 mV s⁻¹ scan rate in an ideal three-electrode system, where a notable difference in current densities could be observed in Ar and N₂ fed electrolyte conditions (Figure 4.7a). The 2 h CA study in Ar at -0.1 V and at OCP in N₂ shows negligible yield of ammonia (inset of Figure 4.7a) that confirmed the authenticity of ammonia production, chiefly from the feeding gas. According to the best of our perception, this is the highest reported yield of ammonia on boron nitride or boron-carbonitride class of materials, where B actively served as the unit for N₂ adsorption and subsequent reduction as shown in Table 4.3. The high production of ammonia was further verified from the isotope labelling experiment, where distinguishable triplet and doublet ¹H NMR signals with coupling constant values of 52 and 72 Hz, respectively, were evident for ¹⁴NH₄⁺ and ¹⁵NH₄⁺, while there was no signal in case of Ar saturated condition of electrocatalysis (Figure 4.7b, c). More



Figure 4.7. (a) Comparative LSV curves of $BNCO_{(1000)}$ catalyst in Ar and N₂ purged 0.1 M HCl at 10 mV s⁻¹ scan rate, inset shows the bar plot of yield of NH₃ in N₂ and Ar, at -0.1 V and in N₂ at OCP for $BNCO_{(1000)}$ catalyst (2 h CA test); (b) CA response of $BNCO_{(1000)}$ catalyst for 1 h at -0.1 V vs RHE in ¹⁵N₂, ¹⁴N₂ and Ar saturated 0.1 M HCl, inset shows the NH₄⁺ formed after concentration and evaporation of electrolyte solution; (c) ¹H NMR spectra obtained after NRR in 0.1 M HCl with Ar, ¹⁴N₂ and ¹⁵N₂ feeding gases showing no peak, triplet and doublet respectively; (d) Quantification of ammonia yield rate and FE by NMR method with ¹⁴N₂ and ¹⁵N₂ feeding gases with BNCO₍₁₀₀₀₎ catalyst.

convincing evidence to the production of ammonia was provided by the quantitative analysis with maleic acid using equation 2.32 (chapter 2), where from the yield and FE of ammonia was calculated and cross verified to be almost similar with both $^{14}N_2$ and $^{15}N_2$ feeding gases (Figure 4.7d).

Boron is well known to have a proper orbital compatibility with N₂ that plays a significant role to lower down the free energy requirement for N₂ adsorption.⁴¹ As schematically shown in Figure 4.8a, the unoccupied sp² hybrid orbital of B took away the electron density from the σ (HOMO) of N₂ and in turn donated the π -electron cloud into the π^* (LUMO) of N₂ from the filled 2p_z orbital of B via back-bonding. This interaction induced the N=N bond weakening and brought about facile first protonation, which is the so-called PDS of NRR on B active sites. While a comparative LSV plot of



Figure 4.8. (a) Energy optimized structures of the BNCO₍₁₀₀₀₎ catalyst with N₂ adsorbed on the edge B site and the molecular orbital interaction between B and ad-N₂; (b) LSV curves of all the synthesized catalysts in N₂ fed 0.1 M HCl solution at 10 mV s⁻¹ scan rate; (c) Linear fits of difference of anodic and cathodic current densities extracted from the CV curves for all the catalysts with respect to different scan rates at definite potentials, where the slopes represent twice the C_{dl}; Comparison in NRR performance of all the synthesized catalysts in 0.1 M HCl at -0.1 V vs RHE in terms of (d) yield of NH₃, (e) mass-normalized production rate and (f) FE.

all catalysts (Figure 4.8b) voted for BNCO₍₁₀₀₀₎ to have better onset potential and cathodic current density, the C_{dl} had a direct co-relation with the electrocatalytic activity, and the results obtained for all our catalysts were absolutely in congruence with the NRR performances of the materials. The C_{dl} was derived from the CV plots at different scan rates for all catalysts and a plot of $\Delta j = (ja - jc)$ against the scan rate was linearly fitted to obtain the slope corresponding to twice the C_{dl} of the materials (Figure 4.8c). While

the role of B active unit was evident from the insignificant NRR performance in NC with NH₃ yield to be 29.83 μ g h⁻¹ mg_{cat}⁻¹, the presence of C had profound role in proliferating the NH₃ yield rate and FE than pristine BN (Figure 4.8d-f). Interestingly, as proper BN architecture was expected to form at a temperature of 900 °C and above, the BNCO catalysts (BNCO₍₉₀₀₎ and BNCO₍₁₀₀₀₎) formed at this high pyrolysis temperature displayed better performance (NH₃ yield for BNCO₍₉₀₀₎ 164.3 μ g h⁻¹ mg_{cat}⁻¹, while for BNCO₍₁₀₀₀₎, the yield was 211.5 μ g h⁻¹ mg_{cat}⁻¹) as compared to BN and BNCO₍₈₀₀₎ (NH₃ yield for BN 86.4 μ g h⁻¹ mg_{cat}⁻¹, while for BNCO₍₈₀₀₎, the yield was found to be 32.38 μ g h⁻¹ mg_{cat}⁻¹). However, the catalyst synthesized at 1100 °C (BNCO₍₁₁₀₀₎) slightly lagged in performance, which could be attributed to the loss of B active sites as shown from the lowered B content in the relative atomic % of the material from XPS analysis (NH₃ yield for BNCO₍₁₁₀₀₎ 161.02 μ g h⁻¹ mg_{cat}⁻¹). The performances of all the catalysts in terms of ammonia yield, production rate and FE are summarized in Figures 4.8d-f. Blessing of the optimized synthesis conditions, our final material BNCO₍₁₀₀₀₎ yielded 211.5 μ g h⁻¹ mg_{cat}⁻¹ ammonia synthesis with 34.7 % FE.

4.3.5 Mechanism of the active material towards NRR from DFT point of view

Theoretical analysis was carried out to unveil the role of carbon and oxygen towards improvement in NRR activity in BN systems. It is known that boron site is more promising active site to adsorb N₂ for NRR as compared to nitrogen sites.³ Therefore, we considered the single boron site at the edge (adjacent to the CO group in Figure 4.1c) in all three models to investigate the NRR mechanism. Firstly, we performed the N₂ adsorption study on boron site of these three models. We found that the end-on configuration of N₂ adsorption is more favourable with lower free energy (equation 4.1) than side-on configuration on boron site.³ Therefore, the alternating and distal pathways could only occur towards NRR, whereas the enzymatic or mixed mechanisms were not feasible. Despite the importance of B in NRR, the pivot of this chapter was to reinforce the local charging effect over B to facilitate the charge transportation from B to N₂, which was successfully accomplished by the presence of foreign dopants like C and O. Through charge density difference analysis and Bader charge study, the adsorption of N₂ on boron site in various models were investigated. In case of pristine BN in Figure 4.9a, b, a lowered charge transfer from B to N₂ was evidenced (0.09e), which in turn resulted in a lower N=N bond cleavage tendency and greater overpotential of PDS ($\Delta G_{N2} - \Delta G_{NNH}$ =1.4 eV) for NRR. In the full free energy profile, we observed the lower value of free

energy of NHNH step compare to the NNH₂ step that prefers the alternating pathway over the distal pathway.^{42,43} Further, the systems BNC and BNCO also showed a same PDS ($\Delta G_{N2} - \Delta G_{NNH}$) and alternating pathway for NRR. However, in the presence of carbon, the edge C atoms had a propagating effect on the B active units that resulted in enhanced charge transfer (from 0.09e in case of pristine BN to 0.22e in BCN) from B to N₂, reinforcing N₂ adsorption at a much-reduced overpotential (from 1.4 to 0.89 eV) (Figure 4.9c, d). Furthermore, edge-functionalized oxygen atom with carbon atoms



Figure 4.9. Charge density difference analysis for (a) pristine BN, (c) BNC, and (e) BNCO systems. Yellow and blue lobes indicate electron accumulation and depletion, respectively (Iso-surface value=0.001 e Å⁻³). The arrow and value indicate amount of Bader charge transferred; Free energy profile for NRR for (b) BN, (d) BNC, (f) BNCO.

formed the stable pentagon ring that made the carbon-boron bond weaker and the boron site became more active to adsorb N₂ strongly. Therefore, this pentagon ring behaved as an electron reservoir to enrich the local electron density over B such that an enhancement of charge transfer (0.26e) could be evident from B to adsorbed N₂ with lowering of the N₂ reduction overpotential to 0.7 eV (Figure 4.9e, f). The N₂ activation is dependent on its bond length after adsorption, where BNCO system shows enhanced N₂ activation due to higher bond length of adsorbed N₂ as follows, 1.13 Å (BNCO)>1.12 Å (BNC)>1.11 Å (BN). Thus, the charging effect and importance of O functionalization along with C dopants could be established for the emerging BN class of materials for NRR. To understand the effect HER on NRR theoretically, we performed the hydrogen adsorption calculation on the boron active site of BNCO system. In the comparison of free energy profile, we find that the NRR is more dominant on HER due to two reasons, (i) Higher N₂ adsorption energy (-0.86 eV) than hydrogen adsorption (-0.77 eV) on boron site, (ii) Lower value of NRR overpotential (0.7 V) than HER overpotential (0.77 V). Therefore, the BNCO catalyst is more favourable for NRR by supressing competitive HER.

4.3.6 Cyclability and stability studies of BNCO(1000) catalyst

The viability of the catalyst (BNCO₍₁₀₀₀₎) performance was ensured from repetitive cyclability measurements, holding -0.1 V vs RHE for 2 h, per cycle (Figure 4.10a). The post-cycling ¹¹B and ¹³C NMR studies for the electrolyte (0.1 M HCl) were performed to verify whether the catalyst was dissolved in the medium in due course of the reaction. Keeping in mind the natural abundance of these isotopes and the concentration of material that could have dissolved in the electrolyte, 8000 scans and 6000 scans were



Figure 4.10. (a) Yield of NH_3 and FE of ammonia production on $BNCO_{(1000)}$ catalyst after cycling experiments, holding -0.1 V vs RHE for 2 h for each cycle; (b) Post-cycling NMR studies of the 0.1 M HCl electrolyte showing ¹¹B and ¹³C NMR spectra in DMSO-d⁶ solvent in a 400 MHz NMR spectrophotometer; (c) Stability of $BNCO_{(1000)}$ catalyst for 48 h at -0.1 V, inset showing NH_3 yield after 2 h and 48 h; (d) FTIR spectra of $BNCO_{(1000)}$ catalyst before and after stability measurements for 48 h; Before and after stability deconvoluted XPS narrow spectra of $BNCO_{(1000)}$ catalyst at (e) B 1s, (f) N 1s and (g) C 1s.

applied prior to ¹³C and ¹¹B NMR measurements, respectively. As can be seen from Figure 4.10b, the ¹³C NMR spectrum displayed only one peak corresponding to the solvent DMSO-d⁶. There was no peak corresponding to the material (BNCO₍₁₀₀₀₎) either in ¹³C or ¹¹B (Figure 4.10b) NMR data, which certainly ensured that the material was not soluble in the electrolyte and the partial deactivation of the active site could be possibly responsible for the minimal drop in FE, while there was a harmony in the yield of NH₃ produced during each of the five CA cycles (Figure 4.10a). In case of N-containing samples, it becomes imperative to show that the catalyst N had no interference in the conversion to N to ammonia. Although, from isotope labelling experiment, the source of the ammonia obtained in the catholyte was verified to be from the feeding gas, a prolonged stability experiment was run to further check the stability and efficiency of the catalyst. After a CA run of 48 h at -0.1 vs RHE under continuous N₂ purging (Figure 4.10c), there was only a trivial loss in the yield rate of ammonia as evident from the inset of Figure 4.10c. This proved that the catalyst was efficient enough to be used for a prolonged time in the N₂ purged electrolyte condition under a continuous -0.1 V potential. The after stability FTIR spectra (Figure 4.10d) of the catalyst displayed identical stretching vibrations of the elemental bonds present in the BNCO₍₁₀₀₀₎ material as that in the fresh sample. In fact, XPS full survey spectra of the material revealed similar percentage of elemental content as the fresh sample, particularly that of N (Table 4.4). More vividly, the narrow spectrum of B 1s, N 1s, and C 1s also showed similar integral areas of the deconvoluted peaks as shown in Figure 4.10e-g respectively. Thus,

Table 4.4. Atomic % of all the elements comprising the $BNCO_{(1000)}$ catalyst before and after stability tests from XPS analysis.

	Boron (B 1s)	Nitrogen (N 1s)	Carbon (C 1s)	Oxygen (O 1s)
Before stability	47.71	28.18	15.48	8.63
After stability	46.44	27.76	14.23	11.57

this material proved to possess enough potential to be used as a metal-free electrocatalyst with target-specific, charge polarized and electrolyte-secured edge B active centres for NRR in 0.1 M HCl.

4.5 Conclusion

In summary, this chapter displayed the significant role of O and C doping within BN architecture to promote NRR on the edge B sites via associative alternating mechanism.

The gradual formation of the ideal structure was systematically studied by means of XPS and the electronic properties were investigated from NEXAFS. A greater impact was found on the charging effect of B centres due to O-functionalized edges that induced a greater charge density from B to the adsorbed N₂, overcoming the potential determining steps for NRR. This chapter simultaneously highlighted the importance of choice of electrolyte, where in 0.1 M HCl our catalyst BNCO₍₁₀₀₀₎ yielded 211.5 μ g h⁻¹ mg_{cat}⁻¹ of ammonia at -0.1 V vs RHE with a FE of 34.7 %. It was experimentally found and theoretically supported that the bulky anions in H₂SO₄ and H₃PO₄ blocked the B active sites by a Lewis acid–base interaction between the B sites and the O ends of the anions, hence not suitable for this class of materials. Thus, this chapter offered an overall idea of catalyst designing and the importance of medium to retain a high and consistent NRR performance.

4.6 References

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Chapler 5

Altered electronic band structure at the interface of NPG@SnS₂ heterostructure promotes electrochemical NRR

Overview: The interface engineering strategy has been an emerging field in terms of material improvisation that not only alters the electronic band structure of material but also induces beneficial effects on electrochemical NRR, which is potentially impeded by the competing HER. To circumvent this issue, catalysts should display a weak affinity for H-adsorption as compared to N₂. In this chapter, we have adopted this approach to synthesis our electrocatalyst NPG@SnS₂, which suppressed HER on Sn active site by deviating proton adsorption on S sites. Experimental work and DFT calculations regarded that due to the charge redistribution, Mott-Schottky effect and band bending of SnS₂ across the contact layer at the interface of NPG, d-band center for the surface Sn atoms in NPG@SnS₂ lowered that resulted in favored adsorption of N₂ on the Sn active site. This phenomenon was driven even forward by a lowering in the work function of the heterostructure that increased conductivity of the material as compared to pristine SnS₂, resulting in 49.3 % FE.



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5.1 Motivation of the chapter

The electronic charge density over the catalyst active site contributes to better kinetics for NRR as it modulates the electronic properties of the material, like work function and conductivity, in favor of its electrocatalytic activity. A better NRR kinetics would, in turn, result in an enhanced FE of NH_3 synthesis on the catalyst surface. The charge carrier density can be artificially induced in a catalyst by creating a local electric field at a metalsemiconductor interface owing to their conductivity difference, by virtue of which (a) the semiconductor counterpart can be utilized for electrocatalysis and (b) the active site can be secured for NRR with a better charge transfer kinetics.

5.2. Introduction

Interface engineering has proved to be an effective strategy for suppressing HER^{1,2} and has already been applied to a few metal oxides and dichalcogenides, where the materials of interest are typically fabricated with a layer of conducting graphene-based 2D materials.³ Two-dimensional dichalcogenides⁴⁻⁶ with atomic-scale thickness, direct bandgap, strong spin-orbit coupling and abundant surface/edge active atoms have attracted attention in the optoelectronic and energy harvesting applications. Interface engineering strategy has been implemented on a popular material MoS₂ to generate $0D/2D^7$ heterostructures. But to improve the interfacial contact area, $2D/2D^8$ heterostructure was designed with MoS₂ that not only improved the electrochemically active surface area but also enhanced the local charge concentration, making the catalyst selective for NRR.^{4,9} Similarly, Sn—based dichalcogenides (mainly SnS₂) have been widely studied for electrocatalytic applications due to their 2D flake like morphology with highly active and exposed edges, tuneable electronic band properties and long-term stability, but are less explored for NRR.¹⁰ However, its inferior electrical conductivity necessitates material fabrication either with a conducting support¹¹ or doping with another suitable metal¹², which not only increase the local electron carriers but also alter the electronic architecture of SnS_2 making it suitable for NRR. Despite of these attempts, this semiconducting material was unable to reach a spectacular FE, on an industrial scale.

However, interface engineering with a metal-semiconductor junction induces a contact layer, where a difference in the contact potential of the metal and the semiconductor at the interface allows a charge flow and eventually modulates the band positions of the semiconductor.¹³ A Mott-Schottky effect operating at the interface induces a lowered work function of the heterostructure with an elevated flat band Fermi

level.¹⁴ This interfacial effect also modulates the d-band center of the surface-active atoms that widely help to suppress the competitive HER.¹⁵ The accessibility of free charge carriers is reflected in the conductivity of the semiconductor that reinforces the kinetics of the proton-coupled-electron transfer process (NRR) that requires six electrons and six protons to completely get reduced to ammonia, whereas HER involves much faster kinetics with only two electrons and two protons.¹⁶ Furthermore, the dissociation of the $N \equiv N$ requires a high energy barrier thus thermodynamically not favourable. Although both HER and NRR theoretically require the same potential for initiation, NRR suffers from a huge overpotential and at the applied voltage window and HER becomes predominant. Furthermore, NRR only functions effectively at voltages ranging from 0.1 to -0.6 V (vs. RHE) at a lower current density. As the current density increases, the FE for NRR is dramatically influenced due to rapid H₂ evolution because of the applied negative potential. In fact, most of the metals favour H-adsorption of their surface and result in a poor selectivity for N_2 . Thus, interface engineering with metal and semiconductor acts like "hitting two birds with one stone" in a way that, it preserves the surface-active metal centers for N_2 activation, thereby suppressing HER with a high FE for NRR and the lowered work function helps to lower the activation energy barrier of the rate determining $*N_2 \rightarrow *N_2H$ step resulting in an improved NRR kinetics.¹⁷ But with SnS_2 as a material of interest, this phenomenon is completely unexplored.

In this chapter, the hexagonal SnS_2 facets have been assembled with an underlying layer of cubic NPG, which served both as a conducting support as well as a current collector. The work function of NPG is smaller than the *n*-type semiconductor (SnS₂), which helps in the transfer of free charge carrier densities towards SnS_2 across the contact layer at their interface. Due to the Mott-Schottky effect, the resultant heterostructure exhibited a lower work function (Φ) of 5.75 eV than pristine SnS₂ (Φ =5.98 eV) with accessible electron carrier density. The repositioning of the d-band center of the surface Sn atoms of NPG@SnS₂ energetically favored the N₂ adsorption on its surface by weakening the competitive H-adsorption. This ensured HER suppression and subsequently a high 49.3 % FE for ammonia formation at -0.5 V in 0.1 M Na₂SO₄ electrolyte.

5.3 Experimental Section

5.3.1 Synthesis of NPG@SnS2 electrocatalyst

The synthesis of NPG@SnS₂ followed several elementary steps to form each of the layers that constituted the electro-active material. Firstly, glass substrates $(1 \times 1 \text{ cm}^2)$ were cleaned successively with IPA, water and acetone and hot-air dried to make it clean from any kind of aerial impurity. This step was followed by the acid etching of gold-silver alloy to obtain fine sheets of NPG, which was then transferred on the glass substrates. This layer was coated with a ~100 nm thick Sn layer *via* e-beam deposition at 0.5 A/s, which was then subjected to sulphurization at 450 °C in Ar atmosphere at 7.5 °C/min to obtain the semi-conducting SnS₂ layer over NPG and a metal-semiconductor interface at their junction. Thus, NPG plays a dual role of a conducting support as well as a current collector.

 SnS_2 was synthesized following the similar experimental conditions, only without the underlying NPG layer. Here, in place of glass, FTO coated glass served as the conductive substrate.

5.3.2 Computational modeling

The Au(111)/SnS₂(101) interface was prepared with QuantumATK S-2021.06 using 5 layer of Au (111) and 4 layers of SnS₂(101) slab.¹⁸ The interfacial orientation was chosen to have the lowest strain for both SnS₂ and Au *via* a pareto optimal analysis such that the simualtion cell is not too large.¹⁹ The geometry optimizations were performed using DFT with the GGA for the exchange-correlation potential.²⁰ The PAW method and a planwave basis set were used.^{21,22} The kinetic energy cut-off for the plane-wave basis were set to 270 eV. A vacuum of ~30 Å was set to avoid the interaction between periodic images. The bottom two layers of gold atoms were kept fixed. The interface geometries were considered converged when the forces all free atoms were lower than 0.01 eV/Å. A dipole correction was applied in z-direction (normal to the slab surface). The first Brillouin zone was sampled with $1\times3\times1$ Monkhorst {Pack k-point mesh. All the computation were carried out using the VASP.²³ Our gold surface work function matched well with state-of-the-art results with similar DFT method.²⁴

5.4 Results and discussion

5.4.1 Synthesis and identification of interfacial structure of NPG@SnS $_2$

The synthesis of NPG@SnS₂ involves several elementary steps (see experimental section for details). Out of which the most crucial step is the synthesis of phase-pure SnS₂ over NPG. To execute the same, the as-assembled NPG@Sn (obtained by e-beam deposition

of Sn over NPG) was subjected to surface chalcogenation at a temperature of 450 °C as depicted in Figure 5.1, keeping a fast reaction rate of 7.5 °C min⁻¹ as the vaporisation



Figure 5.1. Schematic representation of the synthesis of NPG@SnS₂ for NRR.

temperature of Sn and S is ~ 230 °C and ~ 115 °C respectively. In general, temperatures above 350°C are required to form the pure hexagonal crystal of SnS₂, as demonstrated by Amroun et. al.²⁵ The heterostructure thus produced displayed an arrested underlying layer of porous interconnected network of NPG with an irregular flake like morphology of SnS₂ as observed from the SEM image in Figure 5.2a. The thickness of each of the layers (NPG \rightarrow NPG@Sn \rightarrow NPG@SnS₂) was determined from a surface profilometer and it was obtained that NPG on the glass substrate and NPG@Sn had a thickness of about 136.9 nm and 236.9 nm respectively, which was in well accordance with our experimental conditions of e-beam deposition of Sn on NPG. The thickness of the overall catalyst NPG@SnS₂ and pristine SnS₂ were found to be 363.1 nm and 226.2 nm respectively, which were eventually rendered for their conductivity measurements. For a vivid knowledge of the heterojunction of NPG@SnS2, TEM and more precisely, HRTEM analyses were adopted, as can be seen from Figure 5.2b-d. Distinctly, from Figure 5.2e, the selected area (black square) was performed with IFFT masking (inset of Figure 5.2e and Figure 5.2f-h) displayed the planes of (101) corresponding to the sharp lattice fringes of d-spacing value 0.272 nm for hexagonal SnS₂ and (111) plane for NPG, corresponding to 0.232 nm fringe width²⁶ formed at the interface of the highly crystalline heterostructure. It is likely to expect that the (111) plane of NPG would interact with the SnS₂ (101) plane through the S-edges as the adsorption of S atoms is energetically favoured over the hollow sites of the face-centered cubic lattice of NPG.^{27,28} The SAED pattern in Figure 5.2i emphasizes the polycrystalline nature of the NPG@SnS₂ at the interface, predominant with the planes for SnS₂ as well as NPG. As in this case, the SnS₂ phase has been intentionally synthesised as our material of interest, XRD of NPG@SnS2



Figure 5.2. (a) SEM image of flakelike SnS_2 over the NPG layer; (b–d) TEM image of NPG@SnS₂ at different resolutions; (e) HRTEM image of the material; inset of (e) and (f)) show IFFT of NPG@SnS₂ showing distinct layers of NPG and SnS_2 at the heterojunction derived from masking the black box region in (e); line profile for the selected line in the IFFT image of NPG@SnS₂ indicating its d spacing value of (g) 0.232 nm for NPG and (h) 0.272 nm for SnS₂; (i) SAED pattern of NPG@SnS₂ at the interface.

become an inevitable characterization tool to justify the phase purity of the synthesised material. Figure 5.3a displayed a collab of the pure hexagonal phase of SnS_2 (JCPDS Card No. 23-0677) with peaks at 15.39°, 27.80°, 30.42°, 32.63°, 52.42°, 63.28°, 67.18° representing the respective (001), (100), (002), (101), (211), (004) and (202) planes^{29,30} and the face-centred cubic phase of Au crystal (JCPDS No. 04-0784) with peak positions at 38.67°, 44.85°, 64.98° and 77.98° resembling the (111), (200), (220) and (311) planes respectively³¹ with no perceivable impurities. This justifies the formation of pure SnS_2 with no interference of SnS or Sn_2S_3 phases. The more interesting information from the XRD analysis is that, the (101) plane of SnS_2 lied adjacent to the (111) plane of NPG, which makes it obvious that the interface would be formed between these two planes as already proved from the IFFT of the HRTEM image of NPG@SnS₂. The adjunction between the (111) plane of NPG and the (101) plane of SnS₂ was made possible through the S atoms of SnS₂, as mostly this particular plane of Au actively interacts with the S-

atoms (soft-soft interaction) at the cost of low energy barrier, which in turn facilitates the electrocatalytic NRR process as shown in several reports.^{32,33} It was presumed that this interface formation apparently affected the out of plane stretching vibration of the S



Figure 5.3. (a) XRD of NPG@SnS₂ and pristine SnS₂ and NPG catalysts; (b) RAMAN of NPG@SnS₂ and pristine SnS₂; XPS deconvoluted spectra of (c) Sn 3d and (d) S 2p of NPG@SnS₂.

atoms^{34,35}, bonded to the Au atoms of NPG was reflected in the peak shifting of the A_{1g} phonon mode³⁶ at ~311 cm⁻¹ in the Raman spectrum of NPG@SnS₂ in Figure 5.3b, which was positioned at ~307 cm⁻¹ for pristine SnS₂. This interfacial interaction between NPG and SnS₂ would alter the electronic states of the dichalcogenide entity affecting the NRR performance of the hetero-structure material. A detailed discussion about the electronic properties is elaborated in the later sections of this chapter. However, the elemental composition (Table 5.1) from the energy dispersive EDX analysis at the visible

Elements	Atomic %
Gold (Au)	79.28
Tin (Sn)	7.68
Sulphur (S)	13.04

*Table 5.1. Elemental analysis of NPG@SnS*₂ *catalyst obtained from EDX analysis.*

interface of NPG@SnS₂ corroborated the formation of phase-pure SnS₂ over NPG with the atomic weight percentage of Sn being 7.68% and that of S being almost its double that is 13.04%. A more elaborate understanding of the chemical state of the constituent elements of NPG@SnS₂ catalyst was observed from the XPS. Being a surface sensitive technique, it is highly prone to detect surface functionalities and, in our case, a kink of O 1s spectra appeared in the full survey that might have occurred due to slight surface oxidation of our catalyst. The high-resolution deconvoluted spectrum of Sn 3d in Figure 5.3c disclosed Sn 3d_{5/2} and Sn 3d_{3/2} peaks at 489.1 eV and 497.5 eV respectively for the Sn⁺⁴ electronic state with a doublet separation for the spin orbit coupled peaks to be 8.34 eV. For S²⁻, the deconvoluted XPS spectrum of S 2p in Figure 5.3d revealed the respective peaks for S 2p_{3/2} and S 2p_{1/2} at 164 eV and 167 eV.

5.4.2 Role of NPG in fine-tuning the electronic band structure of SnS₂

To fabricate a semiconducting electrocatalyst for any electrochemical reduction process, it is extremely vital to prioritize a noticeable improvement in its conductivity. This could be brought about by lowering the work function that would populate more electronic states near the Fermi level prior to donation. In this context, SnS₂ has been interfaced with NPG with an expectation to observe the desired improvement. The metal under investigation was carefully chosen such that, (a) it follows the Mott-Schottky rule, that is, it should possess an optimum work function, lowering the energy barrier for carrier transport and (b) depending on the n/p-type nature of the semiconductor, the work function of the metal should be either lower or higher, so that a contact layer could be established at the metal-semiconductor interface, resulting in a reduced work function of the final heterostructure. The second point is indeed crucial, as it has been surveyed that, charge transport manifested a lowered work function, which is generally helpful to increase the effectiveness and kinetics of electrocatalytic reactions like oxygen electrocatalysis.³⁷ In the context of NRR, it has been proven to lower the activation energy barrier of the rate determining $*N_2 \rightarrow *N_2H$ step, resulting in improved NRR kinetics and a high FE.

The affirmation of the *n*-type semiconducting nature of SnS_2 was obtained from the negative slope in the Mott-Schottky analysis as shown in Figure 5.4a. So, to attain our desired goal, NPG, being a highly conductive material ($\sigma = 11.124$ kS cm⁻²), was wisely chosen as the current collector and conductive support for SnS₂. The obtained heterostructure, NPG@SnS₂, restored the *n*-type semiconducting nature as evident from



Figure 5.4. Mott–Schottky experiment with (a) SnS_2 and (b) $NPG@SnS_2$ catalysts in 0.1 M Na_2SO_4 ; (c) Tauc plot representing the direct band gap values of $NPG@SnS_2$ and pristine SnS_2 respectively; (d) KPFM analysis of NPG, NPG@SnS_2, and pristine SnS_2 catalysts; (e) modification of the work function of the NPG@SnS_2 surface compared to the pure SnS_2 (101) surface. The black and red solid lines represent the variation of the electrostatic potential profile averaged across the x–y plane (parallel to the surface) as a function of the z-axis of the supercell for SnS_2 and $NPG@SnS_2$, respectively. The work functions of the surfaces are calculated from the vacuum level estimated at the center of the space between two periodic slab images. Au, Sn, and S atoms are represented with yellow, red, and white spheres.

the negative slope in the Mott-Schottky analysis in Figure 5.4b. This Mott-Schottky effect also results in a lower band gap ($E_g = 2.1 \text{ eV}$) of NPG@SnS₂ than the pure hexagonal SnS₂ lattice ($E_g = 2.2 \text{ eV}$) as can be seen from Figure 5.4c (Equation 2.10 and 2.11 of chapter 2).³⁸ As probed from KPFM, the work function (Φ) of NPG was calculated to be 5.55 eV from the V_{CPD} of NPG to be ~ 280 mV as shown in Figure 5.4d (Equation 2.14 from chapter 2), hence fermi level position of NPG was found to be

electronically higher than that of SnS₂, which makes it an ideal support to impart charge density to the semiconductor side across the metal-semiconductor interface. Interestingly, the V_{fb} of NPG@SnS₂, as calculated from Equation 2.12 of chapter 2, was at a higher energy (-0.23 V) as compared to pristine SnS_2 (-0.44 V), which provided an indication of a lowered work function of the final NPG@SnS₂ catalyst. Thus, the KPFM measurements were further applied for the two systems to probe the exact work function of the materials under investigation. Figure 5.4d shows that the pristine SnS₂ surface potential (V_{CPD}) was 712mV, higher than the heterostructure NPG@SnS₂ (V_{CPD}=~476mV), resulting in a lower work function of NPG@SnS₂ (Φ =5.75eV) than pristine SnS_2 (Φ =5.98eV) from Equation 2.14, chapter 2. The lowering of work function of the heterostructure is due to a built-in electric field at the interface that drifted the majority (electrons) and minority (holes) charge carriers apart resulting in the upward deflection of the Fermi level at the contact layer.³⁹ From DFT simulations using five layers of NPG (111) and four layers of SnS₂ (101) slab, the redistribution of electronic charge density and corresponding electrostatic effects led to a shift of the work function of SnS_2 from 5.93 eV on the pure $SnS_2(101)$ surface to 4.96 eV for the NPG@SnS₂ (Figure 5.4e). This reduction of work function is known to increase NRR activity by reducing the energy of the rate determining N_2 to N_2H step,⁴⁰ and thus the interface will significantly increase the overall rate kinetics of NRR with an improved FE.⁴¹

The charge redistribution at our metal-semiconductor junction has been similarly evidenced in metal-oxide⁴² and metal-dichalcogenide interfaces, reported recently.⁴³ An integration of the charge density difference along the z-axis shows an overall accumulation of electronic charge on the SnS₂ layer and an overall depletion of electronic charge in the NPG layer (Figure 5.5a). An overall shift of electron density toward the SnS₂ layer from the NPG layer (Figure 5.5b) has been quantified using the Bader charge analysis (Figure 5.5c). The lower work function of NPG than pure SnS₂ ($\Phi = \sim 5.98 \text{ eV}$) and the weak electron accepting ability of the S atoms withdrew the electronic bands of SnS₂ at the interface of NPG@SnS₂ until the fermi levels of the metal and the *n*-type semiconductor reached an equilibrium state, as schematically represented in Figure 5.5d.⁴⁴ This electronic movement from the metal to the semiconductor sets up a negative charge in its contact layer. As the electrons approached the surface, their energy decreased across the anti-barrier layer and an increment of the free-charge carrier concentration inside the contact layer of the semiconductor eventually increased the



Figure 5.5. (a) Bader charge density analysis of the NPG@SnS₂ interface. Charge accumulation and depletion along the Z-axis; (b) Charge depletion and accumulation on the individual atoms where a blue isosurface indicates depletion and a pink isosurface indicates accumulation; (c) The partial charges of atoms at the interface layer between the SnS₂ and Au layers are indicated with text near the atoms. The total charge shift summed over all atoms in the Au and SnS₂ slabs is indicated in the inset. Color code: red, Sn; gray, S; gold, Au; (d) Schematic representation of the band bending at the interface of NPG@SnS₂ catalyst; (e) I–V (conductivity) measurements and (f) EIS analysis of NPG@SnS₂ and pristine SnS₂ with Nyquist plots and the equivalent circuit (inset of figure f).

conductivity of NPG@SnS₂ (1.35 kS cm⁻¹) about ten times than pristine SnS₂ (0.31 kS cm⁻¹) as calculated using equation 2.15 and 2.16 from chapter 2 (Figure 5.5e). This is in well accordance with the EIS analysis, where NPG@SnS₂ displays a smaller diameter for the charge-transfer resistance as compared to SnS₂ (Figure 5.5f) indicating a faster

Catalyst properties	NPG@SnS ₂	SnS ₂
Conductivity from I-V measurement (kS cm ⁻¹)	1.357	0.308
Surface Potential from KPFM analysis (mV)	476	712
Band gap (\mathbf{E}_{g}) from UV-vis spectroscopy (eV)	2.1	2.2
Flat band potential (E _f) from Mott-Schottky (V vs. NHE)	-0.23	-0.44
Work Function from KPFM analysis (eV)	5.75	5.98
d-band centre of surface Sn from DFT calculations (eV)	-3.47	-2.91

Table 5.2. Electronic properties of NPG@SnS₂ and pristine SnS₂.

charge transfer kinetics for NRR.⁴⁵ All the electronic properties and band position related information of NPG@SnS₂ and SnS₂ have been tabulated in Table 5.2.

5.4.3 Electrochemical NRR performance of NPG@SnS2

High FE and improved NRR kinetics are inevitable if competitive HER is suppressed at the electrode surface. A lowering in the d-band centre of the surface-active site is known to weaken the H-adsorption.^{46,47} DFT simulations for this chapter reflects that, when SnS_2 was interfaced with NPG, the d-band centre of the surface Sn atom, active for NRR shifted from -2.91 eV for pristine SnS_2 to -3.47 eV for NPG@SnS₂ (Figure 5.6a). This deviation reflected that HER would be suppressed at the active site, resulting in the facile adsorption of N₂ initiating NRR. This effect was rather emphasized in Figure 5.6b, where the adsorption of H (*H) on S was energetically favoured (1.39 eV lower in energy) compared to *H on Sn. This led to two effects: (a) the electrocatalytically active surface Sn in NPG@SnS₂ was preserved for facile N₂ adsorption, and (b) the competitive HER was suppressed at the catalyst surface, which contributed to achieve 49.3 % FE with our material.



Figure 5.6. (a) Modification of the d-band center of the surface Sn from the SnS_2 surface (red) to $NPG@SnS_2$ surface (blue); the inset indicates a shift of the d-band away from the Fermi level to weaken the Sn-H interaction; (b) depiction of H-adsorption on S and Sn on the $NPG@SnS_2$ surface; color code: red, Sn; light gray, S; gold, Au; blue, H; (c) LSV polarization curves of $NPG@SnS_2$ in Ar and N_2 purged 0.1 $M Na_2SO_4$ electrolyte; (d) Bar plot showing the yield and FE of ammonia formation at different applied potentials for $NPG@SnS_2$ catalyst, error bars represent standard deviation value from three different data sets; (e) Mechanism for the NRR, showing the facile adsorption of N_2 over protons on the catalyst (Sn) surface.

The electrochemical activities concerning NRR were carried out in an H-type electrolyzer separated by Nafion 115 membrane, which allows only protons to migrate between the anodic and cathodic chambers and restricts the movement of the formed NH₃ to the cathodic compartment, inhibiting its oxidation. To avoid any impurities from the Nafion membrane, it was pretreated in 5 wt% H₂O₂ aqueous solution followed by ultrapure water, for 1 h each and at a constant 80 °C temperature. All the measurements were conducted in a three-electrode system where Ag/AgCl (3 M KCl) and Pt-wire served as the reference and counter electrodes respectively and 0.1 M Na₂SO₄ as the working electrolyte. The working potentials were calibrated with respect to the RHE according to Equation 2.6, chapter 2. The working electrode was composed of NPG@SnS₂ film formed over a glass substrate, where NPG played the dual role of current collector as well as an active catalyst material for the growth of SnS₂ film on it. In the case of the control experiment with only SnS₂, FTO served as the conducting support. The NH₃ produced by each experiment was quantified using the Indophenol method and estimated based on the calibration curve obtained with a known concentration of NH₃ following the equation y = 0.081x + 0.028. A similar procedure was adopted to verify the side product formation (N_2H_4) by the Watt and Chrisp method.

The coveted alteration of the electronic properties of the active material already acknowledged the candidacy of NPG@SnS₂ for NRR, and the deviated proton adsorption secured the Sn active sites for NRR due to which a variation was observed in the cathodic current densities in the LSV curves in Figure 5.6c in Ar and N₂ saturated electrolyte conditions. Taking a range of potentials from -0.3 to -0.7 V vs. RHE, covering the onset region in the LSV curve, potential dependent CA studies produced NH₃ on NPG@SnS₂. The concentration and eventually the yield of NH_3 was calculated to be 20.72 µg h⁻¹ cm⁻ 2 at -0.6 V (maximum value), while the FE was strikingly high (49.3 %) at -0.5 V as evident from the bar plot (with error bar showing the standard deviation of values obtained from repeated experiments thrice) in Figure 5.6d (Equation 2.18 and 2.19 of chapter 2 respectively). This expected outcome was justified by the calculation of the dband centre⁴⁸ from the density of states of the Sn atoms at the surface, where a strong negative shift of the d-band from the Fermi level was observed in case the of the NPG@SnS₂ surface compared to the pure SnS₂ surface, which promoted NRR kinetically as schematically shown in Figure 5.6e. Thus, charge redistribution at the NPG@SnS₂ interface exacerbates a series of effects playing in the background, which eventually improved the FE for NRR with our material: (a) the shift of the d-band weakened the

interaction of *H and energetically favoured N₂ adsorption on the Sn site, thereby restricting HER and producing high FE for NRR; (b) the in-between-planar interaction of NPG and SnS₂ produced an electron-rich interface which helped to lower the work function of NPG@SnS₂ as compared to its pristine counterpart, and (c) accessible charge accumulation over SnS₂ eventually increased the conductivity of our catalyst with easily accessible charge carriers prior to participation in NRR.

To justify the improved performance of NPG@SnS₂, control experiments were conducted with pristine SnS₂ and NPG, where, not only the yield but also the FE for NH₃ production were reduced drastically, as shown in Figure 5.7a. This result is in well accordance with the fact that, SnS₂ is an *n*-type semiconductor⁴⁹ having inferior intrinsic electrical conductivity, hence unsuitable for the proton-coupled-electron transfer during electro-catalysis.⁴⁵ However, NPG (Figure S20 e,f) displayed a better diffusivity of the working electrolyte with an even better active site density owing to its porous interconnected ligaments.⁵⁰ But, surprisingly, it also receded in the NRR performance because it exhibits better kinetics for the HER at low energy expenditure that inhibits



Figure 5.7. (a) Comparative bar plot of NPG@SnS₂ and different controlled catalysts revealing their NRR performance; (b) Bar plot showing yield of NH₃ at -0.6 V in N₂ and Ar and at OCP in N₂ purged 0.1 M Na₂SO₄; (c) NRR performance of NPG@SnS₂ catalyst after five consecutive cycling experiments at -0.6 V; (d) UV-vis absorption spectra for the detection of N₂H₄ at different applied potentials after 2 h of NRR measurements; (e) ¹H NMR spectra of ¹⁴NH₄⁺ and ¹⁵NH₄⁺ developed upon isotope labelling experiment in 0.1 M Na₂SO₄ with ¹⁵N₂ and ¹⁴N₂ as the feeding gases; (f) Stability of NPG@SnS₂ catalyst for prolonged 22 h at -0.6 V, with the inset showing a before and after stability comparison of the XRD data.

the reduction of N_2 on its surface.^{51–54} Besides being the best contender, this NPG@SnS₂ catalyst was also product-selective as at all the different potentials, no N_2H_4 was detected in the UV-vis spectra at 460 nm (Figure 5.7b). As a matter of verification that the NH₃

produced during the experiment was chiefly achieved from the feeding N₂ gas and not from any other nitrogenous impurity source, several blank CA experiments were conducted like 1) NPG@SnS₂ at -0.6 V in Ar saturated with 0.1 M Na₂SO₄, 2) NPG@SnS₂ at OCP in N₂ saturated electrolyte. In both cases the yield of NH₃ was even less than 0.3 μ g h⁻¹ cm⁻² as shown in the bar plot in Figure 5.7c.

The confirmation of the origin of NH₃ produced during NRR was obtained from the isotopic labelling experiment with ${}^{15}N_2$ feeding gas as shown in Figure 5.7d. The ¹H NMR spectrum corresponding to ${}^{14}NH_4^+$ displays a triplet coupling with a J_{N-H} of 52 Hz when ${}^{14}N_2$ served as the feeding gas, while a doublet coupling with non-identical peak positions was observed for the ${}^{15}NH_4^+$ with a J_{N-H} of 74 Hz. This confirmed that the NH₃ was completely derived from the feeding gas only and there were no nitrogenous impurities, either in the electrolyte or in the catalyst.

In practice, two factors must co-exist: (a) an exciting NRR activity and (b) the retainment of the performance for extended periods of time without compromising the material structure or crystallography. NPG@SnS₂ displayed repetitive and reproducible cycling data for NH₃ yield and FE for five CA cycles under the same experimental conditions at -0.6 V in N₂ saturated 0.1 M Na₂SO₄ as can be seen from the bar plot in Figure 5.7e. The potent candidature of NPG@SnS₂ in NRR was examined with a continuous CA run for 22 h (Figure 5.7f). Along with a notably stable current density, there with no change in the crystallographic phases of NPG@SnS₂ as evident from the XRD data (for fresh and used samples before and after stability in the inset of Figure 5.7f). The stability of our active material was verified three times, which thus concluded the superior robustness of the active material amidst the prolonged experimental conditions of NRR. To the best of our knowledge, our synthesized material NPG@SnS₂ forecasted a potential efficiency for NRR with FE as high as 49.3 %, which is the highest among all the dichalcogenide and interfacial-engineering based catalysts reported for NRR till date, as shown in Table 5.3 and Table 5.4.

Catalysts	Electrolyte	NH ₃ yield (μg h ⁻¹ mg _{cat} ⁻¹)	NH ₃ yield (μg h ⁻¹ cm ⁻²)	FE (%)	Potential (V vs RHE)	References
Mo-doped SnS ₂	0.5 M LiClO ₄	41.3	-	20.8	-0.5, -0.4	<i>J. Mater. Chem.</i> <i>A</i> 2020, 8, 7117– 7124
Sn/SnS ₂	0.1 M NaOH	23.8	-	6.5	-0.8	<i>Small</i> 2019, 1902535
pAu/NF	0.1 M Na ₂ SO ₄	-	9.42	13.36	-0.2	<i>Small</i> 2019, 1804769
NPG	0.1 M KOH	30.5	-	-	-0.2	ACS Sustain. Chem. Eng. 2019, 7, 10214– 10220
NPG@ZIF-8	0.1 M Na ₂ SO ₄	-	28.7	44	-0.8, -0.6	Angew. Chem. Int. Ed. 2019, 131, 15506– 15510
Au/CoO _x	0.05 M H ₂ SO ₄	15.1	-	19	-0.5	Angew. Chemie. Int. Ed. 2019, 58, 18604- 18609
S/Au NWs	0.1 M Na ₂ SO ₄	21.04	-	15.34	-0.2	ACS Sustain. Chem. Eng. 2019, 7, 19969– 19974
Au-CNT	0.1 M HCl	-	57.7	11.97	-0.2	ACS Appl. Mater. Interfaces 2020, 12, 42821– 42831
Au(111)@Bi ₂ S ₃	0.1 M Na ₂ SO ₄	-	45.57	3.10	-0.8	ACS Appl. Mater. Interfaces 2020, 12, 55838– 55843
S-mAu film/NF	0.1 M Na ₂ SO ₄	22.7	-	17.2	-0.2	<i>J. Mater. Chem.</i> <i>A</i> 2020, 8, 20414–20419
NPG@SnS ₂	0.1 M Na ₂ SO ₄	-	20.72	49.37	-0.6, -0.5	This chapter
Note: pAu/NF = porous Au film on Ni foam, ZIF = zeolite imidazole framework, NWs = nanowires, CNT = carbon nanotube, S-mAu film/NF = Sulphur-decorated mesoporous Aubased film on Ni foam.						

Table 5.3. Summary of the electrocatalytic performance of the reported SnS_2 and Au based catalysts for NRR.

Catalysts	Electrolyte	NH ₃ yield (μg h ⁻¹ mg _{cat} ⁻¹)	NH ₃ yield (μg h ⁻¹ cm ⁻²)	FE (%)	Potential (V vs RHE)	References
MoS_2/C_3N_4	0.1 M Na ₂ SO ₄	19.86	-	6.87	-0.5	ACS Sustainable Chem.Eng., 2020, 8, 8814–8822
SnO ₂ /RGO	0.1 M Na ₂ SO ₄	25.6	-	7.1	-0.5	ACS Appl. Mater. Interface, 2019, 11, 31806–31815
CoS ₂ /NS-G	0.05 M H ₂ SO ₄	25	-	25.9	-0.2, - 0.05	<i>Proc. Natl. Acad.</i> <i>Sci.</i> 2019, <i>116</i> , 6635–6640
V _{r-} ReSe ₂ @CBC	0.1 M Na ₂ SO ₄	-	28.3	42.5	-0.25	Angew. Chemie 2020, 59, 13320– 13327
MoS_2/C_3N_4	0.1 M LiClO ₄	18.5	-	17.8	-0.3	ACS Appl. Mater. Interfaces 2020, 12, 7081–7090
Au/Ti ₃ C ₂	0.1M HCl	30.06	-	18.34	-0.2	ACS Appl. Mater. Interfaces 2019, 11, 25758–25765
NPG@SnS ₂	0.1 M Na ₂ SO ₄	-	20.72	49.37	-0.6, -0.5	This chapter
Note: $RGO =$ reduced graphene oxide, $NS-G =$ nitrogen and sulphur doped reduced						

Table 5.4. Summary of the electrocatalytic performance of the reported NRR catalysts based on interface engineering.

Note: RGO = reduced graphene oxide, NS-G = nitrogen and sulphur doped reduced graphene, CBC = carbonized bacterial cellulose.

5.5 Conclusion

In this chapter, the entire focus has been devoted to impeding the competitive HER at the SnS_2 surface, which is one of the major hindrances in achieving high FE for NRR. SnS_2 , known to have a poor electrical conductivity and low selectivity for NRR, was interfaced with the (111) plane of NPG, which turned out to be a perfect shot to (a) lower the d-band center of the surface Sn atoms, which weakened the H adsorption over Sn making it accessible and energetically favorable for facile N₂ adsorption, (b) lowering of the work function with an elevated Fermi level of the NPG@SnS₂ interface and hence (c) increase the conductivity of the heterostructure to provide an abundance of charge supply from the interface to the surface active Sn atoms. The inherited strategy for the NPG@SnS₂ material synthesis was well justified from the 49.3 % FE for NRR at -0.5 V in 0.1 M Na₂SO₄ working electrolyte that clearly showed that HER was suppressed at the electrode active site thereby enhancing the NRR kinetics. From DFT calculations, a net electron cloud could be found to accumulate over the SnS₂ surface with a partial charge

of -0.09, while at the NPG end, a charge depletion was noticed with +0.09 partial charge density. NPG, with a lower work function imparted the negative charge density towards the SnS_2 side at their contact layer in order to equilibrate the fermi levels of the metal and the semiconductor at the interface. This Mott-Schottky effect resulted in a lower work function and increased conductivity of the NPG@SnS₂ as compared to pristine SnS_2 .

Besides performance, the stability of the NPG@SnS₂ catalyst in the harsh electrolyte conditions for a prolonged 22 h showed no compromise with respect to the crystal phases as evident from the pre- and post-stability XRD analysis. Thus, this interface engineering strategy between NPG (metal) and an *n*- type semiconductor SnS₂ enabled a wholesome alteration of the electronic band positions of the final material NPG@SnS₂ due to interfacial charge redistribution and thus provided a route to rationally design HER suppressants and high-efficiency candidates for NRR.

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Chapler 6

Group VIB metal doping in Ag₃PO₄ induce compressive strain and altered d-band center reinforcing electrochemical NRR kinetics

Overview: This chapter concerns the implementation of doping strategy with group VIB metals in Ag₃PO₄ to trigger the NRR activity of the host metal and involve the dopant as an active unit initiating d-p orbital mixing at Ag/dopant-N₂ interface. An elaborate study regarding the crystal structure, d-electronic states and charge density deployments reveals that Mo as a dopant serves as the most efficient candidate as compared to Cr and W. All these catalysts variedly influence the NRR overpotential, as confirmed from the detailed kinetic study with RRDE technique that unsurfaced the rate of current exchanged during the electrode reactions at the catalyst-gas-electrolyte interface. The product selectivity of the catalyst is confirmed from the oxidation peak corresponding to the NH₃ detected at the Pt ring. Hence, it is expected that N₂H₄ will remain a stable intermediate on the active site, exploiting all the electrons and protons into the complete conversion of N₂ to NH₃. Experimental observations complemented with theoretical findings reveal a deeper vision into the obscured reaction intermediates and their binding strength on the catalyst surface, verified from in-situ ATR-FTIR spectroscopy.



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6.1 Motivation of the chapter

NRR is majorly dictated by the N_2 adsorption step because usually most of the metal centers are susceptible to proton adsorption more feasibly. Amidst the abundant source of protons in the aqueous electrolytes, material selectivity plays a very important role, otherwise HER dominates over NRR and the FE gets severely affected. In this context, rather than optimizing the active site, it is better to choose the metal center wisely such that it inherently exhibits a better affinity for N_2 . This would not only help in N_2 adsorption but also prevent active site passivation with protons. Thus, the protons would eventually find their way to the adsorbed N_2 and initiate the first protonation step at a comparatively lower overpotential. So, the purposeful selection of electrocatalyst is important for (a) N_2 adsorption and (b) making a proton conducting path for the easy first protonation step.

6.2 Introduction

Transition metal-based catalysts have been revealed extensively for electrocatalytic ammonia synthesis^{1–3} due to the strong affinity of N_2 adsorption over it. It is generally accepted that transition metals can form a facile sigma bond with N2 owing to their availability of electrons in d-orbitals. Furthermore, it can also allow the back donation of electrons to the π^* orbital of N₂ mitigating the kinetic energy barrier, which is required to activate the N \equiv N.⁴ In this regard, the re-positioning of the d-orbital levels is a major concern that mostly results from the splitting of the degenerate energy states. This in turns depends upon the coordination environment and geometry of the unit cell of the catalyst. The d-orbitals of metals that are energetically close to the σ and π^* orbitals of N₂ generally undergo a d-p mixing resulting into the N-N bond polarization.^{5,6} Besides this, the intrinsic behavior of an electrocatalyst towards N₂ depends on the local electronic structure and charge density of the active site.⁷ These could be manipulated in a number of ways by (a) regulation of the co-ordination environment around active metal site, (b) alteration of density of states and electronic spin states leading to modification of the local electronic structure of a material.⁸ A combinatorial effect of these factors influences the N_2 adsorption and control the binding strength of the intermediates on the catalyst surface empowering NRR kinetics.⁹ Even if a catalyst is suitably designed for NRR, so far a major missing in the field is a proper kinetic study that could justify the rate of the ongoing reaction on the active site owing to reasonable improvisation in the catalyst structure.

Literature findings suggest that, doping could be an effective strategy that largely influences the charge distribution in host metals, regenerates the electronic band positions suitable for metal-N₂ interaction and provides extra active sites prior to N₂ adsorption.¹⁰ Usually the early transition metals like Ti, V possess properties suitable for photocatalysis. Beyond that, among the other transition metals, the group VIB transition metals like Cr, Mo and W have been theoretically proven to have better N₂ adsorption capabilities over the late transition metals as shown by Guo et. al.¹¹ In fact, Mo is the main active unit in the biological nitrogenase enzyme.¹²⁻¹⁴ Thus, in this contextualization, we have rendered a simple coprecipitation strategy to synthesize group VI metal-doped Ag₃PO₄ since Ag has less feasibility for the H⁺ adsorption than the other noble metals.¹⁵. The introduction of dopants altered the d-band center of the Ag close to the Fermi level making it a better suited for interaction with N₂, in addition to its HER retarding property. Interestingly, it has also been observed that, while Ag and Cr/Mo/W are known to favor an end-on N₂ adsorption individually, the presence of both in the system offered a combined active site ensuring a side-on N₂ adsorption. A following charge transfer reaction between active site and N2 via d-p orbital mixing at the interface lowered the overpotential for the first protonation step that was kinetically determined with RRDE technique. A combinatorial experimental as well as theoretical finding ascertained Mo as the most efficient dopant to elevate the performance of Ag_3PO_4 with 54.8 % FE for NRR, where the stable NRR intermediates were identified with in-situ ATR-FTIR spectroscopy.

6.3 Experimental Section

6.3.1 Synthesis of group VI metal-doped rhombohedral Ag₃PO₄

The rhombohedral Ag₃PO₄ was synthesized via a simple precipitation method. Typically, 0.588 mmol of AgNO₃ has dissolved into 60 ml of DI water. On the other hand, 5 mL of aqueous 0.15 M Na₂HPO₄ solution was prepared. In this solution, the metal precursor of VI group metal (CrCl₃, Na₂MoO₄, and Na₂WO₄) was dissolved. The AgNO₃ and metal precursor were taken in 5:1, 10:1, and 15:1 ratio. The metal precursor containing Na₂HPO₄ was added dropwise to the AgNO₃ solution under continuous stirring and 60 °C temperature. The solution was kept at the same condition for 1 h till the yellow precipitate. The synthesized materials are named M/Ag₃PO₄-5, -10, and -15, respectively. The M denotes the VI group metals chromium (Cr), molybdenum (Mo), and tungsten (W). To remove the nitrate impurities the synthesized samples are washed

with 0.1 M KOH followed by DI water through centrifugation. Along with these, for a comparative study, bare Ag₃PO₄ was synthesized by a similar method without using the metal precursors.

6.3.2 NRR kinetics study using RRDE

The overall NRR current density (*j*) is a function of $j_{\rm K}$ (kinetic current density) and $j_{\rm L}$ (diffusion-limiting current density). At the higher overpotential region, the reactants (N₂), upon reaching the electrode surface, immediately get reduced, leaving behind a net zero reactant concentration on the electrode surface. This leads to formation of a flat plateau region governed by the $j_{\rm L}$ which is determined by the rate of nitrogen diffusion onto the surface of the electrode, and it is dependent on the rotating speed in the RRDE measurement. On the other hand, $j_{\rm K}$ depends upon the reaction kinetic process, rate of oxygen reduction on the electrode surface, and number of electrons transferred. Thus, the overall current density can be achieved from the K-L equation 6.1.

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K}$$
(6.1)

where, ω is the angular velocity of the electrode ($\omega = 2\pi N$, *N* is the linear rotation speed) and *B* is the Levich slope. From the corresponding K-L plot, 1/*B* and 1/*j*_K can be obtained as the slope and the intercept, respectively. Current densities are expressed in mA cm⁻².

6.3.3 In-situ ATR-FTIR studies

In-situ ATR-FTIR studies were carried out with Si FAC in a spectro-electrochemical cell equipped with a three-electrode set-up. The background was collected with the electrolyte and all the sample measurements were taken with 128 scans and resolution 4 in absorbance mode. All data were further baseline corrected and were collected by holding different cathodic potentials for a definite time-span.

6.3.4 DFT Calculations and Methods

DFT calculations for geometry optimization were conducted using the VASP.¹⁶ The exchange and correlation effects were described by the PBE functional within the GGA.¹⁷ Electron-electron interactions were accounted for using the PAW method.¹⁸ A plane-wave cutoff energy of 450 eV was applied to all simulations, and a k-point mesh of $5\times5\times1$ was used for Brillouin zone sampling. Optimization procedures persisted until the total energy per atom reached below 10^{-6} eV, and the forces converged to 0.01 eV/Å. To prevent interactions between periodic images, a 15 Å vacuum was established in all directions.

The evaluation of catalyst activity towards NRR involved calculating the overpotential (η) through a free energy profile. The Gibbs free energy (G) for this profile was determined using the equation: G = E + ZPE - TS - neU, where E represents the DFT-calculated energy, n signifies the number of transferred electrons, and U is the applied electrode potential.¹⁹ Notably, the entropies and zero-point energies of adsorbed atoms/ions were found to be negligible in comparison to those of the gaseous phase under room temperature and ambient pressure conditions. The reported values of entropies and zero-point energies from the chemical database²⁰ were adopted for free molecules, assuming a situation at U = 0 V within the free energy profile.

6.4 Results and discussion

6.4.1 Interfacial interaction of doped Ag₃PO₄ materials with N₂ influencing NRR

The primary set-back of NRR is the N₂ activation on the catalyst surface. A facile bonding anti-bonding interactions between active site and N₂ initiate N=N bond polarization that is a very crucial need for the first protonation step. Since both Ag and the dopants have preferences towards N₂ adsorption, at the electrode-electrolyte interface, it is expected that N₂ molecules will form a gaseous layer over the catalyst surface. In this condition, the p-orbitals of N=N (σ and π^*) would overlap with the energetically accessible d-orbitals of LUMO and HOMO of the metals (Ag and dopant) in a side-on manner. The electronic strain thus generated in the N₂ would offer charge inequality over the N atoms leading to facile first protonation step at a low overpotential. The extent of charge transfer from the active site to N₂ would determine the rate of NRR kinetics and help to gain an insightful understanding of the NRR mechanism in our designed catalysts.



Figure 6.1. Synthesis strategy and energy optimized crystal structure of Ag₃PO₄, Cr/Ag₃PO₄, Mo/Ag₃PO₄ and W/Ag₃PO₄, where grey, mov, red, cyan, pink, and green colors represent Ag, P, O, Cr, Mo, and W atoms respectively.

The material Ag₃PO₄ has been intentionally doped in this chapter via a very simple mechanical stirring approach for 1 h at 60 °C to obtain the energetically stable catalysts (as shown in Figure 6.1) in order to bring about changes in the d-electronic states of Ag and influence the interaction between the catalyst and N₂. Generally, these systems are prone to experience alteration in electronic structures that eventually act as a descriptor to dictate their NRR performance and can be revealed with XPS. Primarily, the presence of various elements in the developed materials and the corresponding valencies are shown from XPS in Figure 6.2 indicating a successful doping of Cr, Mo and W metals in the Ag₃PO₄ crystal structure. It was more interesting to analyze the deconvoluted Ag 3d spectra for all samples (Figure 6.3a) that showed the two spin-orbit



Figure 6.2. XPS deconvoluted narrow spectra of (a) O 1s and (b) P 2p for Ag_3PO_4 ; (c) O 1s, (d) P 2p and (e) Cr 2p for Cr/Ag_3PO_4-10; (f) O 1s, (g) P 2p and (h) Mo 3d for Mo/Ag_3PO_4-10; (i) O 1s, (j) P 2p and (k) W 4f for W/Ag_3PO_4-10.

coupled 3d_{3/2} and 3d_{5/2} peaks positioned at 374.14 and 368.14 eV, respectively, ascribing the presence of Ag in the +1-oxidation state. The doping of group VI elements apparently lowered the binding energy of the Ag 3d peaks. This marked the possibility that an electron transit prevailed between Ag and the dopant and a local charge accumulation over Ag due to oxygen vacancy (as confirmed from the deconvoluted narrow spectra of O 1s for all samples) that intended to shift the binding energy of the core electrons to a lower end in the order Mo>W>Cr.²¹ This eventually indicated an upshift of the metal dband center close to the Fermi energy state²² as obtained from the VBS using equation 2.17 of chapter 2, shown in Figure 6.3b.^{23,24} Imperatively, there will be less electron occupancy of the anti-bonding states of the Ag active site as discussed in Figure 6.3c.^{25– 27} This phenomenon is best observed for Mo/Ag₃PO₄-10 > W/Ag₃PO₄-10 > Cr/Ag₃PO₄-10 > Ag₃PO₄ according to the trend of peak shifting in the XPS spectra. This would not only ascertain a better orbital overlap tendency of Ag 3d with N 2p but the dopant site would add to the active site density of the materials ensuring a side-on N₂ adsorption, as



Figure 6.3. (a) Deconvoluted Ag 3d narrow spectra of undoped and doped samples; (b) d-band center positions of the materials derived from the VBS, all spectra are Shirley background corrected; (c) schematic representation of the upshifted d-band center along with the significance with respect to bonding and anti-bonding electronic levels.

anticipated.²⁸ The XPS full survey spectra and ICP-MS revealed ~12:1 atomic weight % of Ag and Mo, as shown in Table 6.1. The overwhelming N_2 adsorption was

Table 6.1. Elemental ratio of Ag and Mo from ICP-MS and XPS analysis for Mo/Ag₃PO₄-10 catalyst.

Elements	Concentration (PPb) from ICP- MS	Atomic % from XPS analysis		
Molybdenum (Mo)	3.04	1.32		
Silver (Ag)	37.37	16.94		

experimentally countered with the CV curves at different scan rates in Ar and N₂ purged electrolytes in the non-Faradaic region for Mo/Ag₃PO₄-10 sample as shown in Figure 6.4a, b. The corresponding double layer formation due to the partial charge polarization at the electrode-electrolyte interface was found to shorten in presence of N₂ (Figure 6.4c) indicating migration and occupancy of the electroactive sites of the catalyst with N₂ from bulk electrolyte to the double layer across the diffuse layer as schematically represented in Figure 6.4d. Eventually the ECSA of the catalyst, calculated using equation 2.8 of chapter 2 was found to be reduced in the N₂ environment than Ar.



Figure 6.4. CV analysis at scan rate 10-50 mV s⁻¹ for Mo/Ag_3PO_4 -10 under (a) Ar and (b) N₂; (c) the comparative C_{dl} of Mo/Ag_3PO_4 -10 derived from the CV curves at different scan rates in Ar and N₂ saturated electrolytes; (d) corresponding schematic representation of the N₂ diffusion and adsorption on the catalyst surface across the double layer. The white, cyne, dark pink, green, grey, blue, red, pink color sphere represents the H, Cr, Mo, W, Ag, N, O, P atom respectively.

6.4.2 Crystal lattice deformation and morphological changes

Successful doping depends upon a number of factors, mainly on the size compatibility of the host and the dopant, and results in a modified spacing in the crystal planes and altered electronic states of the host metal. Primarily XRD analysis was employed on all the synthesized materials. Figure 6.5a displays a relationship between the various developed materials and shows Ag₃PO₄ had a cubic crystal structure without any impurities. All the obtained peaks of Ag₃PO₄ were well matched with the JCPDS No. 006-0505²⁹ and justified the synthesis of phase-pure Ag₃PO₄. The successful doping of group VIB metal ions (Cr, Mo, and W) in the Ag₃PO₄ crystal structure was confirmed as in the slow scan, the peak corresponding to the (210) plane shifted to a higher 20 value lowering the interlayer spacing, which indicated that the doping induced compressive



Figure 6.5. (a) XRD spectra of all the doped and undoped Ag_3PO_4 samples, matched with the JCPDS number-00-006-0505; (b) slow scanned XRD spectra of the catalysts between 30 to 35 20 value showing gradual shifting of the (210) plane to a higher value; (c) schematic representation of the altered interlayer spacing in the Ag_3PO_4 crystal lattice resulting from compressive strain due to doping; FESEM image of (d) Ag_3PO_4 (inset shows rhombohedral morpholgy) and (e) Mo/Ag_3PO_4 -10 catalysts; (f) TEM image of Mo/Ag_3PO_4 -10; (g) HRTEM image of Mo/Ag_3PO_4 -10 showing (h) defects originating from doping in Ag_3PO_4 and (i) d-spacing corresponding to (211) plane in Mo/Ag_3PO_4 -10, inset shows the FFT image of the lattice fringes.

strain in the Ag_3PO_4 crystal structure (Figure 6.5b and 6.5c). It is noteworthy to mention that, doping could be fostered in all crystal planes of Ag_3PO_4 but since (210) plane was predominant, the effect was significant in this. While no extra peaks existed for any composite of Mo and Ag_3PO_4 indicating the successful doping of 'M' in the Ag_3PO_4 crystal structure, after the incorporation of 'M' in the Ag₃PO₄ crystal structure the peak intensity of all diffraction peaks decreased slightly, predicting a decrease in crystallinity. This presumably enhanced the active sites, grain refinement, and lattice defects that might favor the improvement of NRR.^{30,31} Any material improvisation strategy should always have a subject to influence the NRR kinetics, which is the ultimate objective of the chapter. As it is known, the primary step of NRR is the proper adsorption of the N₂ on the catalyst surface, which is only possible if the N₂ leads the competition over protons to chemisorb over the catalyst surface more preferably. Although the thermodynamic feasibility of this process is a great challenge but, in the literature, it is reported that compressive strain can lead to a decrease in the H⁺ adsorption due to the increase in Gibbs free energy for H adsorption.³² So, increase in Gibbs free energy deteriorates the HER and favors the NRR.³³

It is imperative that doping can alter the crystal structure and electronic states of the host but should not have an influence on the alteration of the material's surface structure. Since, from the XPS and XRD analyses, it was conclusive that Mo-doping had maximum impact on Ag₃PO₄, this aided for a detailed morphological analysis and comparison between Ag₃PO₄ and Mo/Ag₃PO₄-10. As shown in Figure 6.5d and 6.5e, Ag₃PO₄ and Mo/Ag₃PO₄-10 exhibited a rhombohedral faceted morphology. The rhombohedral morphology of Mo/Ag₃PO₄-10 was further confirmed through TEM in Figure 6.5f. After doping of 'Mo' in Ag₃PO₄, HRTEM results indicated two major conclusions as shown in Figure 6.5g: (a) the presence of 'O' defects and a decrease in crystallinity resulting from loss of regular lattice fringes (Figure 6.5h), which is well augmented with the XPS and XRD analysis, and (b) the lattice fringe width corresponded to the d-spacing value of 0.241 nm resembling the (211) plane for the Mo/Ag₃PO₄-10 material (Figure 6.5i). In congruence with the XPS analysis of the material with respect to the elemental content, the elemental mapping of the Mo doped material (in Figure 6.6) revealed all the elements in distinct colors (O: yellow, P: brown, Mo: blue and Ag: dark pink) that further corroborated homogeneous doping in the synthesized material.

6.4.3 Synergy of doping and vacancy in scavenging the charge carriers in the catalysts

An important outlook of this chapter is the doping-assisted vacancy generation in the samples. Usually, vacancies are always accompanied by local charge accumulation in



Figure 6.6. EDX mapping of Mo/Ag₃PO₄-10 showing the presence of Mo, Ag, P, and O as elements.

the crystal lattice impacting NRR, which nicely gets arrested in the ESR technique (Figure 6.7a). However, it is to be noted that when an oxygen gets away from the regular crystal lattice, it takes away two electrons and leaves behind two positively charged electron holes, which, when bound with the O-vacant sites, enable hole trapping and a g value in the ESR higher than 2.00.³⁴ As obtained from the XPS spectra, Ag₃PO₄ lattice was partly dominated by O-vacant sites. This induced a local negative charge deficit or a majority of hole carriers bound to the vacant oxygen sites within the lattice. This is what was observed in the ESR spectra of Ag₃PO₄ having g value 2.09. The trend follows in the case of Mo/Ag₃PO₄-10 and W/Ag₃PO₄-10 with the respective g values of 2.17 and 2.13. This is unlike the case of Cr/Ag₃PO₄-10, where g value corresponded to that of free electrons this is 2.00. This value could be mostly attributed to the high paramagnetism obtained for Cr/Ag₃PO₄-10. The Eg of all the materials as shown in Figure 6.7b, c corresponded to the anticipated NRR activity trend that followed as Mo/Ag₃PO₄-10 > W/Ag₃PO₄-10 > Ag₃PO₄. The band gap of the materials was estimated using equation 2.10 and 2.11 of chapter 2 derived from the Tauc plot (Figure 6.7c). In



order to shed more light on the charge carrier density due to vacancy generation, PALS

Figure 6.7. (a) Low temperature ESR spectra of all the catalysts, inset shows the g-values; (b) diffused reflectance UV-visible spectra of all the catalysts; (c) corresponding Tauc plot for deriving band gap values obtained by extrapolating the tangents cutting the x-axis.

in all the samples were studied that could be fitted as sum of two exponentials using PALSFit program³⁵ yielding two positron lifetimes and they are called as τ_1 and τ_2 in the increasing order of magnitude as shown in Table 6.2 where the summary of lifetimes and

Table 6.2.	ESR and positron annihilation lifetimes	and intensities in undoped and doped Ag ₃ PO ₄
samples.		

	Positron annihilation lifetimes					
Sample	$\tau_1(ps)$	$I_1(\%)$	$\tau_2(ps)$	I ₂ (%)		
Ag ₃ PO ₄	97 ± 16	6.0 ± 1.0	276 ± 1	94.0 ± 1.0		
Cr-Ag ₃ PO ₄	172 ± 20	10.6 ± 2.6	327 ± 3	89.40 ± 2.6		
Mo-Ag ₃ PO ₄	224 ± 07	38.1 ± 1.9	313 ± 11	61.9 ± 1.9		
W-Ag ₃ PO ₄	210 ± 28	20.0 ± 2.0	302 ± 8	80.0 ± 2.0		

the corresponding intensities are also presented. The undoped Ag_3PO_4 yielded two lifetimes of 97 and 276 ps. These lifetimes are close to minimum lifetimes of 100 ps and 288 ps reported in Ag_3PO_4 systems.³⁶ The lifetime of 97 ps is associated with delocalized

positron in the bulk, while the 276 ps should be due to the presence of Ag⁺ vacancies in the system. This could be possibly due to the charge difference between the dopants (+6 for Mo and W and +3/0 for Cr) and host metal ion (Ag⁺), which could possibly knock off some Ag⁺ ions for the charge-balancing phenomenon. The extremely superior sensitivity of positrons to cation vacancies might be responsible for high intensity of this component. It may be noted that the samples may contain varied types of defects, but it is mathematically impossible to extract different positron lifetimes for each type of defects and close by lifetimes always appear as an average value. The first positron lifetime and corresponding intensities increase with transition metal doping and are in the order Ag₃PO₄ < Cr-Ag₃PO₄ < W-Ag₃PO₄ < Mo-Ag₃PO₄. The increase in the lifetime is due to the creation of oxygen vacancies, which was previously confirmed from the XPS analyses of all samples. These vacancies seem to be aiding the catalytic process.³⁷ The second positron lifetime of more than 300 ps is due to interfacial trapping of positrons and vacancies involving more than one atom like V_{Ag}-V_O. This lifetime is in the order $Cr/Ag_3PO_4-10 > W/Ag_3PO_4-10 > Mo/Ag_3PO_4-10 > Ag_3PO_4$. The reduced crystallinity in the transition metal doped samples as advocated from XRD results along with less oxygen vacancy association with Cr dopant, might have resulted in formation of vacancy clusters near the surfaces and enhanced the lifetimes. The doping induced inherent charge trapping in the systems localized an electron density over the metal centers leading to upshifting of the metal 3d-band center towards the Fermi level. This enabled a greater vacant anti-bonding states prior to the orbital mixing of Ag/M d-orbital and N₂ 2p, intimating N₂ adsorption. This is a direct revelation that group VI metals indeed depicted a sound role in favoring N2 adsorption and the subsequent reduction steps on the electro-active sites, which actually served as the stepping stone towards effective NRR.

6.4.4 Active site determination in Ag₃PO₄ and Mo/Ag₃PO₄ samples

On most of the catalyst surfaces, NRR is accompanied by the competitive HER that impedes the kinetics of the elementary steps of NRR by interfering in the adsorption and subsequent protonation steps. In order to avoid this, the catalyst is desired to be selective towards N_2 adsorption and the protonation should selectively occur on the adsorbed N_2 rather than the active site itself. In this respect, the experimental revelations were corroborated with theoretical findlings where the free energy calculation was chosen as the descriptor to determine the feasibility of the electrocatalytic processes on the catalyst surface. From the literature survey, although it is clear that Ag_3PO_4 itself behaves as an NRR selective catalyst, but we intended to prove this tendency theoretically and for that purpose, we considered 210 surfaces of Ag_3PO_4 as per XRD data and identified three different Ag sites (site-1, site-2, site-3) that are possible for N₂ adsorption (Figure 6.8). Firstly, we calculated the N₂ adsorption energy, where we found that site-1 has more



Figure 6.8. The model structures of N_2 adsorbed on (a) Site-1 (b) Site-2 and (c) Site-3 of Ag₃PO₄ system. The grey, pink, red, blue color sphere represents the Ag, P, O, N atom respectively.

potent N₂ adsorption energy as compared site-2 and site-3 of Ag₃PO₄ surface. Thereafter, in order to offer better active sites and accelerate the NRR process on Ag₃PO₄, the doping strategy with VI-group metals (Cr, Mo, and W) was adopted in the Ag₃PO₄ crystal structure. Usually, in the existing literatures, doping is widely exploited to reinforce the activity of active sites, but in this study, it was interesting to note that the dopants, along with Ag, simultaneously acted as the active centers for NRR. Similar to Ag₃PO₄, there are three different possible sites on Mo/Ag₃PO₄ (site-1, site-2 and site-3) as well where N₂ could be made to interact with the active sites as shown in Figure 6.9. Similar to Ag₃PO₄, the N₂ bond polarization, rather N-N bond length was found to be maximum 1.157 Å on site-1, as compared to site-2 and site-3 and it was even greater than pristine Ag₃PO₄ (N-N bond length: 1.128 Å). This not only emphasized the effect of doping in





Figure 6.9. The model structures of N_2 adsorbed on (a) Site-1 (b) Site-2 and (c) Site-3 of Mo/Ag₃PO₄-10 system. The grey, pink, red, blue, and dark pink color spheres represent the Ag, P, O, N and Mo atoms respectively.

6.4.5 Electrocatalytic NRR performance of all catalysts

The electrochemical NRR performance of all the materials were executed in a typical three-electrode setup in an H-cell. All the potentials are represented with respect to RHE calibrated using equation 2.6 of chapter 2. A primary observation was noted from the LSV curves for all the catalysts shown in Figure 6.10a, where a noticeable increase in the cathodic current density followed Ag₃PO₄ < Cr/Ag₃PO₄-10 < W/Ag₃PO₄-10 ≤ Mo/Ag₃PO₄-10, which was also reflected in the NRR performance of all the materials upon prolonged CA run for 1 h over the potential range of +0.1 to -0.3 V. The concentration of ammonia was colorimetrically estimated by Indophenol blue method, following the calibration and linear regression plots done in 0.1 M Na₂SO₄ with a known concentration of NH₄⁺ (y = 0.359x + 0.0206). From the UV-visible spectra of all the aliquot solutions for all four materials after 2 h of incubation time, the calculated value of the experimental NRR descriptors from equations 2.19 and 2.20 of chapter 2, revealed the maximum NH₃ yield rate and FE for Mo/Ag₃PO₄-10 at 0.0 V to be 461.2 nmol h⁻¹

 mg_{cat}^{-1} and 54.8 %. The other catalysts like W/Ag₃PO₄-10, Cr/Ag₃PO₄-10 and Ag₃PO₄ slightly lagged behind Mo/Ag₃PO₄-10, as represented in the bar plots in Figure 6.10b, c (error bars represent the standard deviation values for three different data sets). Besides the dopant itself, the ratio of doping also played a significant role. The primary optimization studies regarding the loading of dopants in Ag₃PO₄ are concerned with varying the ratio of Ag:Mo as 5:1, 10:1 and 15:1 namely Mo/Ag₃PO₄-5, Mo/Ag₃PO₄-10 and Mo/Ag₃PO₄-15 respectively while maintaining all other synthesis conditions same. The NH₃ yield rate and FE was found in the order Mo/Ag₃PO₄-10 > Mo/Ag₃PO₄-5 > Mo/Ag₃PO₄-15 as shown in Figure 6.10d. So, 10:1 was the optimum Ag:Mo ratio and was considered for all other sample preparation. The developed catalysts were thus



Figure 6.10. (a) CV plots of all doped and undoped Ag_3PO_4 catalysts taken at 10 mV s⁻¹ scan rate in 0.1 M Na_2SO_4 saturated with N_2 ; NRR performance comparison of all the catalysts in 0.1 M Na_2SO_4 in a potential range of +0.1 V to -0.3 V with respect to (b) NH₃ yield rate and (c) FE; (d) NRR comparative yield rate and FE of NH₃ for Mo/Ag₃PO₄-5, -10, and -15 catalysts; (e) yield rate of NH₃ and FE after cycling experiments with Mo/Ag₃PO₄-10; (f) bar plot demonstrating the NH₃ yield rate of Mo/Ag₃PO₄-10 at 0.0 V vs RHE in neutral electrolyte from UV-visible spectroscopy and IC, compared with bare controls like in Ar, at OCP and for blank substrate; (g) CV plots of Mo/Ag₃PO₄-10 catalyst taken at 10 mV s⁻¹ scan rate in 0.1 M Na₂SO₄ saturated with Ar and N₂ respectively; (h) comparative FE under N₂ and Ar at 0.0 V vs. RHE of Mo/Ag₃PO₄-10 and blank graphite plate; (i) NMR spectroscopic data showing distinct triplet and doublet peaks for ¹⁴NH₄⁺ and ¹⁵NH₄⁺. The error bars represent the standard deviation values for three different sets of experimental data.

named as W/Ag₃PO₄-10 and Cr/Ag₃PO₄-10. The conventional cyclability test of Mo/Ag₃PO₄-10 at 0.0 V for distinct five NRR cycles also revealed appreciably similar performance of the catalyst (Figure 6.10e). However, it is not sufficient to control the reactivity of active sites. A significant lookout is the negation of any nitrogenous contamination into the reaction chamber that could perturb the quantitative determination of NH_3 formed as a result of N_2 reduction on the catalyst surface. So, it was reasonable enough to pass on the ¹⁴N₂ feed gas via acid (0.05 M H₂SO₄) and base (0.1 M KOH) traps to check any sort of adventitious N-source and prevent its interference into the reaction chamber. A quantitative analyses of these trap solutions from UV-visible spectroscopy are elaborated in Table 6.3, where a bare minimum that is $<0.001 \ \mu g \ mL^{-1} \ NH_3$ was evidenced from contamination sources. In fact, to avoid taking any chance, the catalyst was washed multiple times with 0.1 M KOH, so any unreacted NO₃⁻ from the catalyst could get away and do not take active part during the NRR process. Thus, with all these preventive measures, the NRR activity of Mo/Ag₃PO₄-10 was quantified with IC and the result was well accorded with the first-hand UV-visible spectroscopic data as shown in Figure 6.10f, which confirmed the reliable data acquisition and NH_3 production on the catalyst active surface.

Table 6.3. Summary of the ${}^{14}N_2$ gas purity analysis.

Gas	Purity	NO _x	NH3	Total N-impurities
	(From supplier)	(μg mL ⁻¹)	(μg mL ⁻¹)	(μg mL ⁻¹)
$^{14}N_2$	99.99 % (Sigma Gases)	0.0005	0.0004	<0.001

As the theoretical data claimed that the material Mo/Ag₃PO₄ was more active towards NRR than HER, a more negative cathodic current density with a better onset potential in presence of N₂ as compared to Ar was visible in the LSV curve in Figure 6.10g. It was quite obvious as; the electrode potential of hydrogen is higher than Ag₃PO₄. So even the doped samples cannot reduce the hydrogen ion or produce hydrogen gas.³⁸ Thus in Ar atmosphere as well its HER activity is not more pronounced than its activity towards NRR in N₂ atmosphere. The corresponding CA and UV-visible spectra in Ar atmosphere at 0.0 V as well as a few other control experiments like in N₂ condition at OCP revealed, negligible NH₃ yield (Figure 6.10f and 6.10h) that verified the absence of other contamination sources in the cathodic reaction chamber. In fact, the blank graphite plate also responded negligibly towards NRR, which confirmed the substrate had no contribution in the NRR and the activity was solely achieved from the active catalyst. A more accurate and thorough examination of authenticity was done with the ${}^{15}N_2$ isotope labeling experiment, where the NMR spectra in Figure 6.10i showed a distinct triplet for the ${}^{14}NH_4^+$, while a doublet with no traces of the triplet peak confirming the formation of ${}^{15}NH_4^+$ chiefly out of the ${}^{15}N_2$ feed gas. The coupling constant values for these peaks were calculated using equation 2.31 of chapter 2 and it matched well with literature as we obtained *j*=52 Hz and 72 Hz, respectively, for the triplet and doublet peaks of ${}^{14}NH_4^+$ and ${}^{15}NH_4^+$.

6.3.6 NRR versus HER and the role of active sites on the charge transfer mechanism during NRR

From the free energy values in Figure 6.11a, it is clear that while the proton adsorption was thermodynamically not favored on site-1 with a positive value of 0.56 eV, N₂ adsorption was reinforced on the Ag active sites with -0.37 eV free energy and the N₂ adsorption was further provoked with doping. Figure 6.11a also revealed that while the thermodynamic feasibility of N₂ adsorption followed the trend Ag₃PO₄ < Cr/Ag₃PO₄ < $Mo/Ag_3PO_4 \leq W/Ag_3PO_4$, the proton adsorption tendency enhanced drastically for W/Ag₃PO₄. Thus, although W/Ag₃PO₄ had a similarly high N₂ adsorption possibility as that of Mo/Ag₃PO₄, the simultaneous affinity of the former towards proton adsorption would eventually lead to proton poisoning effect undoubtedly affecting the NRR performance of W/Ag₃PO₄. The predominance of N₂ adsorption over proton could be attributed to the fact that the catalyst synthesis strategy and doping adopted in this chapter introduced loss of crystallinity and oxygen vacancy formation in the catalysts. These oxygen vacancies rather behave as electron traps making way for electrostatic interaction with the abundant protons from the aqueous electrolyte. This consequently made the Ag and dopant sites available for N₂ adsorption at the cost of low free energy. Now, the potential hurdle for NRR towards the first protonation step could be analyzed by the overpotential between *NN to *NNH and was found to be minimum for Mo/Ag₃PO₄ $(\Delta E=0.50 \text{ eV})$ as shown in Figure 6.11b that indirectly notified a better charge transfer probability between Ag-Mo center and N₂ than the other samples.

Although the theoretical and experimental findings complemented one another in parallel, it called for a reasonable justification to supplement the results. Here XPS played an extremely crucial role in evaluating the electronic structure of the catalysts. An upshift of the d-band center position unpopulated maximum anti-bonding states³⁹ in

Mo/Ag₃PO₄ that exclusively attracted more p-electrons of the N₂ to bind and interact with the d-electrons of Ag and Mo via a so-called d-p mixing. This led to an electronic flux into the anti-bonding orbitals of N₂ from Ag/Mo lowering the N-N bond order and a facile bond polarization process, which could be arrested from the in-situ ATR-FTIR spectra. N₂ molecule being non-polar exhibits an IR silent vibration at 2359 cm⁻¹. However, upon bond polarization when N₂ develops partial positive and negative charges over the distal and proximal N atoms, there occurs a red-shift in the broad peak



Figure 6.11. (a) Free energy comparison of proton adsorption versus N_2 adsorption on all the doped and undoped Ag_3PO_4 samples; (b) Free energy of the N_2 adsorption and first protonation steps on the catalyst surface with Ag-Ag, Ag-Cr, Ag-Mo and Ag-W behaving as active sites for the side-on N_2 adsorption; (c) in-situ FTIR spectra of all samples showing $N \equiv N$ bond polarization; (d) Bader charge distribution analysis of the catalysts with adsorbed N_2 on the active site in side-on fashion, yellow lobes indicate charge depletion while blue lobes indicate charge accumulation; (e) Bader charge distribution analyses in all the catalysts before and after N_2 adsorption revealing the charge transfer order in the catalysts.

corresponding to N=N and for all our materials, this claim appeared to validate from the gradual red-shift in the particular peak position (Figure 6.11c) from 2349.9 cm⁻¹ (Ag₃PO₄) to 2345.5 cm⁻¹ (maximum peak shift being found for Mo/Ag₃PO₄).⁴⁰ This confirmed the maximum rate of charge transfer from the active site of Mo/Ag₃PO₄ to the *N₂ that eventually led to a lower energy barrier between the adsorption and the first protonation step for this material. Bader charge analysis, in this matter, is a very useful tool, which not only ascertains the charge transfer but also identifies the local charge accumulation/depletion regions on the N₂ adsorbed active sites. As seen in Figure 6.11d, the dopant Cr/Mo/W were found to be proactive in the charge transfer phenomenon as compared to the Ag site as advocated from the local charge depletion (yellow lobes) over

Cr/Mo/W and charge accumulation over N₂ (blue lobes) and thus, the N₂ adsorption was more leaned towards the dopants. This was the actual intention of the chapter to accelerate the active site influence on the NRR by doping. The Bader charge calculations on the active site before and after N₂ adsorption revealed a better charge transfer from Mo to N₂ and the trend slightly deviates from the activity of the materials that is Ag₃PO₄ $< W/Ag_3PO_4-10 < Cr/Ag_3PO_4-10 \le Mo/Ag_3PO_4-10$ as shown in Figure 6.11e. But since the NRR involves much complicated reaction steps, this charge transfer phenomenon is only a part of it but not the sole factor determining the NRR activity. Instead, adsorption is much more important to consider and obviously, the proton poisoning effect because only after adsorption all these charge transfers would occur, eventually leading to N-N bond polarization and first protonation.

6.4.7 Kinetic study of all the catalysts with RRDE

It is extremely crucial to compare the kinetics and onset of NRR for the investigating materials, but is mostly not documented for almost all reports in the field. The extensive kinetic study for all the Ag₃PO₄ samples records a vital finding in this chapter where the RRDE was accounted for all the electrochemical measurements. A convection generated



Figure 6.12. (a) Schematic representation of the reactions ongoing at the catalyst-electrolyte interface during NRR with RRDE; (b) LSV polarization curves for all Ag_3PO_4 samples on RRDE taken at 2 mV s⁻¹ in N_2 purged 0.1 M Na₂SO₄ electrolyte at 800 rpm; (c) corresponding Tafel plots of the samples representing overpotential for NRR; (d) CV scans on Pt ring taken in the oxidative region at 10 mV s⁻¹ in Ar and after NRR experiments in N_2 ; (e) comparison of exchange, kinetic and limiting current densities of all samples derived from the intercept of Tafel plot, K-L plot and the diffusion region of the LSV polarization curves respectively.

in the N₂ purged 0.1 M Na₂SO₄ at different rotation speeds applied to the RRDE resulted into three important phenomena likely N₂ diffusion onto the glassy carbon part, followed by reduction to NH₃ and finally detection of NH₃ on the Pt ring and its subsequent irreversible oxidation to NO_x as shown in Figure 6.12a. During the entire process, the



Figure 6.13. LSV curves at various rotation at 0 V vs RHE at 10 mV s⁻¹ and the corresponding K-L plots for $(a, b) Ag_3PO_4$, $(c,d) Cr/Ag_3PO_4$ -10, $(e, f) Mo/Ag_3PO_4$ -10, $(g, h) W/Ag_3PO_4$ -10 samples. All data are acquired in N₂ purged 0.1 M Na₂SO₄ electrolyte and the inset of K-L plots denote the inverse of kinetic current density for the samples represented by j_K .

LSV curves obtained at 2 mV s⁻¹ at 800 rpm for all the samples (Figure 6.12b) were divided into (a) NRR kinetic-dominated region where the reduction actually occurs and is dominated by $j_{\rm K}$, (b) the diffusion region that appears as a plateau at the higher overpotential, where the reactants (N₂), upon reaching the electrode surface, immediately get reduced, leaving behind a net zero reactant concentration on the electrode surface and it is dependent on the rotating speed in the RRDE measurement; this region is dominated by $j_{\rm L}$ and (c) the HER region where the hydrogen evolution dominates at a much negative cathodic potential with a sharp increase in the cathodic current density. The Tafel slope obtained for all samples (from equation 2.22 of chapter 2) at the NRR-onset region showed the lowest overpotential for the Mo-doped sample and is found to increase in the order of $Mo/Ag_3PO_4-10 < W/Ag_3PO_4-10 < Cr/Ag_3PO_4-10 < Ag_3PO_4$ (Figure 6.12c). This technique displayed another important observation proving the material selectivity towards NH_3 synthesis, where the Pt ring is expected to be highly sensitive to detect and oxidize both hydrazine and NH₃ at 0.2 V and 0.7 V respectively.⁴¹ Interestingly, a single oxidative CV scan after the NRR experiment (Figure 6.12d) detected the presence of local ammonia on the Pt ring at 0.7 V vs RHE, while there was no trace of any oxidation peak at 0.2 V for hydrazine. More interestingly, the idle current density obtained for the net charge exchange at the electrode-electrolyte interface (j_0 calculated using equation 6.1 of this chapter), j_L and j_K were found to be maximum for the Mo/Ag₃PO₄-10 sample as shown in the bar plot in Figure 6.12e. It is to note that the $j_{\rm K}$ was derived from K-L plot for all samples obtained from LSV curves at 0.0 V at 10 mV s⁻¹ under different rotation speeds of RRDE in rpm as shown in Figure 6.13

6.4.8 Arrested intermediates in the in-situ ATR-FTIR and determination of NRR pathway on Mo/Ag₃PO₄-10

The selectivity as well as reactivity are important for a material to be a strong contender in NRR. The electronic structure of the catalyst not only determines its favorability towards N₂ reduction but also regulates the binding strength of the intermediates on the catalyst surface. The in-situ ATR-FTIR studies were recorded at different potentials for Mo/Ag₃PO₄-10 ranging from +0.4 to -0.6 V vs RHE. The in-situ data, as shown in Figure 6.14a, revealed few indistinct yet unavoidable peaks at 1145, 1318, 1456 and 2849 cm⁻¹ resembling the N-N stretching, N-N rocking in N₂H₄, N-H bending and N-H stretching vibrations, respectively. It is interesting enough to point out that, the peak intensities maximized in the range of +0.1 to -0.3 V, exactly our investigating potentials for NRR.



Figure 6.14. (a) In-situ ATR-FTIR spectra of Mo/Ag₃PO₄-10 catalyst showing stretches corresponding to the NRR intermediates formed during NRR as schematically shown above the respective FTIR plots; (b) NRR full pathway of Mo/Ag₃PO₄ catalyst, distal pathway being slightly more prone than the alternating one, inset shows the model structures for each of the elementary steps of NRR. The white, dark pink, grey, red, blue color sphere represents the H, Mo, Ag, O, N atom respectively.

The appearance of N-N rocking vibration in N₂H₄ indicated that N₂H₄ was formed on the catalyst surface as one of the stable intermediates and did not interfere in the product formation. Thus, it is significant to mention that there was no disquiet from side product formation (hydrazine) as obtained from the oxidative CV curve from RRDE measurements. Although the alternating and distal pathways followed the same energetics for the initial protonation of N₂ as well as for the last three steps, but the intermediate protonations were in a swing between the two pathways on Mo/Ag₃PO₄ as shown in Figure 6.14b. Here, the distal pathway is more favorable than alternating due to energetically facile adsorption energy of *NNH₂ rather than *NHNH intermediate. In fact, the facile desorption of the end- product NH₃ helped to recover the active site over

time, producing a stable cathodic current density for a CA run for a prolonged 12 h (Figure 6.15a). This was better confirmed by a negotiably similar NH_3 yield rate and FE



Figure 6.15. (a) CA response of Mo/Ag₃PO₄-10 catalyst for a prolonged 12 h at 0.0 V vs RHE in neutral electrolyte, inset shows the comparative NRR performance of the catalyst after 1 h and 12 h of electrocatalysis; (b) EDX spectra of Mo/Ag₃PO₄-10 after electrocatalytic NRR stability, inset shows the FESEM images of Mo/Ag₃PO₄-10 catalyst after stability.

of Mo/Ag₃PO₄-10 (inset of Figure 6.15a). It is interesting to notice that the elemental content of Ag and Mo (from EDX) retained in the after-stability sample as compared with the fresh material (Figure 6.15b) along with the retainment of catalyst morphology as acquired from the FESEM (inset of Figure 6.15b). The XPS and ICP-MS analyses of before and after stability samples revealed similar atomic ratio of Ag and Mo as tabulated

Elements	Before stability	After stability (XPS)	After stability (ICP- MS)
Molybdenum (Mo)	1	1	1
Silver (Ag)	12	12	12

Table 6.4. Elemental ratio of Ag and Mo for Mo/Ag₃PO₄-10 catalyst from XPS and ICP-MS analyses before and after stability test for NRR.

in Table 6.4, which inferred the stability of the sample and its candidature for NRR for prolonged experimental hours.

Therefore, overall group VI dopants turned out to be effective enough to elevate the NRR performance of Ag_3PO_4 catalyst. However, the rationale behind the higher activity of Mo/Ag_3PO_4-10 than Cr/Ag_3PO_4-10 and W/Ag_3PO_4-10 can be explained by several supporting proofs; (a) the more availability of active sites on the surface to adsorb

Table 6.5.	Literature comparison	of recent reports	s on doping in	transition	metal-based	catalysts
for NRR.						

Catalysts	Electrolyte	Potential (V vs RHE)	NH3 yield rate (µg h ⁻¹ mg _{cat} ⁻¹)	FE (%)	References	
Fe-NiMoO ₄	0.1 M Na ₂ SO ₄	-0.5	15.36	26.85	<i>Inorg Chem</i> 2023, <i>14</i> , 11	
Mo-CeO ₂	0.1 M Na ₂ SO ₄	-0.45, - 0.25	10.9	26.5	<i>Chempluschem</i> 2023, 88 (3), e202300023	
Mn-doped Bi ₂ O ₃	0.1 M Na ₂ SO ₄	-0.1	23.54	21.63	ACS Sustainable Chem. Eng. 2022, 10, 20, 6766–6774	
F-Fe:TiO ₂	0.1 M Na ₂ SO ₄	-0.5	27.86	27.67	Appl Catal B 2022, 301, 120809	
Pd-TiO ₂	0.1 M Na ₂ SO ₄	-0.5	17.4	12.7	<i>Chem. Comm.</i> 2022, 58 (19), 3214–3217	
Re-doped TiO ₂	0.1 M Na ₂ SO ₄	-0.3	22.7	18.1	<i>Chem. Engg. J.</i> 2022, <i>434</i> , 134648	
Fe-InVO ₄	0.1 M HCl	-0.4	17.23	14.27	<i>Chem. Engg. J.</i> 2022, 431, 133383	
Ag-Cu _{NS} /CP	0.1 M Na ₂ SO ₄	-0.4	61.5	20.9	<i>Chem. Engg. J.</i> 2022, 433, 133752	
Co-doped Fe ₃ S ₄	0.1 M HCl	-0.55	37.5	17	<i>Inorg Chem</i> 2022, 61 (49), 20123–20132	
Pt/NiO-NSs	0.1 M Na ₂ SO ₄	-0.2	20.59	15.56	<i>Chinese J. of</i> <i>Cat.</i> 2022, <i>43</i> (5), 1371–1378	
V/NiO	0.1 M KOH	-0.3, -0.1	30.55	11	New J. of Chem. 2022, 46 (33), 15831–15837	
Mo/Ag ₃ PO ₄ -10	0.1 M Na ₂ SO ₄	0.0 V	7.84	54.8	This chapter	
Note: CP- carbon paper; NSs-nanosheets.						

the N₂ over H₂, (b) introduction of larger compressive strain with 'Mo' dopant enhances the d-band broadening and lowers the thermodynamic energy barrier for the N₂ adsorption, (c) maximum upshift in d-band center vacating maximum anti-bonding states prior to the N₂ adsorption, (d) greater extent of charge transfer from the Mo site to N₂ leading to a facile reaction kinetics and reduced energy barrier for the potential determining the first-protonation step for NRR. Besides all these, the significant role of oxygen vacancy could not be overlooked where these can act as proton scavengers and substantially suppress HER on the catalyst surface, owing to which Mo/Ag₃PO₄-10 yielded 54.8 % FE for NH₃ synthesis, which was better than many recently reported catalysts utilizing the doping strategy for NRR as summarized in Table 6.5.

6.5 Conclusion

In summary, this chapter spectacle the importance of metal doping in Ag₃PO₄ for boosting the FE, NH₃ yield rate in NRR. Here, a simple precipitation methodology was established to synthesize the Ag₃PO₄ and VI group metal-doped Ag₃PO₄. The optimum metal doping in Ag₃PO₄ improves the electrochemical NRR activity by altering the delectronic states of the Ag such that, the anti-bonding 3d states are sufficiently vacant to overlap with the adsorbate (N_2) 2p orbital. The successful doping and vacancy generation was illustrated from the compressive strain in the XRD lowing the d-spacing values in the crystal lattice of Ag and the upshift of metal d-band center from XPS analyses. These changes in electronic structures enabled charge scavanging in the systems that greatly influenced the elementary steps of NRR. Theoretical along with experimental findings revealed that, while Mo/Ag₃PO₄-10 exhibited the highest NH₃ yield rate of 461.2 nmol h⁻¹ mg_{cat}⁻¹ and 54.8 % FE at 0.0 V vs. RHE, Cr/Ag₃PO₄-10 and W/Ag₃PO₄-10 were also strong contenders. The rate kinetics of NRR was elaborately studied with RRDE technique. In fact, the NRR pathway and the intermediates formed were investigated via in-situ ATR-FTIR. That helped to gain a comprehensive understanding on how group VIB dopant manipulates the active sites of Ag_3PO_4 and impact each of the elementary steps of NRR has been elaborately investigated and this strategy would certainly help to design new catalysts for electrochemical NRR under ambient conditions.

6.6 References

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Chapler 7

Manifesting the kinetics and mechanism of electrochemical NRR on bridge oxygen vacancy dominated SnO₂ lattice **Overview**: This chapter follows the synthesis of oxygen vacancy-engineered SnO_2 displaying a structural transformation owing to in-plane (io_v) to bridge oxygen vacancy (bo_v) dominancy. Resultantly, the electron occupancy of the sp³d hybrid orbital changed leading to an upshifted valence band maxima towards Fermi level. This has a profound effect on the end-on followed by side-on N₂ adsorption and charge-transfer kinetics from the active site (site A and B-Sn atoms adjacent to bo_v) to N₂ across the electrode-electrolyte interface, investigated with RRDE technique. The N₂ bond polarization was further arrested by the in-situ ATR-FTIR studies along with the obscured NRR intermediates formed during the alternating NRR mechanism. A restricted HER on Sn-site (favored over O-atoms) results in 48.5% FE, better than all the literature reports on SnO₂ for NRR. This study thus unveils sufficient insights into the role of oxygen vacancy in the crystal as well as electronic structural alteration of SnO₂ and the identification and distinct role of active site impacting the rate kinetics of NRR.



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Reference: Biswas et al., Mater. Horiz. 2024, doi.org/10.1039/D3MH02141F.
7.1 Motivation of the chapter

Recently, it has been observed that almost all materials synthesized under high pressure and temperature or engineered with dopants inherently displace few lattice atoms and generate anionic/cationic vacancies. Although the metal atoms are regarded as the active sites and their physical, chemical, and electronic properties are thoroughly surveyed to correlate with their electrochemical activities, it is often overlooked that the vacancy sites might also instigate the NRR steps. However, it is coming to focus these days that this vacancy could be a game changer in the NRR process. So, an elaborate understanding is required that how the active site manipulation occurs in relation to the vacancy or whether it is the vacant sites rather than the constituent metals that are responsible for the electrochemical performance of the catalyst.

7.2 Introduction

Two-dimensional metal oxides featuring tunable electronic properties, mechanical strength and electro-active edges are widely researched materials for electrocatalytic NRR.¹ However, these materials are vacancy engineered to activate the basal surface by grafting artificial electron-rich active sites influencing N2 adsorption.^{2,3} DFT calculations have complemented the experimental data showing that oxygen vacancies in these materials could upshift the d-band center of the associated metals towards the Fermi level, which in turn lowers the energy barrier for the PDS of NRR.^{2,4} In fact, the polarized electrons over the dangling oxygen vacancies have been utilized to polarize the N≡N and also determine the binding strength of the reaction intermediates with the active center.⁵ In order to leverage these features, massive research is in progress these days. Although there is enough room for survey in these oxygen-vacant materials, a significant gap in the existing literature is how the oxygen vacancy generation brings about structural changes in the crystal lattice that manipulate the electron occupancy in the hybrid orbitals of the material influencing the elementary steps of NRR. In addition, it should also be made clear how, pivoting the generated vacancy, the charge redistribution on the adjacent metals contributes to N₂ adsorption and stimulates the rate kinetics of NRR.

Thus, we purposively chose two-dimensional SnO_2 as our investigating material to breach this understanding. SnO_2 is known to exhibit two different vacancy types in the lattice, namely the in-plane oxygen vacancy (io_v) and the bridge oxygen vacancy (bo_v). The experimentally synthesized SnO_2 at a higher annealing temperature displayed a greater content of bo_v, the reason being, two-coordinated bo_v is structurally more stable

than the three-coordinated iov as estimated from DFT calculations. Although upon vacancy engineering, the coordination environment around Sn changed, but the sp³d hybridization was retained with a d-electronic contribution due to the charge density imparted on Sn atoms from the vacant sites. Owing to this, the SnO₂-600 sample evidenced an elevated valence band maximum towards the Fermi level, which acted as the driving force to chemisorb and activate N₂ on the Sn site. The NRR was kinetically studied using RRDE, wherein the charge transfer rate from the electrode surface to N_2 across the catalyst-electrolyte interface was found to be maximum in case of SnO₂-600. As anticipated, this material with an optimum vacancy density was found to be most efficient towards NRR with 53 µg h⁻¹ mg_{cat}⁻¹ NH₃ yield rate and 48.5 % FE. This high FE for NRR could be attributed to the fact that H-adsorption was favored more on the electronegative O-atom site than Sn, facilitating NRR over the competitive HER. A thorough theoretical study surfaced the tendency of the bo_v dominated (101) plane of SnO_2 to adsorb the N₂ in a more energetically favorable way than the (110) plane. In fact, centering the boy, an out-of-the-way adsorption mechanism was found for this material where an end-on followed by side-on N₂ adsorption on the Sn active sites (sites A and B) accelerated the first protonation step at a comparatively low overpotential. It was mechanistically presumed that this side-on interaction would enable a better orbital interaction between the respective hybrid-sp³d and 5d orbitals of Sn and π^* and σ orbiitals of N₂ by a "push-pull electronic effect" that facilitated the N=N bond polarization followed by an alternating NRR pathway, as also determined from the insitu FTIR data. The kinetic parameters that determine the rate of NRR on catalyst surface at the electrode-electrolyte interface was studied with RRDE. The detailed investigation in this study not only surfaced several unseen features of vacancy engineered SnO₂ towards NRR but also provided a different outlook by which other metal oxides with oxygen vacancies could be studied (VO₂, $TiO_2^{6,7}$, CeO_2^8 , WO_3^9 , etc.).

7.3 Experimental Section

7.3.1 Synthesis of defect-enriched SnO₂ samples

0.1 M of tin chloride was dissolved in 25 mL DI water to which 0.01 M hydrazine hydrate was added under mechanical stirring condition. Thereafter, the solution mixture was subjected to hydrothermal reaction at 120 °C for 12 h. The as obtained white slurry was collected by centrifugation and dried in hot air oven at 70 °C. In order to elevate the oxygen vacancy density, which is preferably inevitable beyond an annealing temperature

of 400°C, the amorphous SnO₂ sample was subjected to heat treatment in air at different annealing temperatures like 500 °C, 600 °C and 700 °C respectively to obtain SnO₂-500, SnO₂-600 and SnO₂-700 samples.

7.3.2 In-situ ATR-FTIR studies

In-situ ATR-FTIR studies were carried out with Si FAC in a spectro-electrochemical cell equipped with a three-electrode set-up. The background was collected with the electrolyte and all the sample measurements were taken with 128 scans and resolution 4 in absorbance mode. All data were further baseline corrected and were collected by holding different cathodic potentials for a definite time-span.

7.3.3 Computational details

The computational code, known as VASP which is based on density functional theory, has been applied to carry out all the calculations related to the study. To understand the interaction between core and outer valence electrons in the given system, we have used PAW method with plane wave basis set¹⁰ where all plane-waves are expanded within a maximum kinetic energy cut-off of 450 eV. In case of total energy calculations, two types of convergence criteria we have introduced for ionic and electronic relaxations, one is energy convergence and another one is ionic force convergence, by setting the values of 1E-05 eV and -0.01 eV/Å respectively. The effects of exchange and correlation forces among electrons are approximated through GGA of PBE functional¹¹. Long range weak Van der Waal forces also we have considered for the system considered by employing Grimme DFT-D3 dispersion scheme¹². To sample the Brillouin zone in k-space, we have used popular Monk-Horst pack k-point sampling method, with 3 X 3 X 1 k-points for structural optimization. For DOS calculations we have chosen 5 X 5 X 1 k-points.

7.4 Results and discussion

7.4.1 Catalyst development based on gap in literature

 SnO_2 is a large band gap material that inhibits easy charge conductivity. To make use of this material in NRR, SnO_2 has been previously featured with oxygen vacancies only to show how the vacant sites alter the electronic charge over the material helping in elevating the NRR activity.¹³ However, there is a knowledge gap in the precise level about how these vacancies impact the orbital interactions between active site and N_2 affecting the rate of charge transfer kinetics during NRR. An in-depth finding reveals that vacancy-engineered SnO_2 exhibits two different types of oxygen vacancy centers,

namely the in-plane (io_v) and bridging vacancies (bo_v). Now, a major missing in the field is a comprehensive study of which vacancy type is more favored for the kinetically troublesome NRR and how it influences the nature of N_2 adsorption on active site. According to the calculation of surface energy (Table 7.1) of (101) oriented SnO₂ film,

Table 7.1. Stabilization energy of the (101) plane of SnO_2 with bridge and in-plane oxygen vacancies calculated from DFT.

Vacancy Type	Removed Oxygen Percentage	DFT energy (eV)
Bridge Vacancy	1.39 %	-650.06
Bridge Vacancy	2.78 %	-642.85
In-plane Vacancy	1.39 %	-649.54
In-plane Vacancy	2.78 %	-640.60

the plane with bov has a higher (more negative value, hence thermodynamically stable) than iov. So, for further studies, we have considered (101) oriented SnO₂ model structure with bov. Generally, the reported SnO₂-based materials for NRR displayed end-on adsorption of the N₂ molecule.^{14,15} However, in this chapter, we have shown that centering the bov, the two adjacent Sn atoms on either side could be utilized in N₂ adsorption in an end-on followed by side-on manner. It is to be noted that, in side-on case, when both the N atoms are involved in σ donation and π back-donation steps from both ends, the charge redistribution and the extent of N=N bond polarizability increases. This, in turn, provokes the first protonation step at a low overpotential and accelerates the overall rate kinetics of NRR. This interaction basically involves the filled hybrid sp³d orbital of SnO₂ (through Sn end) and the vacant non-degenerate 5d states of Sn with the respective π^* anti-bonding and σ -bonding orbitals of N₂. This embarks the NRR process on bov-dominated SnO₂.

Thus, to turn this theoretical prediction into experimental realization, the tetragonal SnO_2 is synthesized by a solvothermal technique, the simplest method of insitu generation of oxygen vacancies. In order to elevate the oxygen vacancy density, which is preferably inevitable beyond an annealing temperature of 400°C, the amorphous SnO_2 sample was subjected to heat treatment in air at different annealing temperatures like 500 °C, 600 °C and 700 °C, respectively, to obtain SnO_2 -500, SnO_2 -600 and SnO_2 -700 samples.

7.4.2 Oxygen vacancy generation: impact on structural and electronic properties of SnO₂ affecting NRR

The morphological information of all the synthesized samples is obtained from FESEM, where the pristine SnO_2 material displayed compactness in the irregular lump-like morphology (Figure 7.1a), which took shape of a granular architecture upon annealing



Figure 7.1. FESEM images of (a) SnO₂, (b) SnO₂-500, (c) SnO₂-600 and (d) SnO₂-700 samples, (scale bar: 100 nm).

(Figure 7.1b-d). Thereafter, the crystallinity and phase purity of SnO_2 was determined from the XRD study of all the synthesized samples, as shown in Figure 7.2a. The pristine sample produced broad peaks, which not only indicated an amorphous nature of the material but also matched with the tetragonal rutile SnO_2 crystal structure (PDF 00-041-1445) with a space group $P_{42/mnm}$.¹⁶ With gradual increase in temperature, two important observations were evident: (a) the crystallinity of the samples enhanced with gradual peak sharpening and few dormant peaks appeared indicating a grain growth with reduced

<i>Table 7.2.</i> Crystallite size (L_c) determination of the (110) and (101) planes of all Sn	O_2 samples.
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Material	(110) plane		(101) plane	
	20	Lc (nm)	20	Lc (nm)
SnO ₂	26.97	3.28	34.16	3.94
SnO₂-500	26.92	5.96	34.12	6.25
SnO₂-600	26.76	9.27	34.05	8.47
SnO₂-700	26.74	16.12	34.02	14.32

grain boundaries as indicated from the calculation of crystallite size (L_c) following equation 2.9 of chapter 2 (Table 7.2),¹⁷ (b) the major planes (110) and (101) slighted shifted to a lower 20 value, which resembled that with increase in temperature the interlayer spacing of the planes increased owing to tensile strain in the catalysts. This disrupted the regular lattice crystal structure and could be attributed to the presence of oxygen vacancies and tensile strain is known to cause an upshift in electronic levels close to the Fermi level, beneficial for the subsequent steps of the NRR.¹⁸

An interesting observation from the EDX analyses in Table 7.3 reveals that as we

Material	Atomic % of Sn	Atomic % of O
SnO ₂	33.5	66.5
SnO₂-500	34.2	65.8
SnO₂-600	36.7	63.3
SnO ₂ -700	37.1	62.9

*Table 7.3. EDX analyses of all SnO*₂ *samples.*

move from SnO₂ to the annealed samples the atomic % of oxygen decreased suggesting that the SnO₂ lattice gradually became oxygen deficient. While the polycrystalline nature of the material was rightly justified from the diffraction rings in the SAED pattern (Figure (7.2b),¹⁷ more definite morphological evidence was acquired for the SnO₂-600 sample by TEM as shown in Figure 7.2c, where at 5 nm resolution, finely distinct lattice fringes are observed. Precisely, the spacing between the adjacent lattice planes were calculated to be 0.33 nm and 0.26 nm stating that the (110) and (101) planes were the two main exposed facets of the SnO₂ lattice respectively. These planes were further confirmed by FFT pattern as displayed in the left-most corner in the inset of Figure 7.2c, which is also in accordance with XRD results. FFT was employed on the black square-labelled area of Figure 7.2c, masking was applied on the intense spots of the FFT spectrum and the IFFT reconstruction of the resulting image provided the FFT reciprocal lattice that was analysed to determine the interlayer spacing values and thus the planes were derived.¹⁹ Figure 7.2d shows the HRTEM images of the sample at atomic level magnification. However, a magnified version of Figure 7.2d, as shown in Figure 7.2e displayed that the Sn atoms were not in a regular array owing to O-atom extraction (oxygen vacancy) disrupting the regularity of the lattice plane.

Unlike other metal oxides with vacancies, from the Raman spectra for SnO_2 materials in Figure 7.2f, it was observed that while pristine SnO_2 displayed a sharp peak at 571 cm⁻¹ (A) corresponding to the io_v,²⁰ with rising the annealing temperature, this peak weakened with an arousal of the peak at 623 cm⁻¹ (B) (A_{1g} mode) resembling the dangling bo_v.^{21,22} This originated the E_g phonon mode at 481 cm⁻¹ (C) in all the annealed samples corresponding to the vibration of the in-plane oxygen. The lowest occurrence of this peak in the pristine SnO₂ sample corroborated the fact that in-plane oxygen vacancy was predominant in the unannealed sample. The gradual transformation of the dominance of io_v to bo_v has been structurally represented in Figure 7.2g. These oxygen vacancies



Figure 7.2. (a) XRD spectra of all SnO₂ samples matched with the JCPDS file number-00-041-1445; (b) SAED pattern of SnO₂-600 catalyst; (c) HRTEM image of SnO₂-600 (scale bar- 5 nm); inset shows lattice fringes corresponding to (110) and (101) planes, also verified from FFT of the black square region; (d) HRTEM image of SnO₂-600 sample with high magnification (scale bar- 2 nm); (e) Magnified version of figure d presenting the disordered arrangement of Sn atoms due to vacancy generation (scale bar- 0.5 nm); (f) Raman spectra of all SnO₂ samples, where A-E represent different vibrations for SnO₂; (g) model structure showing gradual structural change in SnO₂ from unannealed to annealed samples; (h, i) represent the FTIR spectra of all SnO₂ samples; (j) XPS full survey spectra of all SnO₂ samples.

enriched the adjacent Sn atoms with a local charge density that provided appropriate adsorption sites for N₂ molecules.²³ Besides these another B_{2g} mode at 776 cm⁻¹ (D) persisted in all the samples. The A_{1g} and B_{2g} are related to the expansion and contraction vibration mode of the Sn-O bonds. The peak at 280-320 cm⁻¹ (E) is attributed to the Raman-silent E_u mode. This peak does not appear in the symmetry analysis of the bulk SnO₂, but could be transformed to the Raman mode owing to the nanoscale structural disorders at the surface of SnO₂.²⁰ A visible downshift in the peak frequency in the order of SnO₂<SnO₂-500<SnO₂-600≤SnO₂-700 is attributed to the increasing oxygen vacancy density in the lattice.^{24,25} This plays a major role to alter the electronic structures of the SnO₂, particularly the dominant (110) and (101) planes that have been emphatically proven to be active for NRR.²⁶⁻²⁸ However, there are some IR-active modes that define the different types of oxygen peaks in the SnO₂ lattice, verified from the FTIR spectra . The FTIR peaks in between 1000-1300 cm⁻¹ were designated to the different bending and stretching modes of the Sn-OH bond (Figure 7.2h). The peaks observed at 1622 cm⁻¹ (bending vibration of O-H) and 3355 cm⁻¹ (stretching vibration of O-H) determine the hydrous nature of SnO₂ and advocate the presence of chemisorbed hydroxyl groups at the surface of SnO₂.^{29,30} With increase in annealing temperature, this peak appeared to diminish with a blue shift in the spectra. This could be because as temperature was raised, the chemisorbed oxygen or simply hydroxyl groups got away from the surface and the remaining molecules became bound to the SnO2 open edges and the increase in the Sn-OH bond strength led to the blue shift of this peak. The other signature peaks in Figure 7.2i observed at 554, 603 and 661 cm^{-1} were assigned to the antisymmetric as well as symmetric vibrations of the Sn-O-Sn bond present in the SnO₂ lattice.³¹

To better evidence the effect of oxygen vacancy on surface structure of SnO₂, XPS was exployed for all samples. The full survey spectra displayed peaks corresponding to Sn and O revealing the major as well as the auger peaks for Sn (Figure 7.2j). However, the narrow O 1s XPS spectra for all the samples displayed three deconvoluted peaks corresponding to the lattice O (Sn-O) at 530.68 eV, O-vacancy (531.2 eV) and chemisorbed-O at 531.78 eV (Figure 7.3a). It can be noted that, oxygen vacancies could be formed under the high pressure and temperature conditions maintained during the solvothermal reaction.² Further, for all the materials synthesized at different annealing temperatures, the peak corresponding to O-vacancy retained within the crystal lattice with the peak area in the order of SnO₂ < SnO₂-500 < SnO₂-600 ≤

 SnO_2 -700. There occurred a negative peak shifting of 0.31 eV for the lattice O (inset of Figure 7.3a) from the unannealed to the annealed samples. An in-depth understanding on the prevalent oxygen vacancies in the SnO_2 ascertain a dislocation of the tin sublattice with respect to the oxygen sublattice owing to which an obvious dipole moment generates in the overall lattice. The surface Sn atoms coordinated to five O-atoms show



Figure 7.3. (a) XPS deconvoluted narrow spectra of O 1s for all SnO₂ samples; (b) bar plot representing the ratio of atomic % of Sn²⁺ : Sn⁴⁺ present in the material lattice; (c) XPS narrow spectra of the Sn $3d_{5/2}$ spin-orbit coupled peak fo the unannealed and annealed SnO₂ samples; (d) Tauc plot obtained from diffused reflectance UV-visible spectra of all the catalysts; (e) surface VBS of all samples representing the valence band maxima; (f) relative electronic band positions of SnO₂ samples, considering Fermi energy level (E_f) at 0.0 eV vs NHE.

sp³d hybridization. When an oxygen atom is knocked off from the bridge region, the four coordinated O atoms should involve into sp³ hybridization with Sn. But theoretical charge calculations revealed a d-electronic contribution over both Sn site-A and B (0.57e and 0.33e respectively), retaining the sp³d hybridization in the oxygen vacant samples. This could be attributed to the fact that, oxygen vacancy imparts a partial electronic charge over the adjacent Sn atoms and hence, the narrow Sn 3d spectra for all samples evidenced peaks corresponding to both Sn⁺⁴ (major) and Sn⁺² (minor). The ratio of Sn⁺² appeared to enhance with an incremental oxygen vacancy density in the synthesized samples as shown in Figure 7.3b. The electrons released from the bridging oxygen vacancies contributed to electronic dispersion at the valence band maxima as well as the conduction band minima of the reduced materials that led to the formation of surface gap states. This helped to reduce the surface layer Sn atoms from +4 to +2 oxidation state.³²

Further, a gradual negative shifting in the deconvoluted Sn 3d spectra was noticed for the spin-orbit coupled peaks to a lower binding energy value in the order of $SnO_2 < SnO_2$ - $500 < \text{SnO}_2-700 \le \text{SnO}_2-600$ (Figure 7.3c). The negative charge density induced over the Sn atoms exaggerated the core electron loss and hence such an observation. With increase in annealing temperature, it was observed that a disruption in the regular SnO₂ stoichiometry originated subgap defect states and the free charge carriers arising due to oxygen vacancy resulted into band filling. These factors enabled lowering of the Eg of the materials as derived from the diffused-reflectance UV-visible spectroscopy and the corresponding Tauc plot following equation 2.10, 2.11 of chapter 2 (Figure 7.3d).^{33,34} However, since the oxygen vacancies are known to amplify the valence electrons of Sn, this led to an elevation of the valence band maximum (calculated from the surface VBS in Figure 7.3e) of the annealed samples closer to the Fermi level (positioned at 0 eV vs NHE).^{35,36} The corresponding electronic band level diagram for all the samples is presented in Figure 7.3f. This ensured a better electronic interaction between Sn to N₂ empowering the SnO₂ materials toward proficient NRR performance, maximum for SnO₂-600. This polarizability enabled a better N₂ adsorption on the two-coordinated bo_v sites, which is greatly influenced by the ov density that could be quantitatively determined using PALS.

PALS for SnO₂ yielded single positron lifetime in as prepared sample while all others annealed at different temperatures yielded two positron lifetimes. The summary of positron lifetimes and corresponding intensities and intensity weighted average positron lifetimes are given in the Table 7.4. As prepared SnO₂ sample showed single

Sample	$\tau_1(ps)$	I ₁ (%)	$ au_2$ (ps)	I ₂ (%)	$ au_{av}(\mathbf{ps})$
SnO ₂	-	-	383 ± 2	100 ± 1	383 ± 2
SnO ₂ -500	165 ± 22	6.6 ± 1.3	376 ± 2	93.4 ± 1.3	362 ± 6
SnO ₂ -600	162 ± 7	20.9 ± 1.4	359 ± 2	79.1 ± 1.4	318 ± 6
SnO ₂ -700	172 ± 4	46.9 ± 1.9	343 ± 4	53.1 ± 1.9	263 ± 7

Table 7.4. Positron annihilation lifetimes and intensities in all SnO₂ samples.

positron lifetime of 383 ps. The positron lifetime of this magnitude is due to the large vacancy clusters and due to positron annihilations in the grain boundaries. The crystallite sizes in the samples as seen from XRD are smaller than positron diffusion length of \sim 100 nm in defect free materials and positrons are expected to diffuse out to surface if not trapped in the crystallites. The single lifetime component in as prepared samples is due

to too small crystallite size and due to positron annihilations at the grain boundaries that are rich in vacancy clusters.^[38] The appearance of two types of positron lifetimes in the annealed samples points to two type of positron trapping. The first positron lifetime component in the annealed samples is 160-170 ps and is higher than the defect free positron lifetime of ~155 ps expected in SnO₂.^[39] Based on the theoretically estimated positron lifetimes in various vacancies, the first positron lifetime is attributed to oxygen vacancies, which could be mono-, di- or tri-oxygen vacancies.^[39] With increase in annealing temperature, the second positron lifetime (τ 2) and its intensity (I2) have decreased monotonically. This suggests reduction in the grain boundaries due to crystallite growth, which was also evident by XRD. The fraction of positrons annihilating from the oxygen vacancy is comparatively greater for the SnO₂-600 and SnO₂-700 and is also in accordance with XPS studies.

7.4.3 NRR performance of catalysts on determined active sites: NRR vs HER

To examine the reduction of N_2 in this study, the (101) oriented SnO_2 film was chosen over (110) oriented SnO_2 film, as the (110) orientation is more selective for H_2 , which is experimentally proved as reported in the literature³⁷. We have also verified this fact theoretically with DFT calculations as summarized in Table 7.5 and 7.6. To check the promising active site for NRR on the surface of (101) oriented SnO_2 , we have examined N_2 adsorption on the Sn sites (A and B) near the bo_v (Figure 7.4a). We also considered

<i>Table 7.5.</i> Free energy calculation for the adsorption of N_2 and H at site A and site B	of bridge-
oxygen vacancy induced (101) oriented SnO_2 .	

(101) Oriented SnO ₂							
Adsorption Type	Free Energy (ΔG) at A site	Free Energy (ΔG) at B site	Remarks				
\mathbf{N}_2	-0.28 eV		NRR Favourable Active Site				
Н	0.49 eV						
N ₂		-0.13 eV	NRR Favourable Active Site				
Н		0.16 eV					
H adsorbed on oxygen atom		-1.25 eV	HER Favourable				
NT (D	0 1 2 1		.1				

Note: Because of bridge oxygen vacancies and poor oxygen on the surface, Sn atoms become pronounced active sites for H adsorptions, as reported in literature. But, from the table, we can see the change in free energy is more -ve in the case of N_2 adsorption as compared to H adsorption. So, the (101) oriented SnO₂ is more favourable for NRR.

(110) Oriented SnO ₂						
Adsorption Type	Free Energy (ΔG) at C site	Free Energy (ΔG) at D site	Remarks			
N ₂	-0.10 eV		HER Favourable Active Site			
Н	-0.35 eV					
N ₂		-0.27 eV	NRR Favourable Active Site			
Н		0.92 eV				
H adsorbed on oxygen atom		-0.84 eV	HER Favourable			

Table 7.6. Free energy calculation for the adsorption of N_2 and H at site C and site D of bridgeoxygen vacancy induced (110) oriented SnO₂.

Note: In the case of (110) oriented SnO_2 film, the vacancies of oxygen are less as compared to (101) oriented SnO_2 film. Therefore, O and Sn both are playing as active sites for H and N_2 adsorptions. At Sn site, near oxygen vacancy, the possibility of adsorption of H is more than N_2 adsorption. Also, the H adsorption on oxygen atoms occurs in an exothermic way. So, most of the H atoms are adsorbed on O and Sn atoms and results in HER.



Figure 7.4. (a) shows the optimized structure of (101) plane of SnO_2 with bo_v and probable NRR active sites marked as A and B; (b) shows the optimized structure of (110) plane of SnO_2 with bo_v and probable NRR active sites marked as C and D; (c) comparison of free energies between N_2 and H adsorptions on Sn (A site) and Sn (B site) respectively of SnO_2 (101) with bo_v ; (d) Free energy for H adsorption on O-atom site of SnO_2 (101) with bo_v .

two NRR active sites C and D for (110) plane of SnO_2 (Figure 7.4b) but since the (101) plane was more efficient from free energy point of view, we considered the bo_v

dominated (101) plane for all further calculations. From the free energy change (Figure 7.4c), it is pronounced that the N₂ adsorption over Sn-A and Sn-B was energetically more favoured than H-adsorption. More interestingly, the proton adsorption was found to be dominant on the O-atoms with a much negative free energy value of -1.25 V (Figure 7.4d),³⁷ suggesting that the parallel HER was inevitable on the O-atoms securing the Sn sites for N₂ adsorption and its subsequent reduction.

This tendency of NRR over HER reflected in the LSV curve of the SnO_2 -600 that showed an enhanced cathodic current density in presence of N_2 than in the Ar atmosphere, denoting a better charge transfer between the reactant and active site (Figure 7.5a). However, before commencing further experiments, a thorough purification study was accomplished with the feed gas using acid and base traps as shown in Table 7.7.

Table 7.7. Quantitative analysis of purity of ${}^{14}N_2$ feed gas by colorimetric method.

	Source	NH4 ⁺ (μg mL ⁻¹)	$NO_x(\mu g m L^{-1})$	Total N content (µg mL ⁻¹)
$^{14}N_{2}$	Sigma Gases (99.9 % purity)	0.0004	0.0002	<0.001

Thereafter, in a conventional three electrode system, the working electrode was subjected to a range of applied potentials from -0.1 to -0.5 V for 1 h each (CA) as shown in Figure 7.5b. It is to be noted that the potentials reported in this chapter for NRR are calibrated with respect to RHE following equation 2.6 of chapter 2. The electrolyte solution was then collected and mixed with the colouring agents to produce the Indophenol blue dye after 2 h of incubation that is spectroscopically estimated by the peak at ~630 nm appearing in the UV-vis spectra in Figure 7.5c. The concentration of NH₃ was obtained using the standard calibration spectra plots obtained from the known concentration of NH₄Cl in 0.1 M Na₂SO₄ following the equation y = 0.376x + 0.022. From this concentration value, using equations 2.18 and 2.19 of chapter 2, the NH₃ yield rate and FE were calculated for the SnO₂-600 sample and it was concluded that the maximum material performance was achieved at -0.3 V (53 µg h⁻¹ mg_{cat}⁻¹ yield rate and 48.5 % FE) as shown in Figure 7.5d. The NRR activity was cross-verified quantitively using both IC as well as NMR spectroscopic measurements with both ¹⁴N₂ and ¹⁵N₂ feed gases. ¹⁵N₂ isotope labelling experiment was conducted keeping the experimental conditions same

as ¹⁴N₂ and the comparative NMR spectra revealed a triplet with coupling constant value (*j*) of 52 Hz for ¹⁴NH₄⁺ and a doublet with j=72 Hz for ¹⁵NH₄⁺ (calculated using equation 2.31 and concentration of NH₃ quantified using equation 2.32 of chapter 2) with no traces of the triplet peak for the ¹⁵N₂ experiment (Figure 7.5e).³⁸ All the results from UV-vis, IC and NMR were quite congruent to one another with error bars denoting the standard deviation values obtained from three different sets of experimental data (Figure 7.5f). The blank control experiments in Ar, with bare electrode and at OCP (Figure 7.5g) also confirmed the same and the cyclability experiment in Figure 7.5h ascertained the reliability of the data. For the other control samples, the different annealing temperatures affect the crystal type and morphology of the material that in turn influence the



Figure 7.5. (a) Comparative LSV curve for SnO_2 -600 catalyst at 10 mV s⁻¹ scan rate in N_2 and Ar purged 0.1 M Na₂SO₄; (b) potential dependent CA curves of SnO_2 -600 catalyst for 1 h run (each) in 0.1 M Na₂SO₄ electrolyte; (c) UV-vis absorption spectra of the electrolyte stained with indophenol blue indicator after 2 h of incubation from the NRR experiment; (d) NRR performance of SnO_2 -600 in terms of FE and NH₃ yield rate for five different potentials; (e) NMR spectra acquired for the concentrated solution collected after CA run at -0.3 V in Ar, ¹⁴N₂ and ¹⁵N₂ feed gases; (f) quantitative NH₃ yield rate comparison of the SnO₂-600 catalyst by UV-visible, IC and NMR methods; (g) NRR performance of SnO_2 -600 catalyst for 1 h CA run (each) in 0.1 M Na₂SO₄ electrolyte under N₂ (at -0.3 V as well as OCP), Ar (at -0.3 V) and for blank substrate; (h) Yield rate of NH₃ and FE after cycling experiments; (i) NRR yield rate and FE comparison of all synthesized catalysts. Error bars represent standard deviation values taken from three sets of experimental data.

concentration and effectivity of the created oxygen vacancies. Thus, the vacancyengineering concept works at a certain temperature range with the maximum efficiency of the catalyst at a particular temperature rather than increasing the annealing temperature infinitely.² On the basis of this fact, the maximum NRR performance for our synthesized samples was maximum for the SnO₂-600 material showing NH₃ yield rate and FE, better than SnO₂, SnO₂-500 and SnO₂-700 (Figure 7.5i).

7.4.4 Investigation of nature of N2 adsorption and NRR mechanism

In this study, the N_2 adsorption and the subsequent first protonation steps are inter-related as the former drives the later, unlike all other reports on SnO₂ based materials. The charge density distribution through Bader charge analysis over the Sn (A and B) active sites and *NNH is shown in Figure 7.6a, with side and top views, where yellow and cyan blue colours indicate the accumulation of charges and loss of charges respectively.^{39,40} It is observed that Sn atoms adjacent to the boy exhibited a total occupancy of 3.42e (A) and 2.95e (B) electronic charges. The non-uniformity is due to the electronic charges resulting from oxygen vacancy being more leaned towards site-A in the optimized structure in relaxed state. Consequently, the N_2 adsorption was more favoured primarily over site-A Sn atom and after an initial round of charge exchange, the distal N atom of the partially polarized N₂ got attracted to adsorb over the Sn site-B. This step is expected to manoeuvre the N≡N bond activation. As shown in Figure 7.6b, we tried to protonate the end-on adsorbed N₂ and compare it with the spontaneous protonation over the sideon adsorbed N2 only to find a greater N-N bond length from 1.16 to 1.22 Å for the latter case. In fact, the overpotential (η) improved from 1.6 to 1.0 V, driving the NRR kinetics electrochemically forward. Thereafter, to identify the more feasible NRR pathway, we have considered the lowest thermodynamic barrier (lower value of free energy change) by examining the PDS or limiting potential for both distal and associative pathways³⁹. The reaction intermediates through alternating pathway (PDS = 1.0 V) were more favourable than distal (PDS = 1.5 V), and corresponding free energy profile are presented in Figure 7.6c. In Figure 7.6c, we observe that N2 molecule easily gets adsorbed on Sn atom in exothermic way with free energy change of -0.25 eV. In the next step *NN \rightarrow *NNH, (H⁺ + e) pair attacks and protonation takes place with free energy change of 1 V, which is endothermic in nature and observed to be the PDS.⁴¹ As most of the intermediate steps in the reduction process occurred through the releasing of heat energy,

the accumulation of that heat energy helps to overcome the barrier of free energy change (1.99 eV) of NH₃ desorption process from the catalyst surface.



Figure 7.6. (a) shows the side and top views of Bader charge analysis over the (101) oriented SnO₂ film with *NNH, yellow and cyan blue colours indicate the accumulation of charges and loss of charges respectively; (b) rationale behind end-on followed by side-on N_2 adsorption influencing the first protonation step of NRR; (c) full free energy profile of NRR showing possibilities of alternating and distal mechanistic pathways for N_2 reduction on SnO₂. Grey, red, and blue colors represent Sn, O and N atoms respectively.

7.4.5 Rate-kinetic study of NRR on catalyst surface with RRDE

The NRR is a complex electron-proton transfer process accompanying a diffusion of N_2 and charge transfer from the catalyst surface to N_2 across the electrode-electrolyte interface, which could be arrested with RRDE (Figure 7.7a). Here, when the RRDE was subjected to rotation speed of 800 rpm, a convection current thrusted the dissolved

reactant molecules to diffuse onto the electrode surface where the electrode reaction occurred on the disc part of the RRDE. This provided the mass-transport limited current in the kinetic region of the LSV curves for all the samples at 2 mV s⁻¹ scan rate as shown in Figure 7.7b. Since, the NRR is carried in aqueous environment and owing to the comparatively lower N₂ solubility, HER becomes a predominant counter-reaction at all potentials, which over-runs the NRR kinetics at a more negative potential region with an incremental cathodic current density as demarcated in Figure 7.7b.⁴² However, a slight



Figure 7. 7. (a) Schematic representation of the reactions ongoing at the catalyst-electrolyte interface during N_2 reduction reaction with RRDE; (b) LSV polarization curves for all SnO₂ samples on RRDE taken at 2 mV s⁻¹ in N_2 and Ar purged 0.1 M Na₂SO₄ electrolyte at 800 rpm; (c) corresponding Tafel plots of the samples representing overpotential for NRR; (d) comparison of j_0 and j_D of all samples; (e) CV scans on Pt ring taken in the oxidative region at 10 mV s⁻¹ in Ar and after NRR experiments in N_2 ; (f, g) in-situ ATR-FTIR data of SnO₂-600 during NRR. Error bars represent standard deviation values taken from three sets of experimental data.

difference in the onset, kinetic and plateau region for N_2 and Ar conditions suggested that our investigating potential range from -0.1 to -0.5 V favoured NRR over HER. However, the comparative LSV and the corresponding Tafel plots suggested that the SnO₂-600 incurred the minimum overpotential for (Figure 7.7c), as expected from the highest yield rate of NH₃ and FE. More interestingly, the diffusion current density (j_D) and the idle current density obtained for the net charge exchange at the electrodeelectrolyte interface without a significant energy loss due to activation (j_0 , calculated using equation 2.22 of chapter 2) was found to be maximum for the SnO₂-600 sample as shown in Figure 7.7d. This RRDE technique also reflected product-selectivity of the catalyst. the Pt ring is expected to be highly sensitive to detect and oxidize both N₂H₄ and NH₃ at 0.2 V and 0.7 V respectively.⁴³ Interestingly, a single CV scan after the NRR experiment (Figure 7.7e) detected the presence of local ammonia on the Pt ring at 0.7 V vs RHE, while there was no trace of any oxidation peak at 0.2 V for hydrazine. This suggested that N₂H₄ was formed as a stable intermediate on the catalyst surface.

7.4.6 Identification of reaction intermediates with in-situ ATR-FTIR and long-term NRR stability

The traces of other obscured reaction intermediates during NRR could be evidenced from the in-situ ATR-FTIR analyses (Figure 7.7f) where three peaks at 1123, 1328 and 1436 cm⁻¹ denote the respective stretches for N-N stretching, N-N-H rocking and H-N-H bending vibrations.⁴⁴ More interestingly, although the N \equiv N lacks polarity but a greater tendency of all the SnO₂ catalysts to chemisorb N₂ arises a red-shifted peak as shown in Figure 7.7g corresponding to the polarized N \equiv N. This phenomenon was maximally manifested for the SnO₂-600 catalyst.

This material was investigated for CA study for 24 h at -0.3 V vs RHE, where a stable cathodic current density was seen (Figure 7.8a) with a negotiable retainment of NH₃ yield rate and FE (inset of Figure 7.8a). As it is crucial to determine the material robustness, for the ease of post-stability characterizations, the stability study was accomplished with the material on activated CC. The morphological entity of the post-stability material retained as that of the fresh sample with consistent elemental content as can be seen from the FESEM elemental mapping in Figure 7.8b. The post-stability XPS characterization revealed that, the O atomic wt % increased in the full survey spectra (Figure 7.8c). The narrow spectra of O 1s in Figure 7.8d showed an incremental peak area for the chemisorbed O and a relatively low-area for the peak corresponding to O-vacancy. However, this could not explain the consistent NRR performance. Therefore, the Raman analysis of the post-stability sample was executed that showed, while the inplane and sub-bridging oxygen vacancies were filled up due to prolonged exposure of

the material to the aqueous environment, the bo_v stood dominant contributing to the stable NRR activity for a prolonged time (Figure 7.8e). In addition to this, the lattice planes and crystallinity of the material was found to remain unaffected during the prolonged experimental hours as shown in the comparative XRD spectra in Figure 7.8f. This uninterrupted performance of SnO₂-600 towards NRR proved to outperform almost all the relevant SnO₂ based catalysts reported in literature in terms of FE and NH₃ yield rate, summarized in Table 7.8.

Catalyst	Electrolyte	Potential (V vs RHE)	Yield rate $(\mu g \cdot h^{-1}mg^{-1}_{cat})$	FE (%)	References	
Fe-doped SnO ₂	0.1 M Na ₂ SO ₄	-0.8 V	28.45	6.54	Nano Res. 2022, 15, 6026–6035	
SnO ₂ /RGO	0.1 M Na ₂ SO ₄	-0.5 V	25.6	7.1	ACS Appl Mater Interfaces 2019, 11, 31806– 31815	
SnO ₂ with oxygen vacancy	0.1 M Na ₂ SO ₄	-0.6 V	25.27	11.48	Nanoscale 2021, 13, 16307– 16315	
Ti doped SnO ₂	0.1 M Na ₂ SO ₄	-0.2 V	13.09	42.6	<i>Chinese</i> <i>Chemical</i> <i>Letters</i> 2022, <i>33</i> , 4655–4658	
Janus Fe- SnO ₂	0.1 M Na ₂ SO ₄	-0.3 V	82.7	20.4	Angewandte Chemie 2020, 132, 10980– 10985	
Au@amorp hous SnO ₂	0.1 M HCl	-0.2 V	21.9	15.2	<i>Sci Bull</i> (<i>Beijing</i>) 2020, 65, 350–358	
d-SnO ₂ @C	0.1 M HCl	-0.25 V	16.68	12.7% at -0.15 V	<i>Green Energy & Environment</i> 2022, 7, 672– 679	
SnO ₂ @CC	0.5M K ₂ SO ₄	-0.25 V	38.18	11.33	ACS Appl Energy Mater, 2020, 3, 6735– 6742	
F-SnO ₂ /CC	0.1 M Na ₂ SO ₄	-0.45 V	19.3	8.6	<i>Inorg Chem.</i> 2019, 58, 10424–10431	
SnO ₂ -600	0.1 M Na ₂ SO ₄	-0.3 V	53	48.5	This chapter	
Note: RGO-	Note: RGO- reduced graphene oxide, C- carbon, CC- carbon cloth.					

Table 7.8. Literature comparison of SnO₂ based catalysts for NRR.



Figure 7.8. (a) NRR stability study of SnO_2 -600 for 24 h at -0.3 V, inset shows the NH₃ yield rate and FE after 1 h and 24 h respectively; (b) elemental mapping from FESEM of after stability sample; (c) XPS full survey spectra of SnO_2 -600 before and after stability test; (d) deconvoluted narrow spectra of O1s of the catalyst before and after stability study; (e) Raman spectra of fresh and after stability SnO_2 -600 sample (A-E represent the different vibrations for Sn-O bonds); (f) XRD spectra of SnO_2 -600 catalyst before and after stability test, compared with bare activated carbon cloth.

7.5 Conclusion

This chapter provides sufficient insights about how oxygen vacancy in SnO₂ modulate the crystal structure of the (110) and (101) planes. As anticipated from theoretical studies that SnO₂ with bo_v is structurally more stable than io_v, upon high temperature pyrolysis, SnO₂ displayed a gradually dominating bo_v than the io_v from the Raman spectra. In particular, the (101) plane with bo_v was proved to be energetically more favorable towards N₂ adsorption at the Sn centers on either side of the bo_v enabling end-on followed by side-on N₂ adsorption. A push-pull electronic interaction between the orbitals of Sn and N₂ facilitated a charge transfer from site-A/B Sn to N₂, brought about by the altered electronic structures of the material, as evidenced from XPS. With an optimum oxygen vacancy density, upshift of the valence band maximum, greater N₂ adsorption tendency and enhanced charge transfer kinetics, SnO₂-600 showed maximum NRR performance with 53 µg h⁻¹ mg_{cat}⁻¹ NH₃ yield rate and 48.5 % FE. The NRR site selectivity of the material was observed owing to the energetically favored H-adsorption on the O-atoms, favoring NRR over HER on the Sn active site. This study thus provided a detailed understanding of the structural innovation of the bo_v-SnO₂, electronic interactions between Sn and N₂, kinetic and mechanistic investigations with RRDE and in-situ ATR-FTIR studies, respectively, and opened up avenues for a more explicit study on the vacancy-engineered materials for NRR.

7.6 References

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Regulating the OER kinetics towards an energy-efficient electrochemical NRR

Overview: Electrochemical NRR is imperatively countered with the OER on a conventional Pt counter electrode. Upon focusing on the development of suitable cathode catalysts, it is usually overseen that OER on Pt seeks a significant energy input to overcome the slow reaction kinetics, regardless of the efficiency of the NRR catalyst. Here, we unveil that, on pursuing OER with RuO₂ in KOH, the NRR process reinforces thermodynamically. As a proof of concept, we assembled RuO₂ with an NRR catalyst FePc, in an electrolyzer, preferably in a two-electrode setup, where the catholyte consisted of 0.5 M NaBF4. This system achieved selective cathodic conversion of N₂ to NH₃ with 67.6 % FE at 0.0 V (vs RHE) and simultaneous anodic water oxidation to O₂ with a high electricity-to-chemical energy conversion efficiency of 46.7 %. The electrolyzer forecasted a full cell voltage of 2.04 V, which demands only 603 mV overpotential to attain 0.5 mA current to drive forward the chemical equilibrium of the overall cell reaction.



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8.1 Motivation of the chapter

The electrochemical NRR is regarded because of its several advantages over the Haber Bosch process, majorly its net-zero carbon impact and ambiance. Down the lane, several catalysts are developed with fascinating properties to scale up NH₃ production to the industrial level. But the excessive potential required for this electrochemical process consumes huge electricity, which elevates the overall energy utilization like that invested in the Haber Bosch process. So, to make use of the NRR in an energy efficient manner, one needs to think beyond a fruitful catalyst development or electrolyte improvisation. NRR is a cathodic process accompanied by OER as the oxidation reaction. It is realized that if the current flow could be improved for this full cell reaction, which is possible by kinetically enhancing the reaction rates, it would require a low voltage input and eventually accomplish the reactions at lower energy consumption.

8.2 Introduction

Although NRR at ambient conditions of temperature and pressure with zero-carbon footprint is promising toward a sustainable and green future,^{1,2} it is a challenging quest due to the chemical inertness of the N₂ gas.³ Although a high FE for ammonia synthesis can be achieved by designing NRR catalysts that successfully suppress the competitive HER on its surface,^{4,5} it is very crucial to realize that the kinetics of the thermodynamically controlled NRR process relies largely on the counter oxidation reaction kinetics. Thus, it is not sufficient to solely look out for slowing down the HER kinetics, but a reinforcement of OER kinetics is also necessary to uplift the NRR performance. This, in a broader perspective, affects the production rate and FE of ammonia synthesis and the excess electricity to chemical energy conversion efficiency. Thus, it is important to simultaneously pay attention to both reactions and the gap needs to be bridged if one aims to move toward an energy-efficient electrochemical NRR process; however, it has taken no notice of the researchers to date.

In this chapter, we have tried to establish the concept of inter-dependency of the NRR coupled OER processes to achieve an appreciable production rate and FE of ammonia synthesis. As an anode catalyst, we have taken RuO₂ on Ni foam (1×1) cm² and compared its superiority over the conventionally used Pt counter electrode for OER. Under such conditions, the NRR selectivity not only improved on the FePc cathode in 0.5M NaBF₄ but also the FE shot up to 67.6 % at 0.0 V with 4 mg cm⁻² RuO₂ in 0.5 M KOH for OER. As a proof of concept, an NRR electrolyzer was assembled in a two-

electrode system, where the full cell overpotential for 0.5 mA current was measured to be 1.36 V for Pt, which drastically reduced to half, that is, 0.60 V in the case of 4 mg cm^{-2} RuO₂. Consequently, the spontaneity of the NRR process improved along with the full cell reaction being driven kinetically forward at the cost of lesser electricity consumption. Thus, the energy efficiency of the system was found to be 46.7 %, which is way better than what is conventionally achieved with the Pt counter electrode (20.2 % for this chapter). This concept has a broader importance to work simultaneously on the different parameters of NRR along with the development of efficient catalysts for OER (even better than the state-of-the-art RuO₂/IrO₂ catalysts)⁵ for attaining revolutionary heights of NRR kinetics, thermodynamics, and energetics.⁶

8.3 Experimental Section

8.3.1 Electrochemical characterizations for OER and full cell

For NRR, the conventional electrochemical characterizations are followed as elaborated in section 2.4.19 of chapter-2. 0.5 M NaBF₄ was taken as the working electrolyte with FePc as the cathode material on activated CC, serving as working electrode. For OER, 0.5 M KOH was used as the working electrolyte and Pt wire and RuO₂ (with different mass loading on Ni foam) was used as the working electrode. While Hg/HgSO₄ (sat. K₂SO₄) served as the reference electrode, graphite rod was used as the counter electrode. The OER potentials were converted to RHE using the following equation 8.1:

$E_{RHE} = E_{Hg/HgSO4} + (0.0591 \times pH) + 0.64 (E^0 \text{ at } Hg/HgSO_4, \text{ sat. } K_2SO_4)$ (8.1)

For full cell study, a two-electrode system comprising of FePc on CC (in 0.5 M NaBF₄) was used as the working electrode in the cathodic chamber of the H-cell and the anodic counterpart contained RuO₂ on Ni foam as the reference and counter electrode in 0.5 M KOH to measure the full cell voltage. For a matter of comparison, Pt wire was also used as anode with the same connections as that of RuO₂.

All presented polarization curves were steady-state ones after 10 cycles and were measured at 10 mV s⁻¹ scan rate and the current density values were normalized to geometric surface areas for NRR. Whereas, for OER the polarization curves were taken at 10 mV s⁻¹ to give sufficient time for the surface oxidation reactions to occur. All the polarization curves were without any iR compensation. For an elaborate NRR study, CA tests were conducted in the N₂-fed 0.5 M NaBF₄ solution for 1 h over the potential range from +0.1 V to -0.3 V vs RHE.

8.4 Results and discussion

8.4.1 Motivation of work from current research point of view

The electrochemical NRR is always accompanied by a counter oxidation reaction at the anode compartment, which is imperatively OER. One major aspect of why researchers seek an alternative to the Haber Bosch process is its energy intensiveness and drastic operating conditions.⁷ However, the electrochemical NRR process, owing to several bottlenecks such as the competitive HER, poor solubility of N₂ in aqueous electrolyte, and the poor selectivity of material toward N₂ adsorption, utilizes sufficiently high energy inputs for the production of ammonia, moreover at a much lower production rate.^{8,9} When these issues persist, the sluggish kinetics of the counter OER on the conventional Pt anode surface in the aqueous electrolyte consumes about 90 % of the electricity input, which makes the overall NRR coupled OER process energetically and thermodynamically unfavorable.¹⁰ Thus, we assembled an electrolyzer for a proof of concept and conducted full cell electrolysis by integrating FePc on activated CC as the cathode and Pt wire as well as RuO₂ (0.5–4 mg cm⁻²) on Ni foam as the anode in the H-cell as shown in Figure 8.1. To justify the concept and the interdependence of the two



Figure 8.1. Schematic representation of the cell components used for the full cell study involving cathodic NRR on FePc on CC and anodic OER on Pt wire as well as RuO_2 on Ni foam.

processes (NRR and OER), the commercial FePc catalyst for NRR^{11,12} has been rendered here (the detailed physical characterizations of this commercial rod-shaped FePc catalyst are elaborated in Figure 8.2). It is widely explored theoretically and experimentally that single atom catalysts are beneficial for NRR, and hence, such a cathode catalyst is chosen.^{13,14} From the results of chapter-3, having solved the kinetics related issues of



NRR with NaBF₄, the cathodic compartment of the H-cell comprised FePc as the cathode catalyst and 0.5 M NaBF₄ as the catholyte. However, OER is usually more reliable on

Figure 8.2. (a) FESEM image of commercial FePc catalyst (scale bar: 20 μ m); (b) cumulative and individual mapping of the elements present in the catalyst, (scale bar: 5 μ m); (c) TEM image of FePc, (scale bar: 500 nm); (d) HRTEM image of the FePc catalyst, (scale bar: 10 nm); (e) XRD spectrum of the FePc corresponding to the JCPDS number 00-037-1845 for the β -iron phthalocyanine polymorph; (f) XPS full survey spectrum of FePc showing distinct regions of C 1s, N 1s, O 1s and Fe 2p; High resolution deconvoluted XPS spectra of (g) C 1s, (h) N 1s (inset shows structural representation of FePc, grey colour denotes C, white denotes H, red denotes pyridinic N, blue denotes pyrrolic N and yellow denotes Fe), (i) C 1s and (j) Fe 2p of FePc catalyst.

noble metal oxide surfaces such as IrO₂/RuO₂.¹⁵ Although several noble metal free catalysts are already reported in the literature outperforming these noble-metal catalysts toward OER,^{16–18} but being considered as the state-of-the-art catalysts and RuO₂ having a better intrinsic OER activity than IrO₂, as shown by Lee et al., our anode catalyst was prepared with different mass loading of RuO₂ on Ni foam as a porous self-standing substrate for the electrode material.^{19,20} Nevertheless, the working electrolyte at the anodic side was taken as 0.5M KOH, which is known to reinforce OER.

8.4.2 OER studies with RuO₂

It is to be noted that all the potential values reported in this chapter are calibrated with respect to RHE following equation 2.6 of chapter 2 and equation 8.1. The initial set of electrochemical studies for OER involved LSV curves in a typical three electrode configuration in 0.5 M KOH solution. Figure 8.3a shows the non-iR-corrected LSV profiles for Pt and different mass loaded RuO₂ on Ni foam for OER. With an advent of the positive potential range, an increased current density could be observed with evolution of gas bubbles at the catalyst surface denoting the initiation of OER. While Pt wire exhibited a potential of $1.62 V^{21}$ to reach a current density of 10 mA cm⁻², RuO₂ exceeded far beyond this performance with the minimum potential requirement of 1.45 V and a maximum loading of 4 mg cm⁻². As demonstrated by Niu et al., the OER overpotential at the same current density (η_{10}) was calculated with respect to the standard



Figure 8.3. (a) LSV polarization curves of all the catalysts for OER in 0.5 M KOH at 2 mV s⁻¹ scan rate; (b) Overpotential required by the corresponding catalyst to achieve 10 mA cm⁻² current density during OER; (c) LSV polarization curves of the current against cell voltage from different anodes coupled with FePc; (d) Comparative bar diagram representing the overpotential of the full cell systems with FePc as the cathode and Pt wire and different mass loaded RuO₂ on Ni foam as the anode. Error bars represent the standard deviation values from three different sets of electrochemical studies.

thermodynamic potential for OER, that is, 1.23 V.²² Figure 8.3b demonstrates the gradual lowering of the OER overpotential upon moving from Pt to RuO₂ and with subsequent increase in the loading of RuO₂ on Ni foam providing enhanced active sites for OER.

Ideally, assuming 298.15 K, the overall thermodynamic cell voltage for the full cell reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2O \rightarrow NH_3 + \frac{3}{4}O_2$ becomes 1.424 V (as explained and calculated using equations 2.23-2.26 in chapter 2). LSV without iR compensation of the full NRR electrolyzer cell showed that the maximum cell voltage of 2.78 V was required by Pt as the anode, which subsequently reduced to 2.04 V with a gradual increase in the RuO₂ loading on Ni foam to attain a current of 0.5 mA, as shown in Figure 8.3c. Thereafter, by applying equation 2.27 of chapter 2, the overpotential ($\eta_{OER-NRR}$) was calculated to be 1.36 V for the conventional cathode||Pt system, which reduced to almost half, that is, 0.603 V, in the case of FePc||RuO₂ (4 mg cm⁻²) full cell system, as displayed in Figure 8.3d. A lower overpotential indicated lesser energy consumption for the forward chemical equilibrium of the NRR coupled OER processes.

8.4.3 NRR thermodynamics and kinetics: FePc||Pt versus FePc||RuO2

In general, all the bottlenecks of the NRR process signify the positive ΔG value (+412.18 kJ mol⁻¹) with an equilibrium constant being < 1 according to the ideal reaction conditions of NRR (calculated in this chapter using equations 2.28 and 2.29 of chapter 2).²³ In the conventional method, with Pt as the counter electrode, the OER kinetics required a huge activation energy barrier with a full cell voltage of -2.78 V (far more negative than the thermodynamic requirement). Consequently, the overall system suffered from a positive upsurge of the ΔG impacting negatively on the NRR thermodynamics and energetics. There is no point in developing electrocatalysts for only NRR when it does not anyway improve the spontaneity of the process or drive the reaction equilibrium forward. Thus, this study is of utmost importance in the current scenario of research ongoing on NRR because the counter-oxidation kinetics and the overall NRR coupled OER reaction thermodynamics are at infancy and the research direction should be inclined to this area to earn full out of these environmentally benign electrochemical processes. Considering that none of the processes occurring in nature are truly ideal, at least one should aim to reach the periphery of the thermodynamic values of the different rate determining parameters for any process under the experimental reaction conditions. Interestingly, when RuO₂ was taken as an anode material on Ni foam, not only the full cell potential became less negative but there was also a sharp drop in the ΔG value to +590.19 kJ mol⁻¹ from +807 kJ mol⁻¹ (in the case of Pt). Thus, the trend ΔG (Theoretical) < ΔG (FePc||RuO₂) < ΔG (FePc||Pt) favored the otherwise

thermodynamically unfavorable chemical equilibrium of the exothermic NRR process to increase twofold with RuO₂ than Pt counter electrode as shown in Table 8.1.

Parameters	Thermodynamic values	Values with Pt as counter electrode	Values with RuO ₂ (4 mg cm ⁻²) as counter electrode
Full cell potential $(\Delta E_{\text{NRR-OER}} \text{ in } V)$	- 1.42	-2.78	-2.04
Gibbs' energy change $(\Delta G \text{ in } kJ \text{ mol}^{-1})$	412.2	807	590.2
Equilibrium constant (k in V mol ⁻¹)	0.24	0.06	0.13

Table 8.1. Comparative data evaluating the thermodynamics of NRR with different counter oxidation electrodes.

Before commencing with the NRR studies, it is mandatory to negate all the contamination possibilities. The ¹⁴N₂ feed gas (Sigma-Aldrich; 99.99% purity) was rigorously passed through acid and base traps where the trap solutions were examined by UV–visible and IC techniques and the net impurity was found to be $< 0.001 \ \mu g \ mL^{-1}$ as shown in Table 8.2. To show the significant impact of this study on the NRR performance of FePc, we conducted CV at 10 mV s⁻¹ in the (NaBF4)FePc||Pt,RuO₂(KOH) systems.

Table 8.2. Summary of the ${}^{14}N_2$ gas purity analysis.

Gas	Purity	NO ₂ ⁻	NO ₃ ⁻	NH3	Total N-impurities
	(From supplier)	(μg mL ⁻¹)	(μg mL ⁻¹)	(μg mL ⁻¹)	(μg mL ⁻¹)
$^{14}N_2$	99.99 % (Sigma Gases)	< 0.001	< 0.001	< 0.001	< 0.001

The Nafion membrane also plays a vital role here in a sense, being selectively permeable to protons, it checks the infusion and, hence, interference of electrolyte ions from either of the compartments to the other side. The non-iR-compensated data shown in Figure 8.4a revealed a better NRR onset potential with incremental cathodic current density in the case of RuO₂ as the counter electrode. Thereafter, a CA study over a potential window ranging from +0.1 to -0.3 V in 0.5 M NaBF₄, holding each potential for 1 h, was an obvious experimental protocol to follow to ensure the potential with a maximum yield of ammonia.^{24,25} After each CA measurement, the aliquot solution was subjected to colorimetric tests, namely, indophenol blue methods method for the quantification of NH₃ (details are provided in section 2.8 of chapter 2). The concentration plots obtained





Figure 8.4. (a) Comparative CV curves for NRR in N_2 saturated 0.5M NaBF₄ at 10 mV s⁻¹ scan rate; (b) FE values of NH₃ synthesized over the wide-ranging potential for NRR in FePc//Pt and FePc//RuO₂ systems; (c) NRR performance comparison of FePc catalyst after 1 h CA run at 0.0 V vs RHE in 0.5 M NaBF₄ with RuO₂ as counter electrode in 0.5 M KOH anolyte via UV-Vis and NMR spectroscopic techniques; (d) CA response of FePc catalyst in 0.5 M NaBF₄ under ¹⁴N₂ and ¹⁵N₂ purged gases at 0.0 V vs RHE; (e) ¹H-NMR spectra of the concentrated electrolyte solution obtained after isotope labelling experiment; (f) Comparison of ammonia yield and FE via NMR method with ¹⁴N₂ and ¹⁵N₂ feed gases.

system with an FE as high as 67.6 % at 0.0 V as shown in the bar plot in Figure 8.4b (equations 2.21 and 2.19 of chapter 2). The yield rate of ammonia was cross verified with the most reliable NMR method and was calculated to be identical as obtained from the UV–Vis spectroscopic method (Figure 8.4c). However, to certainly confirm the source of the produced ammonia, the ¹⁵N₂ isotope labelling experiment was conducted quantitatively and compared with that with ¹⁴N₂ (Figure 8.4d). In the ¹H-NMR spectra, while a triplet appeared for ¹⁴NH₄⁺, a clear doublet with coupling constant (J) value 72 Hz was observed for ¹⁵NH₄⁺ (Figure 8.4e). A bar plot in Figure 8.4f shows similar experimental values derived from both ¹⁴N₂ and ¹⁵N₂ feed gases which emphasized the reliability of our experimental data. Additionally, a differential onset potential and reduced current density of the FePc||RuO₂ system in the presence of Ar as compared to N₂ (Figure 8.5a) advocated that such an electrochemical environment was unsuitable for ammonia production, which was also obeyed at the OCP in the presence of N₂ (Figure 8.5b). In fact, blank CC also displayed a much-lowered NRR performance, which reflected the influence of the catalyst for NRR (Figure 8.5b).


Figure 8.5. (a) CV polarization curves for NRR of $FePc/|RuO_2$ system under N_2 and Ar purged conditions at 10 mV s⁻¹ scan rate; (b) Comparative bar plot of yield rate and FE of NH₃ in N_2 and Ar at different conditions after 1 h CA test; (c) CV curves of $FePc/|RuO_2$ systems for NRR in N_2 saturated 0.5 M NaBF₄ at 10 mV s⁻¹ scan rate with different anolytes; (d) Concentration of NH₃ produced during the electrochemical study holding 0.0 V for 1 h each; (e) NRR performance of $FePc/|RuO_2$ at 0.0 V vs RHE in presence of different combinations of electrolytes.

8.4.4 Importance of electrolyte selection

The role of anolyte was further assessed with three different cell systems, namely, FePc(NaBF₄)||RuO₂(KOH), FePc(NaBF₄)||RuO₂(NaBF₄), and FePc(NaBF₄)||RuO₂(H₂O), and we unravelled that these three different electrolyte systems drastically affected the NRR/OER performance of the catalysts establishing the strong influence on the catalyst-reactant interaction. This effect was visibly evident from the NRR CV curves at 10 mV s⁻¹ in Figure 8.5c. The NH₃ concentration produced after 1 h CA study at 0.0 V and the NRR activity trend with different analytes are shown in 8.5d, Although the be Figures e. optimized system was found to FePc(NaBF₄)||RuO₂(KOH), FePc as a cathode material holds a benefit of doubt that the material N might interfere in the NH₃ production and thus a prolonged NRR stability study was performed for 48 h (Figure 8.6a) and hence, the yield and production rate of NH₃ was compared with that obtained after 1 h (inset of Figure 8.6a). It was interesting to find a stable cathodic current retention with consistent performance of the catalyst. A rigorous after-stability material characterization (Figure 8.6b-e) advocated that there was neither metal leaching nor loss of catalyst-N even after the catalyst was exposed to prolonged hours of NRR.



Figure 8.7. (a) Stability study of $FePc(NaBF_4)//RuO_2(KOH)$ system towards NRR; (b) shows the corresponding bar diagram for the calculated yield rate and FE of ammonia after 1 h and 48 h of CA run; (c) TEM image (scale bar: 200 nm) of FePc catalyst after stability measurements for NRR; (d) HRTEM image (scale bar: 5 nm) of the after-stability catalyst; XPS analysis of FePc catalyst after 48 h NRR stability study showing deconvoluted narrow spectra for (e) N 1s and (f) Fe 2p.

However, it is remarkable to note that, not only OER or NRR was highly influenced by KOH but the full cell voltage was also found to be affected with the different anolytes as shown by the LSV curves in Figure 8.7a. While H₂O was unsuitable, the inset of Figure 8.7a revealed that even NaBF₄ was responsible for the much sluggish kinetics of OER resulting in 834 mV full cell overpotential, which reduced to 603 mV in the presence of KOH. Thus, it is understandable that with RuO₂ and KOH, NRR occurred at a low current consumption improving the energy efficiency for the full cell reaction. Considering all the thermodynamic and kinetic improvements in the FePc||RuO₂ system,



Figure 8.6. (a) LSV polarization curves of the current against cell voltage for $FePc//RuO_2$ system in different analyte conditions, keeping $NaBF_4$ fixed as catholyte, inset the full cell overpotential of the two cell conditions; (b) Energy efficiency comparison for the NRR process with the conventional versus our improvised system.

the electricity to chemical energy efficiency of the NRR/OER electrolyzer was obtained to be 46.7 % as shown in Figure 8.7b, derived from equation 2.30 of chapter 2.

8.5 Conclusion

In summary, this chapter has primarily aimed to establish the mutual importance of OER along with NRR kinetics toward an improved electricity to chemical energy conversion efficiency of the full NRR electrolyzer system. Commercial state-of-the-art RuO₂ catalyst on porous Ni substrate not only outperformed Pt for OER but also drastically improved the overall cell voltage of the NRR electrolyzer. This NRR coupled OER system with FePc||RuO₂ imparted a thermodynamic improvement in terms of Gibbs' energy and equilibrium constant. The FePc(NaBF4)||RuO₂(KOH) system improved the spontaneity of the process at a better current and energy conversion efficiencies of 67.6 % and 46.7 %, respectively. The concept furnished in this study is simple yet very important for improving the energy efficiency of the NRR process, where shedding light on the OER kinetics to reinforce NRR and full cell energy consumption has not been implemented beforehand in this manner.

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Summary and future scope of the thesis

Overview: In this chapter, the crucial findings of this thesis are summarized. This thesis is an attempt to explore the various fundamental parameters of the electrochemical NRR to produce green ammonia, which is now one of the research hotspots. This is due to the overwhelming utility of ammonia in fertilizer industries as well as energy sectors as an alternative transportation fuel or hydrogen reservoir. However, the several bottlenecks of the process utilize huge energy along with a sacrificial production rate of ammonia, distant from the industrial scale margins. This has motivated us first to optimize the colorimetric detection methods for quantitative detection of the produced ammonia. This is followed by the development of electrocatalysts and exploration of aqueous electrolytes, focussing on lowering the energy barrier for the potential determining steps of NRR. A structure-function relationship study between the N2-electrolyte-electrode active surface provides an in-depth understanding of the reaction kinetics and enables us to improve the energy-effectiveness of the process. We hope that this thesis work opens new paradigm for developing advanced materials and electrolyzers for NRR to meet the real-time targets of the green ammonia from commercial point of view that can serve as the future economy.

9.1 Overall summary

The present thesis work concentrates on the improvisation of different rate-determining parameters of NRR, majorly focusing on overcoming the bottlenecks of the process such as (a) poor N_2 solubility in aqueous electrolytes, (b) material selectivity issues empowering HER over NRR and (c) sluggish kinetics of OER affecting the rate of NRR. However, in all the chapters, along with material/electrolyte innovation, the prime goal has been to realize the chemistry of active sites that intuitively manipulate the mechanisms and kinetics of the elementary steps of NRR.

Chapter-1 discusses the importance of ammonia from past to present to future and surfaces the motivation of the current study and its relevance in the frontier of future research domains. A subtle transformation from the century-old Haber Bosch process to the zero-carbon electrochemical approach of ammonia synthesis has been interpreted from the point of view of the economy as well as energy consumption and production. Hence the electrochemical NRR has been discussed along with a fundamental understanding of the thermodynamics and mechanisms of the process and the ratelimiting parameters as mentioned above. Consequently, an overview of different genres of electrocatalysts for the purpose has been provided aiming to shed light on the relevant upcoming chapters of the thesis.

But before the commencement of the experimental work, detailed information regarding the instrumentations widely used for the material characterizations (both physical and electrochemical) is summarized in **chapter-2**. This chapter also synopsized the calculations and formulae used in the following chapters to determine the physical and electronic properties as well as the NRR performance of the materials. The second part of this chapter elaborates on the colorimetric methods for the detection of NH_3 , N_2H_4 and NO_2^- followed by an overview of the rigorous optimizations done with the Indophenol blue method for reliable and reproducible quantification of NH_3 .

Primarily, single-atom catalyst (Mn) in an N-doped carbon matrix (Mn-N/C) has been considered in **chapter-3**, where the limelight of the chapter is the innovative aqueous electrolyte NaBF₄, which also acts as a co-catalyst. The Lewis acidic chemistry of the BF₃ counterpart of this electrolyte plays a multitudinous role in enhancing the N₂ concentration in the medium by forming N₂-BF₃ adduct. In fact, unlike other conventional aqueous electrolytes, BF₃ helps to modulate the electronic structure of Mn-N₄ active site and by a push-pull electronic effect, accelerates the metal-N₂ interaction, promoting N₂ activation, bond polarization and first protonation. All these factors, along with the easy desorption of NH₃ (Lewis base-acid interaction with BF₃) facilitate the overall kinetics of the process at a low overpotential with 2.45×10^{-9} mol s⁻¹ cm⁻² production rate of ammonia, approaching the industrial scale periphery.

However, this electrolyte manifests its effect on the M-N₄ coordinated electrocatalysts that limit the scope of material exploration towards improving NRR to a better extent. Thus, the conventional aqueous electrolytes are used in **chapter-4**, while introducing O edge-functionalization in the boron-carbonitride catalyst (BNCO). Boron is already known to have energy-symmetry orbitals ensuring better σ -donation π -back donation interactions with N₂, like metals. The O-functionality at the catalyst edge forms an electron-dense pentagon and imparts a charging effect on the adjacent B active site provoking N₂ adsorption and N=N bond activation. Since B dominantly prefers N₂ adsorption over protons, the competitive HER is suppressed on the active site helping to achieve 34.7 % FE. Additionally, this chapter also discusses that acidic electrolyte with different anions like PO₄³⁻ and SO₄²⁻ cause poisoning effect on the active site by strongly interacting with B through O ends, inhibiting the long-term NRR performance of the material. At the same time, HCl proves to be a better contender for the purpose.

The aqueous electrolytes already have abundant protons and acidic medium adds a feather on the hat for HER, which truly challenges the material selectivity for NRR. Thus, in the following chapters, a neutral electrolyte is accounted and HER is tried to be avoided by a versatile catalyst development approach. Having observed the importance of the charging effect, a hetero-structure material NPG@SnS₂ is developed by interface engineering strategy in **chapter-5**. Here, the work-function difference between NPG and SnS₂ enables band bending at their interface to equilibrate the fermi levels and a charge density accumulation at the SnS₂ site helps lower the work function of the heterostructure material, with a four-fold increase in the conductivity. Sn is anyway favored for NRR and the adsorption of H (*H) on S being energetically favored (1.39 eV lower in energy) compared to *H on Sn led to two major conclusions: (a) the electrocatalytically active surface Sn in NPG@SnS₂ is preserved for facile N₂ adsorption and reduction, and (b) the competitive HER is suppressed yielding 49.3 % FE for NRR with our material.

Now, talking of HER, it is better to seek such catalysts that have inherent HER suppressing ability, then it will add to the advantages of catalyst modification for NRR. Thus, in **chapter-6**, Ag_3PO_4 is taken as the host material and is doped with group-VI metals like Cr, Mo and W, which again possess inherent N₂ adsorption capabilities over

proton adsorption. The doping assisted vacancy generation in the catalysts, assumed from EPR and PALS analyses enriches the material with improved active site density. The materials experience alteration in the d-band center favouring N₂ adsorption in a side-on manner on Ag-Cr/Mo/W site. The NRR kinetics was extensively studied with RRDE, which also depicted product selectivity of our catalyst Mo/Ag₃PO₄-10. Theoretical revelations and in-situ ATR-FTIR studies determine the obscured reaction intermediates and unveil Mo as the best dopant in reinforcing NRR kinetically with 54.8 % FE.

To extend our investigation on the role of vacancy engineering, in **chapter-7** we develop O-vacant SnO₂ purposefully. Since SnO₂ exhibits in-plane and bridge-type oxygen vacancies, so an in-depth study about which type of vacancy holds responsible for NRR and how it manipulates the active site structure electronically is possible with this type of catalyst. It is observed that the bridge vacancy in the (101) plane of SnO₂ rather than the (110) plane gives an energy optimized stable structure for NRR, where centering the bridge vacancy, the two adjacent Sn atoms together serve as an active site for an end-on followed by side-on N₂ adsorption. While the sp³d hybrid orbitals of Sn atoms donate electron density to anti-bonding orbitals of N₂, the vacant 5d energy states of Sn (A and B sites) receive electrons from the bonding σ -orbital of N₂, allowing a facile bond polarization. In fact, the proton adsorption is more favoured on the electronegative O-atom deviating the HER pathway and benefitting NRR with 48.5 % FE. The kinetic and mechanistic investigations are carried out with RRDE and in-situ ATR-FTIR studies respectively together with theoretical support, that provide a wholesome survey of the role of vacancy in NRR, prioritized in this chapter.

After attaining an appreciable NRR performance with several electrolyte-catalyst modifications, our intention deviated to a broader goal of improving the energy efficiency of this process. The several bottlenecks of NRR and on top of that the sluggish OER kinetics intakes about 90 % of the electricity input and raises the overall energy and power demand of the NRR process, disregarding its usefulness in comparison to the industrial Habe-Bosch process. So, **chapter-8** discusses the inter-dependency of the NRR and OER processes and how the kinetics of one impacts the other. Upon replacing the conventional Pt counter electrode for OER, RuO₂ is found to not only improve the OER kinetics in 0.1 M KOH, but also enhances the FE for NRR at a lower overpotential and current consumption. As a proof of concept, the FePc||RuO₂ electrolyzer displays a high electricity-to-chemical energy conversion efficiency of 46.7%. The electrolyzer also forecasts a full cell voltage of 2.04 V, which demands only 603 mV overpotential to

attain 0.5 mA current to drive forward the chemical equilibrium of the overall NRR-coupled-OER cell reaction.

9.2 Contribution from the projects carried out under the thesis work

The contributions and achievements of all the chapters/projects accomplished under the

thesis work are summarized in Table 9.1.

 Table 9.1. Overall work summary with highlights of the chapters and achievements.

Chapters and motivation Highlights and achievement		Results
<i>Chapter-2: Colorimetric method</i> <i>optimization</i>(a) Accurate and reliable quantification of ammonia	Indophenol-blue method for NH_3 detection: Dye is photo-stable for long hours (nitroferricyanide is the unstable light-sensitive element), method is inert to foreign interferants and applicable to universal aqueous electrolytes.	Final medium pH for optimum colour of dye: 9.5 to 11.0
 <i>Chapter-3: Mn-N/C (single atom in N-doped C matrix)</i> (a) Mn has suitable d-electron configuration for NRR (b) Fluorinated moieties enable better N₂ solubility 	$NaBF_4$ as new aqueous electrolyte: Improved N ₂ solubility by N ₂ \rightarrow BF ₃ adduct formation, N ₂ activation by push- pull electronic effect, facile desorption of product via H ₃ N \rightarrow BF ₃ formation.	Production rate: 2.45×10 ⁻⁹ mol s ⁻¹ cm ⁻² FE: 18.6 %
Chapter-4: Functionalized BNCO (a) B has energy symmetric orbitals as N ₂	Charging effect on B active site due to O -edge functionalization: better N ₂ -B orbital overlap and charge transfer, importance of choice of electrolyte towards long term material performance (active-site poisoning).	<i>Production rate:</i> 0.86×10 ⁻⁹ mol s ⁻¹ cm ⁻² <i>FE:</i> 34.7 %
Chapter-5: NPG@SnS ₂ heterostructure (a) Sn is a semi-metal, restricted proton-electron availability, suppressing HER	Band bending at the metal- semiconductor interface: charge accumulation over Sn, NRR>HER (H ⁺ adsorption deviated on S site).	<i>Production rate:</i> 0.34×10 ⁻⁹ mol s ⁻¹ cm ⁻² <i>FE:</i> 49.3 %
Chapter-6: Group-VI metal doped Ag_3PO_4 (a) Ag and PO_4^{3-} has HER suppressant ability (b) Group VI metals: N ₂ adsorption>H ⁺ adsorption	Improved active site density: Ag and Cr/Mo/W together enable side-on N_2 adsorption by orbital d-p mixing effect (Ag-Mo acts best with respect to N_2 adsorption, activation and NRR rate kinetics-studied with RRDE), intermediates arrested in in-situ FTIR.	<i>Production rate:</i> 0.64×10 ⁻¹⁰ mol s ⁻¹ cm ⁻² <i>FE:</i> 54.8 %
 <i>Chapter-7</i>: Oxygen vacant SnO₂ (a) Sn: semi-metal and limited electron-proton density (b) Vacancy: provides enhanced active site density and charge polarization 	Bridge oxygen vacancy: energy optimized structure, end-on followed by side-on N_2 adsorption over adjacent Sn atoms (H ⁺ adsorption on O, NRR>HER), kinetics studies with RRDE, mechanism studied theoretically and by in-situ ATR-FTIR.	<i>Production rate:</i> 0.17×10 ⁻⁹ mol s ⁻¹ cm ⁻² <i>FE:</i> 48.5 %
Chapter-8: FePc//RuO ₂ (a) Fe for NRR (co-factor in nitrogenase bio-enzyme) (b) RuO ₂ : state-of-the-art catalyst for OER	<i>NRR electrolyzer</i> : catalyst (cathode, anode)-electrolyte improvisation and NRR/OER inter-dependency towards improving power and energy input for full cell reaction.	FE: 67.6 % Energy efficiency: 46.7 %

9.3 Future perspectives

This thesis aims to develop and investigate new catalysts (designed with different material synthesis strategies) and electrolytes such that the nitrogen adsorption, bond polarization and first protonation steps can be accelerated at the cost of low overpotential. This eventually improves the power input and energy consumption of the process with a fair production rate and FE for ammonia synthesis. With the execution of required experimental protocols and derivation of sound electrochemical results, we tried to accomplish our goal to reach the industrial scale periphery of green ammonia production in an energy-efficient manner. However, there remain several rooms for exploration in the direction of future possibilities of this thesis work that can be extended as follows:

- Development of ambient aqueous electrolytes having features like ionic liquids, which will help to solvate a better concentration of N₂ in the medium.
- Development of bifunctional catalysts having efficacy towards NRR and OER (better than state-of-the-art catalysts RuO₂/IrO₂), such that a low overpotential for the full cell reaction (in two-electrode cell configuration) can be achieved.
- Development of catalysts efficient towards reversible nitrogen electrocatalysis, such that a membrane-less electrochemical cell can be deployed since the Nafion membrane is often regarded as a "source & sink" of ammonia.
- Fabrication of a flow-cell electrolyzer for NRR, capable of bulk production of ammonia, with a scalable and economic electrocatalyst and other electrochemical conditions.
- Technology development for solidification, segregation, and purification of the produced ammonia from the ions constituting the electrolyte salts.

Therefore, it can be perceived that besides academia, the contents covered in the thesis work have a huge future scope in the industrial sectors that can immensely help to attain the "Net-Zero" pledge of the much-desired sustainable society.



Appendix A

List of Publications (included in thesis)

- Ashmita Biswas, Bikram Ghosh, Ramendra Sundar Dey*, Refining the Spectroscopic Detection Technique: A Pivot in the Electrochemical Ammonia Synthesis. (*Langmuir*, 2023, 39, 10, 3810-3820)
- Ashmita Biswas[†], Samadhan Kapse[†], Bikram Ghosh, Ranjit Thapa, Ramendra Sundar Dey^{*}, Lewis acid-dominated aqueous electrolyte acting as co-catalyst and overcoming N₂ activation issues on catalyst surface. (*PNAS*, 2022, 119 (33), e2204638119)
- 3. Ashmita Biswas, Samadhan Kapse, Ranjit Thapa, Ramendra Sundar Dey *, Oxygen Functionalization-Induced Charging Effect on Boron Active Sites for High-Yield Electrocatalytic NH₃ Production. (*Nano-Micro Letters*, 2022, *14*, 214)
- 4. Ashmita Biswas, Surajit Nandi, Navpreet Kamboj, Jaysree Pan, Arghya Bhowmik, Ramendra Sundar Dey*, Alteration of electronic band structure via metal-semiconductor interfacial effect enables unprecedented Faradaic efficiency for electrochemical nitrogen fixation. (*ACS Nano*, 2021, 15, 20364–20376)
- 5. Ashmita Biswas[†], Mamta Devi Sharma[†], Samadhan Kapse, Ranjit Thapa, Santosh Gupta, Kathi Sudarshan, Ramendra Sundar Dey^{*}, Strain-induced electronic structure modification of group-VIB metal doped Ag₃PO₄ boosting electrochemical ammonia synthesis by d-p orbital interaction. (Under review)
- 6. Ashmita Biswas, Narad Barman, Avinash N., Ranjit Thapa, Kathi Sudarshan, Ramendra Sundar Dey*, Deciphering the bridge oxygen vacancy-induced cascading charge effect for electrochemical ammonia synthesis. (Mater. Horiz., 2024, doi.org/10.1039/D3MH02141F)
- Ashmita Biswas, Ramendra Sundar Dey*, Elevating the Energy Efficiency for the Powerto-Ammonia Conversion: Role of Oxygen Evolution Reaction Kinetics. (J. Chem. Phys. 2023, 158, 201103) This paper is part of the 2023 JCP Emerging Investigators Special Collection

Appendix B

List of Publications (not included in thesis) & Patents

- Ashis Chhetri[†], Ashmita Biswas[†], Sumana Podder, Ramendra Sundar Dey^{*}, Joyee Mitra^{*}, Strategic design of VO₂ encased in N-doped carbon as an efficient electrocatalyst for nitrogen reduction reaction at neutral and acidic media. (Communicated)
- 2. Ashmita Biswas[†], Surajit Samui[†], Ramendra Sundar Dey^{*}, Interlinking electronic band properties in catalysts with electrochemical nitrogen reduction performance: A direct influence. (Communicated)
- 3. Ashmita Biswas[†], Bikram Ghosh[†], Kathi Sudarshan, Santosh Gupta, Ramendra Sundar Dey^{*}, Ample Lewis Acidic Sites in Mg₂B₂O₅ Facilitate N₂ Electroreduction through Bonding–Antibonding Interactions. (*Inorg. Chem.* 2023, 62, 34, 14094–14102)
- Ashmita Biswas, Subhajit Sarkar, Manisha Das, Navpreet Kamboj, Ramendra Sundar Dey*, A No-Sweat Strategy for Graphene-Macrocycle Co-assembled Electrocatalyst toward Oxygen Reduction and Ambient Ammonia Synthesis. (*Inorg. Chem.*, 2020, 59, 16385-16397)
- Ashmita Biswas[†]. Sakshi Bhardwaj[†], Tribani Boruah[†] and Ramendra Sundar Dey^{*}, Electrochemical ammonia synthesis: fundamental practices and recent developments in transition metal boride, carbide and nitride-class of catalysts. (*Mater. Adv.*, 2022, *3*, 5207-5233)
- 6. Renu Rani[†], Ashmita Biswas[†], Raihan Ahammed, Taniya Purkait, Anirban Kundu, Subhajit Sarkar, Mamta Raturi, Abir De Sarkar^{*}, Ramendra Sundar Dey^{*}, Kiran Shankar Hazra^{*}, Engineering catalytically active sites by sculpting artificial edges on MoS₂ basal plane for dinitrogen reduction at a low overpotential. (*Small*, 2023, 2206357)
- Manisha Das[†], Ashmita Biswas[†], Taniya Purkait[†], Tribani Boruah[†], Sakshi Bhardwaj, Sabuj Kanti Das and Ramendra Sundar Dey*, The Versatility of the Dynamic Hydrogen Bubble Template Derived Copper Foam on the Emerging Energy Applications: Progress and Future Prospects. (*J. Mater. Chem. A*, 2022,10, 13589-13624).
- Subhajit Sarkar[†], Ashmita Biswas[†], E. S. Erakulan, Ranjit Thapa, Ramendra Sundar Dey^{*}, Strategic modulation of target specific isolated Fe,Co single-atom active sites for oxygen electrocatalysis impacting high power Zinc-air battery. (*ACS Nano* 2022, *16*, 5, 7890–7903)
- Manisha Das[†], Ashmita Biswas[†], Ramendra Sundar Dey^{*}, Electrons on Play: Understanding the Synergism of Binary Transition Metals and Role of M-N-S Active Sites Towards Oxygen Electrocatalysis. (Chem. Commun., 2022, 58, 1934 – 937)
- Sakshi Bhardwaj[†], Sabuj Kanti Das[†], Ashmita Biswas, Samadhan Kapse, Ranjit Thapa, Ramendra Sundar Dey^{*}, Engineering hydrophobic-aerophilic interface to boosts N₂ diffusion and reduction through functionalization of fluorine in second coordination sphere. (*Chem. Sci.*, 2023, 14, 8936-8945)
- Manisha Das, Ashmita Biswas, Zubair Bashir Khan, Ramendra Sundar Dey*, Tuning the Electronic Structure of Cobalt Selenide on Copper Foam by Introducing a Ni Buffer Layer for Highly Efficient Electrochemical Water Splitting. (*Inorg. Chem.*, 2022, *61*, 33, 13218– 13225)

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- Manisha Das, Zubair Bashir Khan, Ashmita Biswas, Ramendra Sundar Dey*, Inter-Electronic Interaction between Ni and Mo in Electrodeposited NiMoP on 3D Copper Foam Enables Hydrogen Evolution Reaction at Low Overpotential. (*Inorg. Chem.* 2022, 61, 45, 18253–18259)
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- 21. Ramendra Sundar Dey and Ashmita Biswas, An electrocatalyst and a process for its preparation. Indian Patent Application No. 202011047861, Publication date: 30-09-2022.
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- 23. Ramendra Sundar Dey, Sakshi Bhardwaj, Sabuj Kanti Das, Ashmita Biswas, An electrocatalyst, method of preparation, and applications thereof. Indian Patent Application No. 20231100511, Date of Filing: 25-01-2023.

Appendix C

Awards/Achievements/Conferences/Symposia/Workshops

Awards and Recognitions:

- 1. **International travel grant** from CSIR-HRDG (Ref No.TG/12480/23-HRDG) and DST-SERB (File Number: ITS/2024/000522) -2024
- 2. **Best poster award** at International Conference on Nanomaterials for Electro-Catalysis Technology (I-CONECT), IIT Delhi (March 2023).
- 3. **Best poster award** in the ChemNano'22, Energy and Environment Unit, INST Mohali (September, 2022).
- 4. Received Gold medal at iGEM, as an instructor for the team IISER-Mohali (October, 2022).
- 5. **Winner** under chemical science category at SARANSH-2022 Three minutes thesis presentation competition in chemical science discipline, organized by INYAS in October, 2022.
- 6. **Best poster award** in the annual meeting of Energy and Environment Unit, INST Mohali (February, 2021).
- 7. The work "Lewis acid-dominated aqueous electrolyte acting as co-catalyst and overcoming N₂ activation issues on catalyst surface" (PNAS, 2022, 119 (33), e2204638119) was release Information Bureau, GOI highlighted in а press by Press (https://www.pib.gov.in/PressReleseDetailm.aspx?PRID=1888858) and by DST (https://dst.gov.in/new-electrolyte-found-can-help-better-ammonia-synthesis)
- 8. The work "Lewis acid-dominated aqueous electrolyte acting as co-catalyst and overcoming N₂ activation issues on catalyst surface" (*PNAS*, 2022, 119 (33), e2204638119) was highlighted as a special feature in the magazine "Shaastra" by IIT-Madras under the topic "Green is the new black"

Conferences/Symposia/Workshops:

RSC Poster-2024 LinkedIn Conference (Poster presentation)	
Trends in Emerging Nano Science: Energy, Healthcare & Quantum Materials (TENS), International conference, INST Mohali (<i>Poster presentation</i>)	
CHASCON-CRICK, National Conference on Global Science for Global Wellbeing, Punjab University (SODH-SAMWAD story writing competition)	2023
Innovations in Materials for Energy & Environmental Technologies (<i>i</i> - Meet), CSIR-CSIO and ACS-AcSIR CSIO (<i>Oral presentation</i>)	
International Conference on Nanomaterials for Electro-catalysis and Technology (I-CONECT), IIT-Delhi (<i>Poster presentation</i>)	

Smart Materials for Energy and Environmental Technology (Smart- MEET), INST Mohali and CSIR-CSIO (<i>Poster presentation</i>)		
IISER-INST bilateral conference, INST Mohali (<i>Poster presentation</i>)		
241st ECS Meeting (<i>Abstract submitted</i> : <u>Ashmita Biswas</u> , Ramendra Sundar Dey*, Synergism of Co and B Dopants in Carbon-Nitride Framework Toward High Yield of Electrochemical Ammonia Synthesis)		
Energy Conclave, national conference, INST Mohali (<i>Poster presentation</i>)		
INSA-SERB workshop on Science Writing, Indian National Science Academy (INSA), New Delhi		
In-house workshop on Interfacing Tools (Hands-on-training on Arduino and Labview), INST Mohali		
Catalysis Science & Technology 10th Anniversary symposium , Royal Society of Chemistry (<i>e-poster presentation</i>)		
A Three Days International Conference on Recent Developments in Chemistry (RDC), National Institute of Technology, Durgapur (<i>Oral presentation</i>)		
RSC sponsored-chemical science symposium (ChemSci), JNCASR (<i>Poster presentation</i>)	2021	
India International Science Festival (IISF), Government of India (virtual)	2020	
Young Scientists' Conference , India International Science Festival, Ministry of Science and Technology, Ministry of Earth Science and Ministry of Health and Family Welfare, Govt. of India in collaboration with Vijnana Bharati (VIBHA)		
National Conference on Quantum Matter Heterostructure, IISER- Mohali and IIT-Ropar		
RSC sponsored- chemical science symposium (ChemSci), IISER Kolkata (<i>Poster presentation</i>)		
DST&ACS workshop, INST Mohali		
International Seminar on Chemistry in Modern Day Cancer Research, (CMCR), St. Xavier's College, Kolkata		
National Symposium on Recent Advances in Chemistry and Industry, IIEST Shibpur		

Other participations:

1 st and 2 nd Research Scholars' Day, INST Mohali (<i>Poster presentation</i>)	2021, 2022
NanoDay, INST Mohali (Poster presentation)	2021

AWSAR story writing competition	2020, 2021
International Poster Presentation Competition (IPPC), NYAB, INYAS, SLAYS and TYSA	2020

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Article

Refining the Spectroscopic Detection Technique: A Pivot in the Electrochemical Ammonia Synthesis

Ashmita Biswas, Bikram Ghosh, and Ramendra Sundar Dey*

Cite This: https://doi.org/10.1021/acs.langmuir.3c00201

III Metrics & More

Article Recommendations	SI	Supporting Information

ABSTRACT: Ammonia has been recognized as the future fuel because of its immense advantages over liquid hydrogen. The research trend nowadays is mostly inclined toward the electrochemical ammonia synthesis since it offers a sustainable method for green ammonia production. The indophenol blue method is one of the largely used colorimetric techniques to detect ammonia spectroscopically but lacks a proper experimental protocol. The unresolved speculations related to this method concerning stability of dye, sequence of mixing of reagents, importance of pH in the dye formation, or sensitivity of the method is to be set up for a reliable and reproducible data. This work thus aims to unveil the artefacts of this method and explore the mechanisms involved such that it becomes easy for a newcomer as well as existing researchers in the field to understand the requirement of rigorous optimizations in this technique.



■ INTRODUCTION

Since the early ages, the Haber-Bosch process has been largely relied for the industrial scale production of ammonia. But the growing energy related concerns in the current world scenario tend the research community to focus on the electrochemical ammonia synthesis from molecular nitrogen sources as it is fascinating in terms of sustainability. 1 Being emerged from a recent past, a lot of progress is evidenced in this field pivoting versatile catalyst development, electrolyte modifications, and kinetics study with non-conventional approaches, majorly with an aim to suppress the competitive hydrogen evolution reaction acting as a hindrance toward efficient electrochemical ammonia synthesis.²⁻¹¹ Several researchers from all over the world have been working on setting up protocols for a reliable detection method for ammonia from electrochemical nitrogen reduction reaction (NRR) and elimination of interferences from impurities and any other resources.^{12–15} However, the synthesis of ammonia with a high production rate and Faradaic efficiency makes sense when it is properly and accurately quantified. Usually, the primary detection and quantification of ammonia is done using the UV-visible spectroscopic technique derived from a century-old Berthelot reaction of formation of indophenol dye or (i.e., produced by salicylate method). 16,17 This is further validated with alternative nuclear magnetic resonance (NMR) or ion chromatography techniques, where to-date NMR is considered to be most reliable.^{18,19} However, the use of expensive apparatus and standard reagents limit the extensive use of NMR as a preliminary detection technique. Thus, in order to have a valid guidance at the first hand, the UV-visible spectroscopic methods like the Nessler's reagent method, salicylate method,

and indophenol method are widely followed and need proper optimization with a full-fledged knowledge of all the prospects and consequences of the methods. 20

From rigorous literature survey, it was found that Biswas et al.²¹ recently worked on the sequence of addition of reagents in the salicylate method and have compared several literature reports to show that varied reports with non-identical procedures produced different absorbances for the ammonia of known concentration. However, for the indophenol method, Horn and Squire²² showed that the reaction between NH₃ and NaClO was indeed pH dependent and in the alkaline phenol solution, NaClO should be added at once in order to negate any loss of NH₃ owing to medium alkalinity. However, they proposed that it was preferable to add NaClO before phenol for a more rapid and intense color development. Another very recent report by Zhao et al. studied about the detection limit of ammonia by several techniques and cumulatively put forward a protocol that suggested while the Nessler's reagent method worked best in the neutral pH and ion chromatography technique worked well at pH universal condition.²³ However, the ion chromatography technique could be disregarded owing to the large interference of Na⁺ or K⁺ ions from the electrolyte in the same region of the trace amount of NH₄⁺ formed, thereby

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RESEARCH ARTICLE CHEMISTRY



Lewis acid–dominated aqueous electrolyte acting as co-catalyst and overcoming N₂ activation issues on catalyst surface

Ashmita Biswas^{a,1} @, Samadhan Kapse^{b,1} @, Bikram Ghosh^a, Ranjit Thapa^b @, and Ramendra Sundar Dey^{a,2} @

Edited by Alexis Bell, University of California, Berkeley, Berkeley, CA; received March 16, 2022; accepted June 2, 2022

The growing demands for ammonia in agriculture and transportation fuel stimulate researchers to develop sustainable electrochemical methods to synthesize ammonia ambiently, to get past the energy-intensive Haber-Bosch process. However, the conventionally used aqueous electrolytes limit N₂ solubility, leading to insufficient reactant molecules in the vicinity of the catalyst during electrochemical nitrogen reduction reaction (NRR). This hampers the yield and production rate of ammonia, irrespective of how efficient the catalyst is. Herein, we introduce an aqueous electrolyte (NaBF₄), which not only acts as an N₂-carrier in the medium but also works as a full-fledged "co-catalyst" along with our active material MnN₄ to deliver a high yield of NH₃ (328.59 µg h⁻¹ mg_{cat}⁻¹) at 0.0 V versus reversible hydrogen electrode. BF₃-induced charge polarization shifts the metal d-band center of the MnN₄ unit close to the Fermi level, inviting N₂ adsorption facilely. The Lewis acidity of the free BF₃ molecules further propagates their importance in polarizing the N≡N bond of the adsorbed N₂ and its first protonation. This push-pull kind of electronic interaction has been confirmed from the change in d-band center values of the MnN₄ site as well as charge density distribution over our active model units, which turned out to be effective enough to lower the energy barrier of the potential determining steps of NRR. Consequently, a high production rate of NH₃ (2.45 × 10⁻⁹ mol s⁻¹ cm⁻²) was achieved, approaching the industrial scale where the source of NH₃ was thoroughly studied and confirmed to be chiefly from the electrochemical reduction of the puter 2 was.

 $\label{eq:nabla} NaBF_a \mbox{ aqueous electrolyte } | \mbox{ Lewis acid base adduct } | \mbox{ d-band center } | \mbox{ electrochemical nitrogen reduction reaction } | \mbox{ industrial-scale ammonia production }$

Ammonia is considered the most abundant and widely used synthetic fertilizer in the world. The sole mean of large-scale ammonia production relies on the century-old Haber-Bosch process, which takes in more energy than it can produce, while the electro-chemical nitrogen reduction (NRR) offers a carbon-free and sustainable way of ammonia synthesis (1-4). However, electrochemical NH3 synthesis is often arrested by a few factors, such as NH3 detection, contaminations from source gases, nitrogencontaining chemicals, and the presence of labile nitrogen in the catalysts. In the recent past, several protocols have been proposed to correct the fallacious results (5, 6). Recently, Choi et el. concluded that it is difficult to believe from the too-low yield rate of NH_3 that the reduction of N_2 has actually occurred in the aqueous medium (6). However, to overcome this issue, several strategies include the material selectivity allowing selective N₂ adsorption rather than proton adsorption, production of sole product NH₃ rather than N₂H₄, one of the stable intermediates of NRR, and facile desorption of the end product (NH3). Besides this, it is noteworthy that the electrolyte plays a crucial role and offers a suitable environment for any electrochemical reactions to occur. However, the issue with the solubility of N2 in conventional aqueous electrolytes is a real hindrance to achieving a high yield and production rate of NH₃ during electrochemical synthesis. Therefore, it is necessary to solve the most important issue, that is, to solvate a promising concentration of N2 molecules into the electrolyte such that it becomes accessible to the catalyst surface for its subsequent reduction.

A recent study by Ren et al. has elaborated that about 90.7% of the research works related to NRR have focused on the suitable catalyst development, while only 4.7% have been devoted to work on the electrolytes, which is indeed a very crucial factor for NRR, but is mostly overlooked and in infancy (7). In order to do away with the competitive hydrogen evolution reaction (HER), several researchers have sought the help of organic-based or molten hydroxide electrolytes that would lower the proton content in the electrolyte medium. Nonetheless, most organic electrolytes become unstable in the reducing environment of the catholyte, and the requirement of large amounts of organic solvents deviates from the goal of green NH₃ synthesis (8–12). Tsuneto et al. tried to further increase the NH₃ formation efficiency by incorporating Li⁺ into the

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Significance

The electrochemical ammonia synthesis is majorly limited by the poor solubility of N₂ in the aqueous electrolyte environment, besides the competitive hydrogen evolution reaction. In an attempt to solve these issues, the "ambient" conditions are mostly overlooked. This work is an approach to examine the longstanding issues about the solubility of N₂ in aqueous medium and achievement of industrial-scale production rate of ammonia by nitrogen reduction reaction (NRR) at ambient condition. Mechanistic investigation shows that Lewis acid (BF₃) has the capability to hold N₂ by forming a Lewis acidbase adduct, which further adsorbs on catalyst surface by a push-pull electronic effect. Therefore, this report may open new vistas to studying and understanding the role of the NRR in aqueous medium.

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Author contributions: A.B. and R.S.D. designed research; A.B., S.K., and B.G. performed research; R.T. and R.S.D. contributed new reagents/analytic tools; A.B. S.K., R.T., and R.S.D. analyzed data; and A.B. and R.S.D. wrote the paper.

The authors declare no competing interest. This article is a PNAS Direct Submission.

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Nano-Micro Letters ARTICLE



Cite as Nano-Micro Lett. (2022) 14:214

Oxygen Functionalization-Induced Charging Effect on Boron Active Sites for High-Yield Electrocatalytic **NH₃ Production**

Ashmita Biswas¹, Samadhan Kapse², Ranjit Thapa², Ramendra Sundar Dey¹ ⊠ Accepted: 4 October 2022 Published online: 5 November 2022

© The Author(s) 2022 HIGHLIGHTS

Received: 3 August 2022

- O-functionalization at the edges of boron carbonitride induces charge polarization effect on B.
- 0.1 M HCl serves to preserve the catalyst active site from poisoning effect by electrolyte anions.
- Experimental and theoretical findings go hand-in-hand towards high yield of ammonia.

ABSTRACT Ammonia has been recognized as the future renewable energy fuel because of its wide-ranging applications in H₂ storage and transportation sector. In order to avoid the environmentally hazardous Haber-Bosch process, recently, the third-generation ambient ammonia synthesis has drawn phenomenal attention and thus tremendous efforts are devoted to developing efficient electrocatalysts that would circumvent the bottlenecks of the electrochemical nitrogen reduction reaction (NRR) like competitive hydrogen evolution reaction, poor selectivity of N2 on catalyst surface. Herein, we report the synthesis of an oxygen-functionalized boron carbonitride matrix via a two-step pyrolysis technique. The conductive $\text{BNCO}_{(1000)}$ architecture, the compatibility of $\text{B-}2p_{\text{z}}$ orbital with the $N-2p_z$ orbital and the charging effect over B due to the C and O edge-atoms in a pentagon altogether facilitate N2 adsorption on the B edge-active sites. The optimum electrolyte acidity with 0.1 M HCl and the lowered anion



crowding effect aid the protonation steps of NRR via an associative alternating pathway, which gives a sufficiently high yield of ammonia $(211.5\,\mu g\,h^{-1}\,mg_{cat}^{-1})\,on\,the\,optimized\,BNCO_{(1000)}\,catalyst\,with\,a\,Faradaic\,efficiency\,of\,34.7\%\,at-0.1\,V\,vs\,RHE.$ This work thus offers a cost-effective electrode material and provides a contemporary idea about reinforcing the charging effect over the secured active sites for NRR by selectively choosing the electrolyte anions and functionalizing the active edges of the $BNCO_{(1000)}$ catalyst.

KEYWORDS C-doped boron nitride; O-functionalization; Density-functional theory (DFT); Charging effect; Nitrogen reduction reaction; Ambient ammonia synthesis

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Alteration of Electronic Band Structure via a Metal–Semiconductor Interfacial Effect **Enables High Faradaic Efficiency for Electrochemical Nitrogen Fixation**

Ashmita Biswas, Surajit Nandi, Navpreet Kamboj, Jaysree Pan, Arghya Bhowmik, and Ramendra Sundar Dey*

Cite This: ACS Nano 2021, 15, 20364-20376 Read Online ACCESS III Metrics & More Article Recommendations S Supporting Information ABSTRACT: The interface engineering strategy has been an emerging field in terms of material improvisation that not only 49.3 % 40 alters the electronic band structure of a material but also 30 induces beneficial effects on electrochemical performances. Particularly, it is of immense importance for the environ-20 mentally benign electrochemical nitrogen reduction reaction 10 5.2 % (NRR), which is potentially impeded by the competing hydrogen evolution reaction (HER). The main problem lies in the attainment of the desired current density at a negotiable

circumvent this issue, catalyst development becomes necessary, which would display a weak affinity for H-adsorption suppressing the HER at the catalyst surface. Herein, we have adopted the interfacial engineering strategy to synthesize our electrocatalyst NPG@SnS22 which not only suppressed the HER on the active site but yielded 49.3% F.E. for the NRR. Extensive experimental work and DFT calculations regarded that due to the charge redistribution, the Mott–Schottky effect, and the band bending of SnS₂ across the contact layer at the interface of NPG, the d-band center for the surface Sn atoms in NPG@SnS₂ lowered, which resulted in favored adsorption of N₂ on the Sn active site. This phenomenon was driven even forward by the upshift of the Fermi level, and eventually, a decrease was seen in the work function of the heterostructure that increased the conductivity of the material as compared to pristine SnS₂. This strategy thus provides a field to methodically suppress the HER in the realm of improving the Faradaic efficiency for the NRR. KEYWORDS: interface engineering, d-band center, Mott-Schottky effect, electrochemical nitrogen reduction reaction (NRR), Faradaic efficiency

INTRODUCTION

The electrochemical nitrogen reduction reaction (NRR) at ambient conditions aids in getting past the bottlenecks of the energy-intensive Haber-Bosch process, which gives off approximately 3% of the total $\rm CO_2$ emissions into the atmosphere. $^{1-3}$ However, the major shortcoming of such an electrocatalytic process is attributed to the complex six electron-proton coupled reaction pathway and too much intermediate formation, which in turn affects the yield and Faradaic efficiency (F.E.) of ammonia (NH_3) synthesis. Another major cause for this is the competitive hydrogen evolution reaction (HER), which impedes the kinetics of the NRR.4,5 Over the past few years, major attempts have been focused on developing potential candidates for the NRR. However, a very

potential where the NRR would dominate over the HER, which

in turn hampers the Faradaic efficiency for the NRR. To

little attention has been devoted to realizing the major bottlenecks of the NRR and solving them thoroughly. In order to promote a hassle free NRR, either materials with intrinsic HER suppression ability or catalysts tailored to restrict H-adsorption on their active surface can be employed. The latter is more challenging and can be accomplished through a variety of methods such as (a) strain engineering,^{6,7} (b) blocking the HER

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ed d-band center of surface Sn

Lower work function Higher conductivity



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cascading charge effect for electrochemical ammonia synthesis†

Deciphering the bridge oxygen vacancy-induced

Ashmita Biswas, 🗓 ‡ª Narad Barman, ‡^b Avinash Nambron, ª Ranjit Thapa, ^{bc} Kathi Sudarshan^{de} and Ramendra Sundar Dey 🗐 *ª

Oxygen vacancy engineering has recently been gaining much interest as the charging effect it induces in a material can be used for varied applications. Usually, semiconductor materials act poorly in electrocatalysis, particularly in the nitrogen reduction reaction (NRR), owing to their inherent charge deficit and huge band gap. Vacancy introduction can be a viable material engineering route to make use of these materials for the NRR. However, a detailed investigation of the vacancy-type and its role for the structural reorientation and charge redistribution of a material is lagging in the field of NRRs. This work thus focuses on the synthesis of oxygen vacancy-engineered SnO2 with a gradual structural transformation from in-plane (io_v) to bridge-type oxygen vacancy (bo_v) density. Consequently, the electron occupancy of the sp³d hybrid orbital changes, leading to an upshifted valence band maxima towards the Fermi level. This has a profound effect on the nature of N2 adsorption and the extent of $N\!\equiv\!N$ bond polarization. Sn atoms adjacent to the bo_{v} are found to have a fair density of dangling charges that accomplish the NRR process at a comparatively low overpotential and determine the binding strength of the intermediates on the active site. The obscured yet stable reaction intermediates are thereby identified with in situ ATR-IR studies. A restricted hydrogen evolution reaction Faradaic on the Sn-site (favored over O-atoms) results in a Faradaic efficiency of 48.5%, which is better than that reported in all the literature reports on ${\rm SnO}_2$ for the NRR. This study thus unveils sufficient insights into the role of oxygen vacancies in a crystal as well as electronic structural alteration of ${\rm SnO}_2$ and the effect of active sites on the rate kinetics of the NRR.

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New concepts

miconducting materials often suffer from huge band-gap and charge deficits that limit their extensive use in electrocatalysis, particularly in the nitrogen reduction reaction (NRR). Although vacancy engineering can substantially introduce an in-built charging effect in these materials, whether this can be experimentally controlled is not clear. This study reveals that there is a lot more to understand beyond just the concept of oxygen vacancies in metal oxides. Herein, SnO2 is chosen as the investigating material, and we observed that the coordination of oxygen in the crystal lattice determines the type of oxygen vacancies and largely manipulates the structural stability of a catalyst as well as its electronic properties. This not only ascertains a sound electrochemical activity of the material but also ensures long-term material performance, entirely based on the type of vacancies fostered in the SnO_2 material. We also found that a two-coordinate bridge oxygen vacancy and a three-coordinate in-plane oxygen vacancy had varied roles towards N2 adsorption, and the dominance of the vacancy type can be experimentally controlled by varying the a nealing temperature. Naturally, the electron occupancy in the hybridized orbitals of SnO₂ is altered, affecting charge density over vacancy-centered Sn atoms and their bonding interaction with N2 prior to the NRR.

Introduction

Metal oxides or dichalcogenides featuring tunable electronic properties, mechanical strength and electro-active edges are widely studied materials for the electrocatalytic nitrogen reduction reaction (NRR).¹ However, these materials are vacancy-engineered to activate the basal surface by grafting artificial electron-rich active sites influencing N₂ adsorption.^{2,3} DFT calculations have complemented the experimental data showing that oxygen vacancies in these materials can upshift the d-band center of associated metals towards the Fermi level, which in turn lowers the energy barrier for the potential-determining steps of the NRR.^{2,4} In fact, polarized electrons over dangling oxygen vacancies have been utilized to polarize the N—N bond and determine the binding strength of reaction intermediates with the active center.⁵ In order to leverage these features, massive research is in progress these days.

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COMMUNICATION

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Elevating the energy efficiency for the power-to-ammonia conversion: Role of oxygen evolution reaction kinetics

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ABSTRACT

Electrochemical nitrogen reduction reaction (NRR) is imperatively countered with the oxygen evolution reaction (OER) on a conventional Pt counter electrode. Upon focusing on the development of suitable cathode catalysts, it is usually overseen that OER on Pt seeks a significant energy input to overcome the slow reaction kinetics, regardless of the efficiency of the NRR catalyst. Here, we unveil an out-of-the-box concept with state-of-the-art catalysts that, on pursuing OER with RuO₂ in KOH, the NRR catalyst. Here, we unveil an out-of-the-box concept with state-of-the-art catalysts that, on pursuing OER with RuO₂ in KOH, the NRR catalyst, iron phthalocyanine (FePC), in an electrolyte simultaneously help to elevate a reaction mechanism in terms of Gibbs' energy and equilibrium constant. As a proof of concept, we assembled RuO₂ with an NRR catalyst, iron phthalocyanine (FePC), in an electrolyter, preferably in a two-electrode setup, where the catholyte consisted of 0.5M NaBF₄. This system achieved selective cathodic conversion of N₂ to NH₃ with 67.6% Faradaic efficiency at 0.0 V (vs reversible hydrogen electrode) and simultaneous anodic water oxidation to O₂ with a high electricity-to-chemical energy conversion efficiency of 46.7%. The electrolyzer forecasted a full cell voltage of 2.04 V, which demands only 603 mV overpotential to attain 0.5 mA current to drive forward the chemical equilibrium of the overall cell reaction. This study not only emphasized the importance of electroly-electrolyte improvisation but also provided a wider outlook in terms of different thermodynamic parameters to be considered to determine the efficiency of the overall NRR coupled OER process.

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Although the electrochemical nitrogen reduction reaction (NRR) to NH₃ at ambient conditions of temperature and pressure with zero-carbon footprint is promising toward a sustainable and green future,¹⁻³ it is challenging enough due to the chemical inertness of the N₂ gas.⁴ Being emerged in the recent past, the associated methods and procedures of NRR require rigorous standardizations and optimizations, which have been crucially done by several researchers.⁴⁻⁷ Although a high Faradaic efficiency for ammonia synthesis can be achieved by designing NRR catalysts that successfully suppress the competitive hydrogen evolution reaction on its surface,⁴⁻¹² it is very crucial to realize that the kinetics of the thermodynamically controlled NRR process relies largely on the counter oxidation reaction kinetics. Thus, it is not sufficient to solely look out for slowing down the HER kinetics, but a reinforcement of OER kinetics is also necessary to uplift the NRR performance. This, in a broader perspective, affects the production rate and Faradaic

efficiency (FE) of ammonia synthesis and the excess electricity to chemical energy conversion efficiency. Thus, it is important to simultaneously pay attention to both reactions and the gap needs to be bridged if one aims to move toward an energy-efficient electrochemical NRR process; however, it has taken no notice of the researchers to date.

In this work, we have tried to establish the concept of interdependency of the NRR coupled OER processes to achieve an appreciable production rate and FE of ammonia synthesis. As an anode catalyst, we have taken RuO₂ on Ni foam (1 × 1 cm²) and compared its superiority over the conventionally used Pt counter electrode for OER. Under such conditions, the NRR selectivity not only improved on the FePc cathode in 0.5M NaBF₄ but also the FE shot up to 67.6% at 0.0 V with 4 mg cm⁻² RuO₂ in 0.5M KOH for OER. As a proof of concept, an NRR electrolyzer was assembled in a two-electrode system, where the full cell overpotential for

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