Exploring low-cost elements-based nanostructured electrocatalysts for sustainable energy conversion

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

by

Reeya Garg



Department of Chemical Sciences

Indian Institute of Science Education and Research (IISER) Mohali

Knowledge City, Sector 81, Mohali, Punjab- 140306

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CERTIFICATE

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

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

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

Date-

Place- Mohali

Reeya Garg

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

Dr. Ujjal K. Gautam

(Supervisor)

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Dedicated to My Beloved Family

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Thesis Synopsis

The thesis entitled "Exploring low-cost earth-abundant elements-based nanomaterials for electrocatalytic energy conversion" comprised of three parts along with two initial chapters describing the scope of research in the field of heterogeneous electrocatalysis, and the characterisation tools and measurement techniques utilized in this thesis work. Part 1 is focused on sustainable production of atomically dispersed first-row transition metals over nitrogen-doped carbon nanosheets (M-N-C) and deriving governing factors behind achieving atomic dispersion instead of nanoparticle formation. Part 2, which is divided into two sub chapters, demonstrates the benefits of combining M-N-C and minute amounts of Pd nanocrystal on its surface towards achieving enhanced durability along with increased electrocatalytic efficiency. Part 3, which also contains two sub chapters, depicts the potential of the composite of M-N-C and carbon nanotubes in achieving high electrocatalytic efficiency with long durability without any dependence on expensive noble metals. A brief description of each chapter is given below.

Chapter 1 introduces the significance of developing appropriate materials to catalyse the energy conversion reactions involved in fuel cell and energy storage batteries in order to bring sustainability in global energy production and supply. Identifying the gaps in the existing catalytic systems, a potential research scope was established keeping the focus on electrocatalysis. Keeping the ease in reusability in mind, nanostructures were explored in the literature towards efficient electrocatalysis. To achieve cost-effectivity and sustainability in the rational design of futuristic efficient and durable electrocatalysts, cheap and highly abundant elements were chosen. Along with exploring cheap and abundant elements, many attempts made to bring sustainability in the synthetic strategies to produce highly active electrocatalysts have been discussed. While sometime a minimum dependence on noble metal was noticed to be unavoidable in the past work to bring long durability along with high catalytic efficiency, it was felt that efforts should be put to completely rule out the dependence on expensive noble metals and several works were planned accordingly in this thesis work.

Chapter 2 depicts the characterisation tools to identify the chemical entities built in a certain catalytic system. The measurement techniques to determine the electrocatalytic activities of assynthesized catalysts were also explained in detail. The materials and precursors used to execute the experimental procedures were also described here.

Chapter 3.1 introduces an emerging class of electrocatalyst possessing cheap, highly abundant first-row transition metals atomically dispersed on the nitrogen doped carbon nanosheets, known as M-N-C. The structural novelty of M-N-Cs were discussed along with insights into the catalytically active centers responsible for high electrochemical performances. The shortcomings of previously reported M-N-Cs were discussed in nutshell and a prospective future research scope was drawn in this chapter.

Chapter 3.2 demonstrates a sustainable pathway to achieve highly efficient M-N-C as bifunctional electrocatalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The atomically dispersed earth-abundant metals in N-doped carbon (M-N-Cs), an emerging electroactive material not only can catalyse both the cathodic and the anodic reactions due to their bifunctional behaviour but also can match the performance of the precious metals. This cheap, sustainable electrocatalyst demands a sustainable production route. This inspires the development of simpler strategies for scale-up production since the existing ones rely on precursors whose commercial viability is not yet ascertained. We demonstrate the insertion prospects of $M-N_x$ (M = Fe, Co, Ni) moieties, the electrocatalytic centers in the M-N-Cs, into commercial carbon to establish that a single-step heating of the inexpensive precursors is sufficient to impart bifunctional electrocatalytic activity with efficiencies that bypass the majority of the known catalysts. Furthermore importantly, quantification of both the ORR and OER trends and the metal insertion limits for each metal while maintaining an atomic dispersion, without the formation of surface migration-induced clustering, because such clustering is inevitable in the existing processes to necessitate an extra acid-leaching step to remove them. It was further quantified and explained for each metal a negative mass balance originating from anomalous mass loss of both metal and carbon contents, and a massive reconstruction of the carbon backbone catalyzed by the very metal, an event documented for the first time though it ought to be associated with other M-N-C syntheses too. The study establishes an incredibly simple and inexpensive strategy for the realization of M-N-Cs and outlines the parameters to be considered during mass-production.

Chapter 3.3 summarises the key observations and future prospects of the studies described in chapter 3.

Chapter 4.1 discusses the electrocatalytic activities of Pd nanoparticles and the bottlenecks towards large-scale implementation despite high electrocatalytic activity and durability. However, the potential of compositing Pd nanostructures with low-cost electrocatalysts to

achieve highly stable superior electrocatalysts keeping minimal dependence of expensive Pd were depicted in this chapter. Furthermore, the limitations of the existing synthetic strategies of such composite formation were highlighted and a scope of sustainable composite fabrication was established.

Chapter 4.2 reveals the photo-response of M-N-C and utilizes this unique property to bring a green synthetic pathway to incorporate Pd nanoparticles at the surface of M-N-C. This is important because realizing highly active Pd-electrocatalysts under mild conditions is a challenge for industries. Herein, atomically dispersed Co-containing N-doped carbon (Co-N-C) was introduced as a catalyst-support for Pd with multiple benefits. Theory and experiments establish that the Co-N₄ moieties in the carbon-matrix act as semiconducting centers to generate excitons under sunlight, which are capable of reducing Pd-salts to deposit Pd nanoparticles (NPs) on Co-N-C at room temperature. The size of Pd-NPs is comparable to those used in commercial catalysts due to anchoring to the support, despite not using any capping agents, resulting in improved mass transfer on its surface. Importantly, it was found that the Co atom mediates a superior charge transfer between the Pd-NPs and support, leading to a very high ORR efficiency (E_{1/2} of 0.92 V *vs*. RHE) and stability (7 mV shift in E_{1/2} after 20,000 cycles) of these catalysts. These findings should inspire the use of transition metal (M) based M-N-Cs as a new class of support for electrocatalysts with improved activities and also, their use in photocatalysis.

Chapter 4.3 demonstrates the role of synthetic strategies to tune the metal-support interaction. Sluggish ORR kinetics remains a bottleneck in the utilization of palladium in alkaline fuel cells, which can potentially be improved by tailoring Pd -support interactions. Herein, a synergy between uniform distribution of metal active centers throughout the support and strong metal-support interaction has been established. The resulting catalyst showed superior electrocatalytic ORR performance ($E_{1/2}$ of 0.94 V *vs.* RHE) and stability (3 mV shift in $E_{1/2}$ after 20,000 cycles). The enhancement in the activity was rationalized by experimentally determining the extent of metal-support interaction in different electrocatalysts synthesized in different manner. From DFT calculations, the reaction mechanism of ORR for the optimized catalyst was derived and the rate determining step was found out. The pitfalls in different individual synthetic pathways were identified and finally the benefits of rationally combining two synthetic strategies together have been described.

Chapter 4.4 summarises the key observations and future prospects of the studies described in chapter 4.

Chapter 5.1 depicts the potential of one of novel allotropes of carbon, carbon nanotubes (CNT), towards achieving sustainable carbon based electrocatalysts. Emphasis was given on the synthetic protocols and growth mechanism along with the discussion of its structural features contributing to its high electrocatalytic activity.

Chapter 5.2 portrays the effect of various reaction parameters to yield highly electrocatalytically active CNTs. CNTs have large surface area and high conductivity, making them promising for electrocatalysis. Unlike graphene, CNTs possess one-dimensional conductivity, minimizing electron scattering, and lack grain boundaries, enhancing electron transport and mechanical strength. CNTs' electrocatalytic activity arises from various chemical moieties such as tube ends, edge defects, doped nitrogen centers, and encapsulated iron nanoparticles, if any, due to the use of Fe at growth catalyst. Understanding the contribution of these active sites originating from different reaction parameters is essential to uncover their individual mechanisms and synergies, enabling diverse applications. In this study, bamboolike multi-walled CNTs were synthesized using the floating catalyst technique. By optimizing the catalyst dosage, an effective approach to enhance CNT conductivity was found. The limit of scalability was also explored by varying the carbon precursor amount, determining thus the optimal reaction conditions for high-quality CNTs. Additionally, the effect of different reaction atmospheres on CNTs' metallic iron content and electrocatalytic activity was studied. The bestperforming catalyst demonstrated superior electrocatalytic activity towards ORR with an $E_{1/2}$ value of 0.85 V vs. RHE. This study provides valuable insights into rationalizing reaction parameters for producing highly efficient CNTs for electrocatalysis, contributing to advancements in sustainable energy generation.

Chapter 5.3 describes a strategy to completely rule out the dependence on expensive noble metals in order to achieve highly efficient electrocatalysis. Achieving high electrocatalytic performance by completely metal-free electrocatalyst remains a challenge. Alternatively, an efficient composite of carbon nanostructure and non-noble metal with minimum dependence on metal holds immense potential. Although single atom catalysis brings superior performance, its complex synthetic strategy limits its large-scale implementation. Previous investigation in this thesis work has shown that atomic dispersion (Fe-N_x-C) is accompanied by higher metalloss compared to nanoparticle formation (Fe-NPs-N-C). Therefore, to achieve minimum metal

loss, firstly incorporation of iron nanoparticles (Fe NPs) on N-doped carbon (N-C) was achieved and then exposed to a cheap carbon source, melamine at high temperature, resulting in the growth of carbon nanotube (CNT) catalysed by the very Fe NPs loaded on N-C (Fe-NPs-N-C). Thermogravimetric analysis showed that the metal-retention in the composite is higher than the bare carbon nanotube and even the atomically dispersed Fe-active sites on N-C. The composite material (Fe-NPs-N-C/CNT) shows a high half-wave potential (0.89 V *vs.* RHE) which outperforms commercial Pt/C towards ORR. The enhanced activity is attributed to the synergistic effect of high conductivity of CNT and active Fe-sites as the composite and the performance exceeds the individual electrocatalytic performance shown by Fe-CNT & Fe-NPs-N-C, even atomically dispersed Fe-active sites on N-C.

Chapter 5.4 summarises the key observations and future prospects of the studies described in chapter 5.

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Chapter 1

Introduction to sustainable heterogeneous electrocatalysis

CHAPTER 1

1.1 Sustainable energy conversion

According to Forbes's report in 2020, oil can last up to 50 years, natural gas up to 53 years, and coal up to 114 years.¹ The global atmospheric carbon dioxide concentration is almost certainly higher than it has been for one million years.² Therefore, the rapid consumption of fossil fuels led to a decrease in traditional energy resources along with severe threats to the environment by the emission of greenhouse gases like CO_2 . CO_2 accounts for about 76% of total greenhouse gas emissions, where 65% of CO_2 in the atmosphere originates from the use of fossil fuels and other industrial processes.³ Hence, there is an essential need to expand our dependence on abundant, clean and renewable energy resources.

In 2019, only 11% of global primary energy came from renewable technologies.⁴ Hydroelectric power has been one of our oldest and largest sources of low-carbon energy as it accounts for more than 60% of renewable generation. After hydroelectricity, wind energy contributes to most of the global renewable energy harvesting (20%). Among the rest, solar energy produces 9% of the total renewable power generation worldwide. Biofuels, geothermal electricity, etc. are also among many other possibilities. But, the scalability of different renewable energy resources varies significantly across the world. Also, the efficiency of these sustainable energy harvesting technologies is not satisfactory.⁵

The most promising global solution is the use of locally available sustainable energy sources to convert molecules present in the environment (e.g. water, carbon dioxide and nitrogen) into high-value added products (e.g. hydrogen, hydrocarbons and ammonia) via highly efficient sustainable energy conversion pathways. Electrocatalysis has huge potential in this regard. It can act as an alternative option for the establishment of "zero emission" clean energy conversion systems based on 'water', 'hydrogen' and 'oxygen'. Thus, electrocatalysis is at the center of many sustainable energy conversion technologies developed to reduce the dependence on fossil fuels. In fact, during the past decade, significant progress has been made for developing several such energy conversion systems like water electrolyzers, fuel cells, and rechargeable metal-air batteries.⁶

According to a report published in 2021, Norway produces 70% of energy supply from renewable energy resources.⁷ Although China generated the highest amount of hydroelectricity (1300 TW^{-h}) in 2021, its 85% primary energy is coming from the conventional energy resources. Denmark has 75% of electricity from renewable energy sources, where 45% of it arises from wind energy. India has secured the third largest place in terms of solar energy

generation, although it contributes to only 9% of the total primary energy consumption of the whole country. Therefore, its clear that renewable energy generation technologies are highly specific to the different geographic locations throughout the world. But with advancements in electrocatalysis based energy conversion technologies such as fuel cells, zinc-air batteries, etc., all those locally feasible alternative power generation can potentially be utilized to the fullest extent with maximum efficiency. Therefore, it is of utmost important to focus on research and development in electrocatalysis.

1.2 Brief description of catalysis: heterogeneous & homogeneous catalysis

With the continuous rise in the world's population, humanity faces numerous challenges having an impact on energy demand, water resources, and food accessibility. One of the alternative solutions for some of these challenges is catalysis, which can contribute in an environmentally and economically sustainable way. In 1894, Ostwald wrote, "*Catalysis is the acceleration of a slow chemical process by the presence of a foreign material*".⁸ A catalyst accelerates the rate of reaction by opening a new reaction pathway via lowering the activation energy and does it by attaching itself to the reactant molecule. Among industrial chemical transformations, 75 % have taken the help of catalysts in diverse areas like petrochemicals, agrochemicals, and pharmaceuticals. Moreover, newly developed processes also use catalysts.⁹

Generally, the term catalysis can be classified into two parts, i.e. homogenous and heterogenous catalysis. Catalytic process in which reaction substrates as well as catalyst components are present in the same phase, either in gas or in liquid phase are classified as homogenous catalysis.^{10–12} Catalysts involved in homogenous catalysis are generally well-defined coordination or organometallic complexes which are dispersed in the reaction medium along with the reactants. Due to the easy accessibility of active centers to the reactants, they possess high activity performance. Apart from this, homogenous catalysis has other advantages like high selectivity, high turnover number (TON) and turn-over frequency (TOF).¹³ In this, tuning of chemo-, regio- and/or enantioselectivity of the catalytic systems can be easily achieved by modifying the catalytic active sites.¹⁴ Examples of homogenous catalysis include transition metal complexes (rhodium carbonyl complexes in oxo synthesis).

Although many advantages possessed by homogenous catalysis, these suffer from drawbacks like low stability, difficulties associated with the separation of the final product from the reaction mixture and recovery of expensive metals after catalysis.^{10–12} The problem of product separation arises because the distillation procedure is most commonly used which works at high temperatures unless the product is volatile. During distillation, thermal stress

causes decomposition of homogenous catalysts as most of the homogenous catalysts are temperature sensitive (mostly decompose below 150 °C).^{10–12} Chromatography is another technique used for extraction but it also leads to catalyst loss. Thus, the homogenous catalysts which have been commercialized either involve volatile substrates and products or contain thermally less sensitive organic ligands. Besides, the recovery of transition metal catalysts from the reaction mixture is very difficult as a trace amount of catalyst may still present in the recovered product (at ppm or ppb level).¹² This is crucial problem in drug and pharmaceutical industries because trace amount of metal residues lead to serious health issues. One effective way to overcome these problems is to make a heterogenous catalytic systems.

In the case of heterogenous catalysis, catalytically active centres are in a different phase than that of reacting substrates. There are various advantages of heterogenous catalysis over homogenous catalysis, as follows:¹⁵

- a) Facile recovery: The advantage lie in the easy separation of the catalysts from the reaction medium. Heterogenous catalysts are either automatically removed or can be easily separated by simple methods such as filtration or centrifugation.
- b) High recyclability and stability: In a heterogenous system, catalytic sites remain intact due to the presence of different phases, resulting in high stability at elevated temperatures and pressures. Therefore, catalysts having a heterogenous nature can be used in more number of catalytic cycles with minimal loss of catalytic activity.
- c) High catalytic activity: Activity of heterogeneous catalysts can be as high as homogenous ones, if their surface area is high that causes the better interactions between reactant molecules and catalyst surface.

By virtue of these benefits, heterogenous catalysts dominate in large-scale industrial processes such as. In spite of this, heterogeneous catalysts might suffer from formation of the non-uniform aggregates of hundreds or thousands of metal atoms, out of which, only a small fraction is exposed to reactants. Thus, it is an essential to increase the utilization of metal atoms in the heterogeneous catalyst, which can be done by making the heterogenous catalysts that feature the atomically dispersed metal atoms to act as catalytically active centres, providing 100% atom utilization efficiency.¹⁶ Therefore, such an approach carries both the advantages of homogenous and heterogenous catalysis and is believed to be able to bridge the gap between homogenous and heterogenous catalysis.¹⁷

1.3 Nanomaterials: a pillar of heterogenous catalysis

Nanomaterials play an immense role in the development of various chemical industries and new energy storage technologies like lithium-ion batteries and fuel cells.¹⁸ These materials are in high demand for a range of applications in various research fields like catalysis, photocatalysis, photovoltaics, a sensing, electrocatalysis, etc.¹⁹ Materials having a size or at least one of their dimensions in the range of 1-100 nm is defined as nanomaterials. The physical and chemical properties of a material are completely different from the bulk form depending upon their size, shape and composition. As the dimension of particles reaches towards nanoscale, an effect associated with the small size of nanoparticles becomes more pronounced due to an increase in surface to volume ratio. Thus, the properties of nanomaterials can be tuned by controlling the size, shape, composition, and crystallinity that makes them suitable for specific applications. Additionally, understanding the topography of surface sites such as vacancies, steps, kinks, terraces and their effect on catalytic properties is another key parameter for designing nanomaterials with improved performance.²⁰

The difference of nanomaterials from bulk materials is not in the scale of dimension alone, but they possess very different physical properties also. For example, reducing the dimensions of semiconductors below a certain size led to increasing the band gap through the quantum confinement effect.²¹ Tuning of band gap can be simply done by varying the dimensions of a material so that optical absorption and emission spectra can be optimal to meet the particular requirements for desired applications. When the size of gold is reduced to a few tens of nanometres, its colour changes to pink due to surface plasmon resonant absorption and shows many application prospects in surface enhanced Raman scattering.^{22,23} Their catalytic activity can be further enhanced by reducing the size of gold nanoparticles to less than 3 nm due to relatively less shrinkage of d-orbitals in comparison to s- and p-orbitals.²⁴ In addition to this, the smaller size of nanoparticles makes them viable carriers to deliver drugs to specific targets.²⁵ However, the reduction in size of nanomaterials has some adverse impact on some of the applications. For example, the electric conductivity of nanowires can be much lower than that of bulk materials due to the smaller mean free path resulting from scattering.²⁶ Note that, the mobility of charge carriers in polycrystalline semiconductors is smaller than that of a single crystals which reduces further when particle size is in nanometre scale.²⁷

1.3.1 Classification of nanomaterials

Nanomaterials can be classified into different groups based on various criteria. Generally, they are classified on the basis of their dimensionality as shown in **Figure 1.1**. Based on their dimensional classification, nanomaterials can be of three types, i.e. zero-dimensional (0 D), one-dimensional (1D) and two-dimensional (2D).²⁸ In zero-dimensional nanomaterials, electrons cannot flow in over a long length scale, due to their confinement in all three dimensions, such as in nanoparticles or quantum dots. One-dimensional nanomaterials (1D), like nanorods or nanotubes, one dimension is not in the nanoscale while the other two are in the nanoscale. In other words, electrons can move in one direction while their electron flow is confined in the other two dimensions. In 2D nanomaterials such as nanosheets or nanoplates, the flow of electrons is facile in two dimensions.²⁹ According to the chemical composition, nanomaterials can be classified as single constituent metallic nanoparticles (Pt, Ag Au, Pd etc.), their alloys (Pt₃Co, PtAg, etc.), metal oxides (SiO₂, TiO₂ etc.) metal-free carbon-based materials such as graphene, N-doped graphene, carbon nanotubes etc.²⁹

1.3.2 Application of nanomaterials

Nanomaterials provide a great platform for the advancement of existing technologies and development of new technologies. They find commercial roles in various fields like cosmetics, surface coatings, electronics, sports-equipment and energy storage devices as shown in **Figure 1.2**.³⁰ Since energy conversion devices involve physical/chemical interactions at the interface, so the specific surface area, surface energy and surface chemistry play an important role. Inorganic nanostructured materials offer excellent charge mobility, longer lifetime, photon trapping, or light scattering capability for sustainable applications. For example, in the case of photovoltaics, a large surface area offers more sites for charge recombination, and small size of pores hindered the penetration of electrolyte ions in the supercapacitor.³¹ Fullerenes are vital members of carbon-based nanomaterials and have greater potential to use in the development of superconductors.³² The presence of strong covalent bonds in fullerenes helps them in making nanomaterials having improved mechanical strength. By making composites with fullerene, polymers show good flame retardant and thermal properties.³³ They have medicinal applications too due to their anti-cancer, antioxidant, and antibacterial properties.³⁴



Figure 1.1 Classification of nanomaterials on the basis of dimension with examples in each case.



Figure 1.2 Schematic representation of application of nanomaterials.

Another the most important applications, these nanostructured materials are used as electrodes in lithium-ion batteries in energy storage devices. They provide certain characteristics properties including a large surface area for fast interfacial Faradaic reaction, a small distance for charge and mass transportation and also accommodate change in volume due

to their small dimensions during the lithium-ion insertion or extraction.³⁵ In addition to this, nanostructured electrodes should have more open space to facilitate the diffusion of ions in a more effective manner and hence achieve high energy and power density with long-term cyclic life. Nanomaterials having porous structures have been used in electric double-layer capacitators or supercapacitors.³⁶ This is because the capacitance is directly proportional to the total surface area and hence, the presence of nanopores is essential to achieve high surface area. However, smaller pores offer significant resistance for diffusion, which leads to low power density, demonstrating the complexity in designing such structures.

1.4 Single atom catalysis: a bridge between homogeneous & heterogeneous catalysis

The term "*Single atom catalysis*" was first introduced in 2011 by Prof Zhang Tao and co-workers ^{37,38} describing the high CO oxidation activity of single Pt atoms supported on FeO_x. Single-atom catalyst (SAC) refers to a catalyst that contains isolated single atoms dispersed on support. SAC maximizes the atom utilization efficiency (**Figure 1.3**) that is particularly important for the economics of catalytic reactions. It also provides unique electronic and geometric properties coming from the absence of metal-metal bonds and the cationic (or anionic) nature of isolated active sites. Moreover, well-defined and uniform active sites offer SACs great potential for achieving high activity and selectivity compared to common heterogeneous catalysts containing various kinds of active sites.³⁹ Briefly, SACs are heterogenous catalysts and easy to separate and quite stable. Most importantly, they possess isolated active sites similar to homogenous catalysts and come up with advantages of both homo- and heterogenous catalysts. Therefore, the development of SACs is an elegant way to bridge the gap between homo- and heterogenous catalysis and have attracted a lot of attention in recent years as a new frontier in the heterogeneous catalysis.

SACs can exhibit excellent performance in many industrially important reactions like thermochemical reactions with superior activity and selectivity compared to clusters or nanoparticles.^{40,41} Inspired by the nearly 100% utilization of metals in SACs, the application of SAC in electrochemical and photochemical reactions is becoming an active research area.^{41–45}



Figure 1.3 Proportions of surface atoms w.r.t to different particle dimensions. Reproduced with permission.³⁹

1.5 Electrocatalysis: a way of sustainable energy conversion

The continuous depletion of fossil fuels and the potential risks of climate change forced researchers to develop strategies to harvest energy from renewable energy sources like solar, wind, rain, tides, and geothermal energy. However, the supply of renewable energy depends on weather and is hampered by the inability to store and send power adequetly when required. Thus, intermittence in supply versus demand has put research focus on the development of efficient and affordable clean energy technologies. Electrochemical energy storage devices are better alternatives in future energy networks to fulfill the criteria of unpredictable energy generation and supply from renewable sources.⁴⁶ Among these, metal-air batteries and fuel cells are two promising energy storage devices that have the potential to be used as grid smoothing devices for the production of clean energy.^{47,48}

Batteries have been known for their excellence in converting and storing chemical energy from past years. These can be used in a large number of applications from very small button cells like portable electronic devices to very large batteries for electric vehicles and large-scale energy storage. So far, lithium-ion battery (LIB) is the most successful energy storage technology. But the rare lithium sources lead to high costs and having low specific energy density (200-250 Wh/kg), and safety concerns limit their further development and commercialization in industrial applications.^{49–52} For example, a lithium-ion battery pack alone would cost over \$30,000 for 240 miles range passenger vehicle at 400-800 \$ kW⁻¹h⁻¹, which is equal to the cost of an entire gasoline-powered car.⁵⁰ To overcome these issues, great research efforts have been adopted for the development of alternative inexpensive and rechargeable battery technologies. Recently, the "EV Everywhere Grand Challenge" was launched by the U.S department of energy for motivation to produce electronic vehicles (EVs) with improved batteries having low cost and becoming as affordable as today's gasoline powered vehicles.



Figure 1.4 Bar diagram representing the theoretical energy densities of various metal-air batteries. Reproduced with permission.⁵³

Metal-air batteries are one of the best alternatives to lithium-ion technologies and have received great attention in the last few years due to their low cost and environment friendliness.⁵³ These systems are assembled from metal anode and air-breathing cathode through a suitable electrolyte. Alkali metals (e.g. Li, Na, K), alkaline-earth metals (e.g. Mg), or first-row transition metals (e.g. Zn, and Fe) can act as metal anode and air-breathing cathodes have an open porous structures which allow the continuous supply of oxygen from the surrounding air. Depending upon the nature of the anode, the electrolytes can be aqueous or non-aqueous. The design features of metal-air batteries are likely by the combination of both

conventional batteries and fuel cells. They possess a high theoretical energy density of about 3-30 times greater than lithium-ion batteries (**Figure 1.4**). Most commonly used anode material in primary air-batteries is Zinc due to its low cost and high capacity. **Figure 1.5** illustrates the basic structure of the Zn-air battery. It consists of a metal Zn anode, membrane separator and air cathode assembled together in an alkaline electrolyte.⁵⁴ During discharging, metal is oxidized at anode and O_2 from the surrounding air is reduced at the cathode according to the following equations:

Anode:
$$M \longrightarrow M^{n+} + ne^{-}$$

Cathode: $O_2 + 4e^{-} + 2H_2O \longrightarrow 4OH^{-}$

where M represents the metal and n is the oxidation number of the metal ion. During the recharging process, the above electrochemical reactions are reversed meaning oxygen evolving at the cathode and metal plated at the anode.^{55,56} The oxygen reduction reaction that take place at the air cathode is similar to ORR in fuel cells.



Figure 1.5 Schematic illustration of electrode reaction for Zn-air batteries. Reproduced with permission.⁵⁴

Fuel cells are another type of electrochemical conversion device in which a continuous supply of fuel (hydrogen, methanol etc.) and oxidants such as oxygen or air is needed to generate electricity.⁴⁸ There are many different examples of fuel cells summarized in **Figure 1.6**. It consists of two electrodes; one is the cathode where the reduction of oxygen takes place and the second is anode where oxidation of hydrogen occurs (if hydrogen is used as fuel). There is a need of a gas diffusion layer also so that gaseous fuels can efficiently reach the electrodes and the redox-generated ions can easily migrate.⁴⁶



Figure 1.6 An overview of the reactions and processes taking place within different fuel cell systems. Reproduced with permission.⁴⁶

Depending on the nature of the electrolytes used, fuel cells can be classified into two types i.e. acidic and alkaline fuel cells shown in **Figure 1.7**. Alkaline fuel cells have attracted significant attention due to several advantages like reduced fuel cross over effect and less corrosive alkaline environment.⁵⁷ Additionally, the working potential of the electrochemical process shifted by -59 mV for every one pH unit increase of reaction condition according to the Nearst equation, leading to lowering the transformation of anions i.e. 0.059 eV for monovalent ions such as OH⁻ in alkaline media compared to acidic medium.⁵⁸ Most commonly used alkaline electrolytes are KOH and NaOH for electrochemical reduction of oxygen. Many of the physiochemical properties like oxygen solubility, oxygen diffusion coefficient, solution viscosity, electrode interfacial phenomenon etc. are different in both the electrolytes due to the difference in the size of sodium and potassium cations. Most of the catalysts show superior

performance in KOH compared to NaOH because the former has low viscosity and provides better oxygen solubility and hence improves ORR performance.⁵⁹



Figure 1.7 The operation diagram of (a) an alkaline fuel cell and (b) a proton exchange membrane fuel cell. Reproduced with permission.^{57,58}

Thus, metal-air batteries and fuel cell technologies depend on oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) for electrochemical energy conversion. Since the electrochemical environment is less corrosive in alkaline media compared to acidic medium, a possible reaction mechanism occurring at the cathode and the anode are discussed in detail in the alkaline medium in the following section.

1.5.1 Cathode reaction: oxygen reduction reaction (ORR)

The cathode reaction occurring in batteries and alkaline fuel cells is an oxygen reduction reaction i.e. reduction of oxygen molecules to water. The complete reduction of oxygen takes place via four electron transfer process consisting of many elementary steps depending upon the catalyst and nature of the electrolyte used in the device



Figure 1.8 (a) Schematic representation of two potential modes of O_2 molecule adsorption on N-doped CNT (up panel) and non-doped CNT (down panel). (b) Mechanistic pathway of ORR in N-doped carbon materials. Reproduced with permission.⁶⁰

1.5.1.1 Mechanism of ORR

In general, depending upon the type of adsorption mode of oxygen on the catalyst surface i.e. bidentate and end-on O_2 adsorption mode⁶⁰ (**Figure 1.8**), ORR mainly takes place via two mechanisms discussed below:

 In direct four-electron reduction pathway, based on bidentate oxygen adsorption mode, two oxygen atoms are coordinated with the catalyst and oxygen is directly reduced to generate hydroxide ions shown in following equation:⁶¹

 $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ (E^o = 0.40 V vs. SHE)

It was found that the four-electron process takes place by two mechanisms i.e., an associative mechanism involving HOO* and a direct O_2 dissociation mechanism in alkaline electrolyte. The associative mechanism goes through the following steps:⁵⁶

$$*+O_2 + H_2O + e^- \longrightarrow HOO^* + OH^-$$


In the case of the dissociation mechanism, the first splitting of adsorbed O_2 molecule takes place followed by the reduction of adsorbed oxygen atoms to water via the following elementary steps:⁵⁶

```
O_2 + * + * \longrightarrow O^* + O^*O^* + H_2O + e^- \longrightarrow HO^* + OH^-HO^* + e^- \longrightarrow OH^- + *
```

where, * represents the surface active sites and there is the formation of several reaction intermediates such as surface adsorbed oxygen (O*), hydroxyl (OH*) and superhydroxyl (HOO*) species.

ii. In two-electron pathway reduction, only one oxygen is coordinated to the catalyst to form hydrogen peroxide as an intermediate based on the end-on adsorption mode of oxygen. This peroxide species is further reduced to form water as given below:⁶¹

$$O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^- (E^\circ = -0.07 \text{ V vs. SHE})$$

$$HO_2^- + H_2O + 2e^- \longrightarrow 3OH^- (E^\circ = 0.87 \text{ V vs. SHE})$$

From these two mechanisms, the four-electron pathway is considered as a more desired pathway in ORR because in case of two-electron pathway, the generation of corrosive HO_2^- (peroxide) species causes degradation of the catalyst and hence reduces the overall efficiency and stability of metal-air batteries and fuel cells.

The mechanism of ORR involving either a 4 e⁻ inner-sphere electron transfer or a 2 e⁻ outer-sphere reaction pathway⁶² was summarized in **Figure 1.9**. In case of acidic media, there is less amount of OH⁻ species and thus ORR strictly follows the inner-sphere electron transfer mechanism. While in alkaline media, there is competition between inner- and outer-sphere

mechanisms due to more coverage by OH^- species. These adsorbed OH^- species interact with the dissolved oxygen and result in the formation of HO_2^- intermediate. Desorption of this peroxide intermediate as a reaction product from the catalyst surface by less noble metals led to the outer-sphere electron transfer mechanism. Since noble metals have the ability to stabilize the HO_2^- intermediate and hence dominate by the 4 e- inner-sphere electron transfer mechanism. Thus, noble metals can show the best activity in alkaline media as well.



Figure 1.9 (a) Schematic representation of a double layer structure during ORR in different environments i.e. acidic (left) and alkaline (right). Insets (a) and (b) illustrate the inner and outer electron transfer processes. Reproduced with permission.⁶²

The mechanism of ORR can be determined by calculating the adsorption/dissociation energies of these elementary steps. In 2004, during the electrochemical process of ORR,

Norskov and its co-workers calculated the reaction free energy (Δ G) of different reaction intermediates by density functional theory (DFT) integrating with the standard hydrogen electrode (SHE) model.⁶³ The theoretical volcano plot (**Figure 1.10**) can be used as a measure for activity and selectivity of a catalyst based on the relationship between the adsorption energy of oxygen adsorbates and their catalytic activity.⁶⁴ Metals that bind with oxygen too strongly, their activity is limited by proton-electron transfer to O* or OH*. However, in the case of metals that bind with oxygen too weakly, activity is limited by proton-electron transfer to O₂* (associative mechanism) or splitting of O-O bond in O₂ (dissociative mechanism) depending upon the applied potential. As can seen in (**Figure 1.10 a, b**), location of Pt is not at the "summit of volcano" and further improvement can be done by making alloying with transition metals.⁶³⁻

Apart from the theoretical calculations, rotating-disk electrode (RDE) and rotating ring disk electrode (RRDE) measurements are powerful methods to evaluate the ORR performance of catalysts. Linear sweep voltammetry (LSV) curves of current versus applied potential can be recorded to estimate the performance of the catalyst. The number of electrons involved in ORR can be estimated by the Koutecky-Levich (K-L) equation (detailed discussion in section 2.2.2 of Chapter 2).⁶¹ Kinetic current (intrinsic activity of catalyst) can be calculated from the K-L equation and the corresponding mass activity can be determined by dividing the kinetic current with the loading of the catalyst. Another important parameter is half-wave potential ($E_{1/2}$) defined as the potential needed to actia a current that is half that of the saturation current. Higher $E_{1/2}$ means less overpotential needed to achieve $1/2 I_d$ (diffusion-limited current density) hence better catalytic activity.

1.5.2 Anode reaction: oxygen evolution reaction (OER)

The anodic reaction that takes place in metal-air batteries is the oxygen evolution reaction (OER). It is the reverse process of ORR. OER involves a complex process compared to ORR. It is known that Pt is the best ORR catalyst, but it does not show OER activity. This indicates that OER has a different reaction mechanism from ORR on Pt.^{66,67} Generally, microscopic reversibility of the reverse reactions holds only when the process takes place close to equilibrium conditions. In electrochemical reactions, when a large overpotential is required to carry out the reaction in reverse directions, the requirements of the catalysis in each direction could be significantly different.^{68,69} Additionally, OER needs a high positive potential and metals like Pt undergo oxidation at this potential, resulting the formation of a different type of surface from that under ORR conditions. Thus, it is important to determine the surface structure

and active chemical composition of the material to know about the mechanism of OER electrocatalytic reaction.⁷⁰



Figure 1.10 (a) Volcano plot of ORR for metals. b) The theoretical limiting potential plot of ORR for fcc (111) and (100) facets of metals and alloys. c) Volcano plot of metal oxides towards OER. Reproduced with permission d) Relation between the OER catalytic activity and the occupancy of the e_g -symmetry electron of the transition metal (B in ABO3). Reproduced with permission.⁶⁵

Mechanism of OER

In general, OER occurs via four discrete electron transfer steps in which a series of oxygen adsorbates are formed according to the following equations:^{41,56}

*+
$$OH^{-}(aq) \longrightarrow HO_{ads} + e^{-1}$$

$$HO_{ads} + OH^{-}(aq) \longrightarrow O_{ads} + H_2O(l) + e^{-l}$$

where * and "ads" represent the active sites of the catalyst surface and adsorption on the surface of the catalyst, respectively.

After that, the formation of oxygen takes place via two possible pathways. First is the direct combination of two O_{ads} intermediates to produce $O_2(g)$ shown below:

$$2O_{ads} \longrightarrow O_2(g)$$

In the second one, there is the formation of OOH_{ads} intermediate first by reaction of O_{ads} with OH- followed by combination with OH- and decomposition to O_2 (g) as follows:

$$O_{ads} + OH^{-}(aq) \longrightarrow OOH_{ads} + e^{-}$$

$$OOH_{ads} + OH^{-}(aq) \longrightarrow * + O_{2}(g) + H_{2}O(l) + e^{-}$$

$$Overall: 4OH^{-}(aq) \longrightarrow O_{2}(g) + 2H_{2}O(l) + 4e^{-}$$

The reaction kinetics of OER are mainly controlled by the binding strength of oxygen adsorbates on the active sites of the catalyst surfaces like ORR. According to the Sabatier's principle, if the binding with oxygen is too weak, then oxidation of OH_{ads} would be the rate-determining step. On the other hand, strong oxygen binding makes the formation of OOH_{ads} as rate-limiting step. Since OH_{ads} and O_{ads} intermediates are always involved in the OER process so, $\Delta G_O - \Delta G_{OH}$ can be used as a descriptor for the evaluation of OER electrocatalyst efficiencies. The OER volcano plot shown in **Figure 1.10c** has been constructed by $\Delta G_O - \Delta G_{OH}$ for various metal oxides.⁶⁵ It has been found that experimental overpotential at 1mA/cm² is correlated well with this theoretical overpotential volcano peak when plotted against this descriptor. Furthermore, Shao-Horn et al. described a simple activity descriptor that provides a similar correlation between surface adsorbate binding and catalytic activity of transition metal oxides.⁶⁵ They show that the intrinsic activity of the catalyst towards OER reveals a volcano-shaped dependence (**Figure 1.10d**) on the occupancy of the 3d electron with an e_g symmetry of surface transition metal cations. It was predicted that the highest OER activity can be achieved when e_g occupancy close to one.⁶⁵

Overpotential (η) is one of the most important parameters to evaluate the electrocatalytic activities of different catalysts towards OER.⁷¹ For this, linear sweep

polarization (LSV) curves of current vs applied potential are recorded in alkaline media. In general, overpotential is the extra potential from the thermodynamically reversible potential of OER and measured at a current density of 10 mA/cm². The overpotential is logarithmically related to the current density (j) and its linear portion gives the Tafel slope.⁷² This slope reveals the kinetics of the OER reaction. Low overpotential means less potential is required to overcome the thermodynamic potential (1.23 V *vs.* RHE) and an excellent performance towards OER.

The overall reaction of oxygen electrocatalysis i.e. oxygen reduction reaction (ORR) and oxygen evolution (OER) discussed in detail in the above section consists of elementary oxygen redox steps shown in the form of the catalytic cycle in **Figure 1.11 A, B** and the energetics of oxygen redox intermediates in **Figure 1.11 C, D**.⁷³

1.5.3 Scope of research

As we have already discussed in metal-air batteries and regenerative fuel cells, both ORR (discharging) and OER (charging) are parallel in important and these face some critical challenges. One is the sluggish kinetics of the ORR and OER that creates large overpotential on the air cathode, which significantly decreases the efficiency and power density of metal-air batteries. The round-trip efficiency of these batteries is usually < 55-65% because of this high overpotential.⁷⁴Another one is stability, which is less than a quarter of the commercial Li-ion battery. Both these factors hinder its practical applications.⁷⁵ Based on this, there is a urgent need for developing highly efficient and well-tolerated catalysts that act as bifunctional ORR/OER air electrodes.

The following basic requirements should be fulfilled by an ideal catalyst:

1. *Activity:* The activity of the catalyst can be correlated to the intrinsic active site and also to the number of active sites available. Heteroatom doping (N, O, S, B, P and metal atoms) and controlling the defects i.e. vacancy and edge promote electron transfer and change the electronic structure, therefore reducing the adsorption energy of oxygen-containing reaction intermediates, resulting in the improvement of intrinsic activity of catalyst. Controlling the porous structure also exposes a large number of active sites and is another method to increase the catalytic activity. The large specific surface area is provided by meso/micropores are able to increase the

availability of reactants to the active centers, while macropores impart more mass transfer pathways.

- 2. *Conductivity:* Since all the electrochemical reactions involve the transfer of electrons, high conductivity is one of the key parameters for electron transport. It can be increased by using π -conjugated conductive ligands and unbound electrons from the sp² carbon network resulting in enhanced electrocatalytic activity.
- 3. *Stability:* It is the most important factor affecting the commercialization of batteries or fuel cells. The ideal catalyst should have chemical and structural stability under harsh reaction conditions (acid/alkaline environment). Otherwise, agglomeration of particles or change in oxidation state on the surface of the electrocatalyst during the continuous operation of devices terminate the activity of the catalyst.
- 4. *Low-cost and environmental-friendly:* Noble metals like Pt and Ru/Ir exhibit excellent electrocatalytic activity towards ORR and OER, respectively. But the high cost, scarcity, and low stability restrict their practical applications. Due to low cost and intrinsic catalytic activity, metal-free carbon-based catalysts and precious metal-free catalysts can act as better electrocatalysts in near future. Therefore, the synthesis of an electrocatalyst should be designed in such a manner that meets the requirements of low cost and environmentally friendliness.
- 5. Selectivity: Molecular oxygen can be reduced to water by 4 e⁻ or generation of H₂O₂ by 2 e⁻ in the electrochemical process. The production of water is preferred in fuel cells while latter is used for green synthesis production of H₂O₂. Thus, catalysts should be highly selective towards a specific processes.



Figure 1.11 Depiction of the catalytic cycle and energy changes of oxygen redox intermediates in oxygen electrocatalysis. (A, B) Fundamental reactions (in an alkaline environment) involved in the catalytic cycle of OER and ORR, respectively, where M^* denotes the adsorption site on the catalyst's surface. OOH* and OH* may exist on the surface in a deprotonated form as O^{2-} and O-, respectively. The formal oxidation state of the oxygen atom is explicitly presented to provide a general representation of oxygen redox; however, it should be noted that the charge localization may not be so ideal. For instance, surface-bonded OH* is not identical to the \cdot OH radical. Lewis structures of reactants are displayed in each figure. The reaction kinetics are closely related to the electronic structure of the reactants. (C) Potential energy diagram of a typical catalyst under an applied potential E = 0 V vs. RHE. The surface reactivity of the depicted catalyst is excessively high for OER but too low for ORR. (D) Activity volcano plot for OER and ORR. The RDS that form the volcano plot is shown. Reproduced with permission.⁷³

1.5.3.1 Bifunctional oxygen catalysis

Devices in which oxygen reduction reaction (ORR, discharging process) and oxygen evolution reaction (OER, charging process) occurs on the same electrode, that electrode is known as "bi-functional".⁷⁶ So far, most unifunctional ORR or OER electrocatalysts like Pt or Ru/IrO₂ have been developed having high catalytic performances. Since Pt-based catalysts undergo oxidation at high positive potential which is required for OER, this limits their catalytic ability towards OER. Similarly, the most active catalysts for OER like noble metal oxides do not show good ORR catalytic performance.^{65,77} Therefore, there is a great necessity for developing bifunctional oxygen catalysts.

Criteria for efficient bifunctional oxygen electrocatalysts

In the case of bifunctional electrocatalysts, ORR and OER proceed via four elementary reaction steps. ORR occurs by the formation of OOH* from the adsorbed O_2 and then further reduction to O* and OH*, while in OER, a reverse reaction takes place as given below:

*+
$$O_2(g) + H_2O(l) + e^- \longrightarrow HOO^* + OH^-$$

HOO* + $e^- \longrightarrow O^* + OH^-$
O* + $H_2O(l) + e^- \longrightarrow HO^* + OH^-$
HO* + $e^- \longrightarrow OH^- + *$

where * represent the active sites of the catalyst surface.

Overall, in alkaline electrolyte:

$$O_2 + 2H_2O(1) + 4e^- \rightarrow 4OH^-$$

The theoretical calculation of the adsorption energy of oxygen intermediates, **Figure 1.12** shows that the activity of ORR is limited by the reduction step of OH* (black line) and O₂ (blue line). In spite of this, OER activity is limited by the formation of OOH* (green line) and O* (red line).⁶⁵ It is found that the binding energies of intermediates (O*, OH* and OOH*) for ORR and OER catalysts are not identical. Thus, the best catalyst for ORR is much less effective for OER and vice-versa.^{78,79}

Based on this analysis, the catalyst should have moderate adsorption energies of oxygen containing species close to theoretical equilibrium potential (shown by the dashed line in **Figure 1.12**) to show excellent ORR/OER bifunctional performances.⁶⁵ The evaluation of the bifunctional electrocatalyst is done by recording the LSV polarization curves for OER and ORR. The current density at -3 mA/cm² is close to the half-wave potential of the best catalyst of ORR (Pt/C), and for OER, the potential required to achieve a current density of 10 mA/cm² is equivalent to the expected current density for ideal solar cell. Thus, the potential gap (Δ E) between ORR half-wave potential (E_{1/2}) and OER potential at 10 mA/cm² is used as an indicator for evaluating the overall performance of a catalyst towards oxygen electrocatalysis.



Figure 1.12 Initial activity volcano patterns of the ORR and OER. The theoretical activity on (a) the surface of metal oxides and (b) the surface of metals is presented as a correlation with the oxygen binding energy. Reproduced with permission.⁶⁵

The development of a bifunctional oxygen catalyst with high activity and durability is the ultimate goal for the commercialization of metal-air batteries and fuel cells. Various strategies have been adopted such as morphology-, interface-, and defect engineering, to obtain better bifunctional catalysts. The important points for efficient bifunctional electrodes can be summarized as follows:

1. Electrocatalyst should be low-cost and environmentally friendly having a large number of dispersed active sites.

- 2. The surface area of the electrocatalyst should be high so that it can easily make contact with the electrolyte and have suitable surface adsorption energy in contact with O_2 and H_2O .
- 3. Conductivity should be high for facile electron transportation.
- 4. The electrocatalyst should have high corrosion resistance under strong oxidizing conditions and applied potentials.
- 5. It should be stable to prevent leaching off from the electrode surface during the longterm electrocatalytic process.

1.5.3.2 Existing bifunctional materials

A variety of bifunctional ORR/OER electrocatalysts have been developed as aircathode for rechargeable metal-air batteries which can be summarized in three categories: (i) Metal-free carbon catalysts, such as heteroatom-doped carbon and porous carbon; (ii) Metalbased catalyst and (iii) their composite materials.

a) Metal-free carbon materials

Carbon nanomaterials including amorphous carbon black, carbon nanotubes, graphitic carbon nitride (g-C₃N₄) and graphene oxide are promising alternatives for precious metal free carbon-based catalysts. They have been proven to be able to facilitate electron transfer and mass diffusion in catalytic processes because of their low-costs, high specific surface areas and excellent electrical conductivity and therefore, show significant potential in the field of electrocatalysis.^{60,80,81} Heteroatoms or defects are generally introduced into metal-free carbon-based catalysts for achieving high catalytic activity. They help in changing the charge distribution of neighbouring carbon atoms and hence increase the catalytic activity. Heteroatoms like N, S, O, B, and P are introduced in heteroatom-doped carbon materials to attain high catalytic efficiency for various reactions.⁸² Due to certain differences in the electronegativities of these heteroatoms and carbon, they effectively adjust the charge/spin distribution in the sp² conjugated carbon frameworks and thereby enhancing the electrocatalytic activity.

Carbon materials doped with mono-atoms (N, P, S or B) generate a large number of active sites in the carbon matrix and reduces the reaction energy barrier and hence act as efficient bifunctional electrocatalysts in metal-air batteries and fuel cells.^{86,87} N-doped carbon materials are most used as metal-free bifunctional electrocatalysts for ORR and OER. Notably,

Peng et al. synthesized highly efficient N-doped hierarchically porous carbon plates (N-E-HPC) from the natural timber by enzyme treatment followed by pyrolysis with NH₄Cl (**Figure 1.13a**).⁸⁸ Due to the presence of both pyridinic and graphitic N sites in the carbon network, this catalyst shows excellent ORR and OER performances. A reversible Zn-air battery (ZABs) fabricated with this catalyst shows a high peak power density of 192.7 mW/cm², a specific capacity of 801 mA h/g and attain high stability for 110 h (**Figure 1.13b-d**) without any decay in performance. Moreover, this N-E-HPC catalyst is also used as air-cathode in ZABs (**Figure 1.13e**). Such performance of this catalyst is comparable to the commercial catalysts. Hence the direct conversion of wood into nanostructured catalyst is advantageous for practical applications.



Figure 1.13 a) Schematic representation of the bulk transformation process using the enzymeassisted method for synthesis of N-E-HPC using NH₄Cl. b) polarization and power density curves, c) galvanostatic discharge curves of ZABs, and d) galvanostatic discharge/charge cycling curves of rechargeable ZABs with N/E-HPC-900 powder and Pt/C + RuO₂, respectively. e) Schematic representation of a rechargeable quasi-solid-state ZAB using N/E-HPC-900 plate cathode. Reproduced with permission.⁸⁸

Likewise, B-doped carbon nanomaterials also attract a lot of interest for enhancing the electrocatalytic activity. For example, Choi and co-workers⁸⁹ synthesized a carbon-based composite using a hydrothermal method which is made up of B-doped graphene quantum dots

fastened to a graphene hydrogel (GH-BGQD). The synthesized catalyst shows remarkable bifunctional performance for ORR ($E_{1/2} = 0.87$ V) and OER ($E_{10} = 1.6$ V). The excellent catalytic activity is due to the presence of lower electronegative B atoms than carbon which induces charge separation and hence promote an efficient chemisorption with the oxygen atoms. Fabrication of battery using this GH-BGQD catalyst as air electrode shows good performance with enhanced cycling stability (more than 15 h at 10 mA/cm²).

Dual-doping in the carbon network by the presence of two heteroatoms develops a synergistic effect to increase the electrocatalytic activity. Generally, N connected with other heteroatoms like N-S, N-B and N-P are reported.⁹⁰⁻⁹³ There are also reports of N, O dual-doped carbon materials for ORR and OER. A facile route was developed for the synthesis of dual doping of N and O in graphene (NOGB) by using polymer-coated prussian blue as precursors (Figure 1.14).⁹⁴ Introducing oxygen to N-doped graphene accelerates the formation of more carbon positive charge active sites and promotes the activity of OER. Based on this catalyst, ZAB shows small potential gap of 0.72 V between ORR and OER and remarkable stability up to 30 h (Figure 1.14). Besides, mono- or dual doping of heteroatoms, ternary-doped carbon materials as bifunctional catalysts were rarely reported. For instance, ternary (N, F and P) doped carbon materials (NFPC) prepared by Ma et al. using electrospinning and thermal annealing method.⁹⁵The synthesized catalyst shows efficient bifunctional performance due to their high conductivity, large surface area and porous structure, and synergism of doped heteroatoms (N, F and P). When this catalyst is assembled into ZAB, it shows a high potential gap of 0.8 V and poor stability. Thus, the activity of the catalyst was not the only factor for their commercialization.

Thus, extensive research on metal-free carbon materials has shown that they exhibit excellent ORR activity and selectivity, but their bifunctional performance is not good due to lower OER catalytic activity. The improvement in oxygen electrocatalysis is due to the presence of hetero-atoms or defects in the carbon matrix. It is difficult to prepare a specific catalytic active center in metal-free carbon-based materials. Another critical issue is the corrosion of carbon influenceing the cyclic stability during charging mainly occurring because of the absence of metal active sites. So, the activity and the stability of the catalyst are important factors for ZABs performance, thus improvement of both these factors in metal-free carbon materials simultaneously is an important challenge.



Figure 1.14 a) Fabrication process including high-temperature pyrolysis and subsequent acid etching of hybrid precursors for the synthesis of NOGB. b) HAADF-STEM image with EDX mapping of NOGB. c) Polarization profiles during charging and discharging for the aforementioned two Zinc-Air Batteries (ZABs). (d) Galvanostatic charge and discharge experiment conducted on the ZAB utilizing NOGB-800 as the catalyst at a current density of 10 mA cm⁻². (e) Image capturing two series-connected ZABs, based on NOGB-800, powering light-emitting diodes (3 V) for illumination. Reproduced with permission.⁹⁴

b) MOFs- derived metal-based catalysts

Metal-organic frameworks (MOFs) consisting of metal ions or clusters coordinated with organic ligands like zeolite imidazole frameworks (ZIFs) have attracted a lot of interest in catalysis due to their high porosity, ultra-high surface area and tunable structure.⁹⁶⁻⁹⁹ MOFbased catalysts have of following advantages compared to non-porous noble metal catalysts: (i) the morphology, size and porosity structure of pristine MOFs can be regulated to expose the active sites and facilitate the mass transfer in electrocatalytic reactions; (ii) the incorporation of heteroatoms (like metal atoms, N, O, S and P) in the linkers changes the electronic structure of catalysts, improving the catalytic activity by decreasing the adsorption energies of intermediate species; (iii) presence of conductive ligands improve the conductivity of MOFs to attain better electron transfer; (iv) precursors can be encapsulated into the pores of MOFs is another advantages for well-dispersion of species on the resultant carbon-based materials like single-atom metal sites.

c) Other metal-based catalyst & their composites

Recently, MOF-derived metal/metal compound carbon-based materials have been considered as powerful strategies for the preparation of bifunctional ORR/OER electrocatalysts due to their unique features like brilliant electronic conductivity, activity and stability.⁹⁹⁻¹⁰¹ Among these, metal-nitrogen-doped carbon materials (M-N-C, M = Fe, Co, Ni etc.) have attracted a lot of attention in catalysis due to their outstanding ORR activity.¹⁰²⁻¹⁰⁵ This is due to the presence of M-N_x sites distributed in the carbon matrix, which are the main active sites for O₂ adsorption and O=O bond breaking during ORR. Besides this, they are also composed of carbon ligands having N and transition metal sites responsible for exhibiting excellent OER performance. For example, Huang and co-workers described a template approach for the synthesis of atomically dispersed Co single atoms on N-doped 2D carbon nanosheet (SCoNC) (Figure 1.15a).¹⁰⁶ Scanning electron microscopy (Figure 1.15b) images revealed that the resultant SCoNC has 2D sheet-like morphology with an ultrathin feature. The resultant catalyst showed efficient bifunctional activity with $E_{1/2} = 0.91$ V for ORR and $E_{10} = 1.54$ V for OER (Figure 1.15c). Due to the presence of highly dispersed single Co-N moieties in the carbon network, it also shows good performance in ZABs with a power density of 194 mW/cm² (Figure 1.15 c, d). Another approach is the formation of MOF-derived metal alloys in order to acquire highly efficient bifunctional catalysts due to the synergistic effect between bimetallic components. Lu et al. reported a catalyst composed of FeNi alloy dispersed on N-doped CNTstangled hierarchically porous carbon fibre (FeNi/NCPCF) synthesized by pyrolysis of respective metal salts and ZIF-8 derived PAN electrospun fibres.¹⁰⁷ Due to the presence of porous carbon structure which is grafted on N-doped CNTs and also the existence of a synergetic effect between FeNi alloys, the catalyst demonstrate excellent bifunctional activity with a low potential gap of 0.69 V between ORR and OER.

1.5.3.3 Challenges in the existing catalysts

The discussion on the existing non-noble metal bifunctional ORR/OER catalysts, including metal-free carbon catalysts and MOFs-based catalysts possess their own advantages and disadvantages. As for metal-free carbon catalysts, they include heteroatom doped carbon, which helps to improve the catalytic activity by regulating the electronic structure. Significantly, the presence of various heteroatom doping enhances the diffusion of oxygen and boosts the ORR activity by the forming OH⁻ via four electron pathways. However, under high oxidation potentials of the OER, corrosion of carbon takes place, which cannot be avoided

causing catalyst agglomeration and decrease in the activity in consecutive cycles, leading to poor cycling stability. This dissatisfactory bifunctional ORR/OER performance of carbon nanomaterials restricts their practical implementation in ZABs.



Figure 1.15 (a, b) Schematic illustration of the synthetic procedure and SEM image of the SCoNC catalyst. c)ORR polarisation curves of catalysts at 1600 rpm with a scan rate of 5 mV/s in 0.1 M KOH. d) Schematic diagram of customized Zn-air battery. d) Polarization and power density curves of primary Zn-air batteries using Pt/C and SCoNC as ORR catalyst (mass loading of 1 mg cm⁻²) and 6 M KOH electrolyte. Reproduced with permission.¹⁰⁶

In terms of MOF-based catalysts, apart from several advantages like high surface area, porosity, metal active sites and controllable morphology, they are limited by certain disadvantages. As the design of MOF materials requires the careful selection of metal nodes and organic linkers, suitable matching of the MOFs pore structure and encapsulated metal particles and also the high cost of the MOF precursors, prevents wider use of MOF derivatives in large-scale industrial production. Another factor is that high temperature pyrolysis is required for the transformation of MOFs into carbon-based materials, which is also a harsh condition for material synthesis. Moreover, due to high temperature, the materials with low-thermostability cannot be obtained directly in MOF-derived carbon-based materials. In

addition to this, the original pore structure of MOF collapses during pyrolysis. Hence, it is difficult to control pore structure which will ultimately affect the mass transport in electrocatalytic reactions.

1.5.3.4 Probable Remedies

a) Role of improving surface characteristics

There is a lot of potential in tuning surface functionalities for improving the existing electrocatalysts.¹⁰⁸ It is always desirable to have a highly conductive surface of an electrocatalyst to yield a highly efficient product in an electrochemical pathway.¹⁰⁹ There is an important role of functional groups present in catalyst support in order to anchor metal active sites and hence the metal-support interaction is one of the governing factors behind efficient catalytic activity. The kinetic pathway of any reaction depends on the stability of the intermediates. In this regard, the surface charge of the catalyst plays a crucial role. But, the adsorption of intermediates and products should not be too strong otherwise products will be attached to the catalyst surface for the longer time, leading to deactivation of the catalyst.¹¹⁰ Besides, the kinetics of the electrocatalysis is largely dependent on surface area and the porosity of the catalyst material as it indicates the abundance of the active sites present in a catalyst surface.¹¹¹

b) Sustainable synthesis

The harshness of experimental conditions for synthesis of electrocatalysts is the biggest barrier towards sustainable large-scale implementation of most of the existing synthetic strategies for making an efficient electrocatalysts. Furthermore, the requirement of posttreatment often limits the applicability of synthetic proton in industrial standards due to multistep processes. Therefore, it is important to explore the possibilities in producing a catalyst in a single-step.

c) Potential low-cost elements for electrocatalysis

To achieve sustainability and environmental feasibility it is of utmost important to use cheap, high-abundant precursors for catalyst synthesis. But, according to the current scenario (**Figure 1.16**) the third-row transition metals are the most efficient ones whereas they are highly toxic, low-abundant and hence expensive. Therefore, recently, electrocatalysts based on first-

row transition metals are emerging fast. But their both efficiencies and durability's are yet far to reach the industrial standards.



*Figure 1.16 Histogram describing the relative abundance and cost of noble metals and firstrow transitions metals. Reproduced with permission.*¹¹²

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Chapter 2

Materials, general characterization and experimental procedures

CHAPTER 2

2.1 Materials and Characterization techniques

2.1.1 Materials

Cobalt chloride hexahydrate (CoCl₂.6H₂O, Alfa Aesar), Nickel chloride hexahydrate (NiCl₂.6H₂O, Alfa Aesar), Iron chloride hexahydrate (FeCl₃.6H₂O, Sigma Aldrich), Melamine (C₃H₆N₆, Alfa Aesar), Palladium chloride (PdCl₂, < 99%, Alfa Aesar), Pt/C (40 wt% Pt on a carbon support, Sigma Aldrich), Pd/C (30 wt% Pd on a carbon support, Sigma Aldrich), Vulcan-carbon (XC-72), Iron nitrate nonahydrate (Fe(NO₃)₃.9H₂O), Nafion solution (5 wt% in aliphatic alcohol and water, Sigma Aldrich), Iridium oxide (IrO₂, Sigma Aldrich), Potassium hydroxide (KOH, Himedia), Methanol (CH₃OH, Himedia), Ethanol (ACS grade, Merk), HCl (Himedia), H₂SO₄ (Himedia), Sodium bicarbonate (NaHCO₃). All the above reagents were obtained from commercial sources and used without further purification. All the experiments were conducted in ultrapure water with a resistivity of 18.2 MΩ cm⁻¹.

2.1.2 Characterization techniques

The morphology of the prepared samples was investigated by Transmission electron microscopy (TEM) using a JEOL JEM-F200 microscope operated at 200 kV. High-resolution TEM (HRTEM) images, high angle annular dark-field scanning TEM (HAADF-STEM) images, selected area electron diffraction (SAED) patterns, energy dispersive X-ray spectroscopic (EDS) elemental mapping data to know about the chemical composition of the sample were also recorded. TEM grids were plasma cleaned for 30 seconds before use by using Solarus plasma cleaner (Gatan). The samples for TEM were prepared by drop-casting an ethanolic dispersion of the sample on a holey carbon-coated Cu grid and then dried in the air, followed by vacuum drying.

Field emission scanning electron microscopy (FESEM) images were recorded using JEOL JSM-7600 F, operating with an accelerating voltage of 20-30 kV and a chamber pressure of 10⁻⁵ Torr. SEM samples were prepared by making an ethanolic dispersion of the sample by ultrasonication and drop cast on silicon wafer substrate and then allowed to evaporate the solvent at room temperature using a vaccum-dessicator.

Powder X-ray diffraction (PXRD) patterns of all the prepared samples were recorded using a Rigaku-Ultima IV diffractometer with Cu K α radiation (generator power setting: 40 mA and 40 kV) with DTex Ultra detector using parallel beam geometry at a scanning rate of 1°/min and scan step of 0.02° in 2 θ range of 10-80°. Using mortar and pestle, fine powder of the samples was made before the measurement.

Raman spectra were obtained at room temperature using a Renishaw Raman Spectrometer equipped with a 514 nm laser as an excitation source. The data were recorded in the range of $1000-2000 \text{ cm}^{-1}$.

Nitrogen adsorption-desorption measurements were performed on an autosorbiQ2Quantachrome instrument (AutosorbIq-c-XR-XR). The apparent surface area was calculated by the Brunauer–Emmett–Teller (BET) method. A suitable relative pressure range was selected in such a way that a positive x-axis intersects of multipoint BET fitting (C > 0) could be obtained, and V_{ads} (1 – P/P₀) would increase with P/P₀. Before the measurements, the samples were degassed at 120 °C for 2 h under vacuum.

To investigate the elemental composition of the samples, X-ray photoelectron spectroscopy (XPS) measurements were carried out by a Thermo Kalpha+ spectrometer using microfocused and monochromated Al K α radiation (1486.6 eV). The measurement base pressure was more than 5×10^{-9} mbar. An electron flood gun was used for charge compensation during data acquisition.

Atomic absorption spectroscopy (AAS, Labindia AA7000) was used to estimate the metal content in various samples at concentrations as low as one part in 1 million. The samples were dissolved in conc. HNO₃ acid and diluted with water for AAS analysis.

2.2 Electrochemical measurements

All the electrochemical measurements were performed on electrochemical workstation CHI760E using a three-electrode system. Catalyst-coated glassy carbon rotating disk electrode (GC-RDE, working area = 0.0707 cm^2) was used as the working electrode. As a reference electrode, Hg/HgO (0.1 M NaOH) in an alkaline medium, Hg/Hg₂SO₄ (sat K₂SO₄) in acidic media and Ag/AgCl (3 M KCl) in a neutral medium were used. A platinum wire or graphite rods were used as counter electrodes. All potential values were converted and plotted with respect to the reversible hydrogen electrode (RHE) by using the Nernst equation:¹

$$E_{RHE} = E_{observed} + E^{0}_{ref} + 0.0591 pH$$

where $E_{observed}$ is the experimentally measured potential and E^{0}_{ref} is the standard electrode potential of the reference electrode at 25 °C.

 $E^{0}_{Hg/HgO} (0.1 \text{ M NaOH}) = 0.165 \text{ V}$ $E^{0}_{Hg/Hg_2SO_4} (\text{sat. K}_2SO_4) = 0.658 \text{ V}$ $E^{0}_{Ag/AgCl} (3 \text{ M KCl}) = 0.21 \text{ V}$

2.2.1 Preparation of working electrode

The catalyst ink was prepared by dispersing the desired amount of the sample in the required amount of Nafion solution (Nafion:isopropanol: water = 0.05:1:4 (v/v/v)) by ultrasonication for 30 min. The working electrode was prepared by drop-casting the desired amount of catalyst ink on a clean and polished glassy carbon (GC) rotating disk electrode (RDE) with a geometric surface area of 0.0707 cm². It was allowed to dry overnight at room temperature before the electrochemical measurements. The corresponding catalyst loading on GC is 0.707mg/cm² (with cobalt loading only10 μ g/cm²) for the Co_{1.4}-N-C-700 sample. For Pd-loaded samples, the total loading of Pd was maintained near 20 μ g/cm² on the electrode surfaces. For comparison, the commercial Pt/C catalyst dispersion was prepared by dissolving 1.39 mg in 1 ml of the above prepared Nafion solution, and 3 μ l of dispersion was drop-casted on GC-RDE. A 20 μ g/cm² Pt loading was maintained thus on the electrode.

2.2.2 Oxygen reduction reaction (ORR) measurements

For the electrochemical activity test towards ORR, linear sweep voltammogram (LSV) was recorded in oxygen-saturated 0.1 M KOH solution in the potential range of 0.14 V to 1.24 V (*vs.* RHE) at a scan rate of 10 mV/s. To eliminate the background current, LSV was also recorded in N₂ saturated 0.1 M KOH electrolyte with the same scan rate and subtracted from the LSV recorded in O₂ saturated condition.

For the estimation of a number of electrons involved in the oxygen reduction reaction, first ORR LSVs were recorded at different rotational speeds shown in **Figure 2.2.1a**. After that, the Koutecky-Levich (KL) equation (Eq-1) given below was used to calculate the electron transfer number and kinetic current density.²

$$1/I = 1/I_k + 1/I_d$$

where, *I* is the experimentally measured current density, I_d is the diffusion-limited current, and I_k is the kinetic current density. I_d can be obtained from the Levich equation:

$$I_d = 0.62n FAC_0 \omega^{1/2} (D_0)^{2/3} v^{-1/6}$$

where, *n* is the number of electrons involved in ORR, F is Faraday constant (96485 C/mol), the area of the electrode (0.0707 cm²), ω is the angular frequency of the rotating electrode ($\omega = 2\pi f/60$, f is the rotation rate of RDE in rpm), C₀ is the concentration of oxygen (1.21 *10⁻⁶ mol cm⁻³), D₀ is diffusion coefficient of O₂ (1.9*10⁻⁵ cm²/s), v is kinetic viscosity of electrolyte (1.01*10⁻² cm²/s).



Figure 2.2.1 (a) ORR polarization curves (or LSVs) of Pd/C catalyst recorded at different rotation rates in O₂ saturated 0.1 M KOH with a scan-rate of 10 mV/s, b) the corresponding K-L plots at different potentials vs. RHE.

The plot between 1/I vs. $\omega^{1/2}$ shown in **Figure 2.2.1b**, number of electrons and kinetic current can be estimated. The slope gives us the value of the number of electrons participating in the reaction, and the intercept talks about the kinetic current at the particular potential. The comparable slopes at various applied potentials (in the range of 0.7 - 0.85 V *vs*. RHE) signifies that ORR kinetics follows first order kinetics. The mass activity was calculated from the kinetic current by dividing it with Pd/Pt mass loading at 0.85 V *vs*. RHE.

2.2.3 Rotating Ring-Disk electrode (RRDE) measurements

Catalyst ink was prepared similarly as described above. The percentage of hydrogen peroxide yield and electron transfer number were obtained from ring and disk current by following these equations:³

$$\%H_2O_2 = \frac{200 \times \frac{I_{ring}}{N}}{I_{disk} + \frac{I_{ring}}{N}}$$
$$n = \frac{4I_{disk}}{I_{disk} + \frac{I_{ring}}{N}}$$

where I_{disk} and I_{ring} is disk and ring current respectively. N is the collection efficiency of H₂O₂ on the ring electrode and the N value was 0.42.

The durability of the catalysts was checked by performing chronoamperometry measurements for different time periods in O_2 saturated 0.1 M KOH at a constant potential of 0.6 V (*vs.* RHE) with an electrode rotation rate of 1600 rpm or by performing the accelerated durability test (ADT) carried out between 0.6 V and 1.1 V (*vs.* RHE) at a scan rate of 100 mV/s for the desired number of cycles.

2.2.4 Methanol tolerance test

The methanol tolerance of the catalyst was tested by adding 1 M methanol at 100 s during the chronoamperometry measurement at 0.6 V (*vs.* RHE) in O₂ saturated 0.1 M KOH.

2.2.5 Electrochemically active surface area (ECSA) determination

For the estimation of electrochemical active surface area (ECSA), the electric doublelayer capacitance (C_{dl}) of catalysts was measured from CVs recorded in the non-faradaic potential range of 1.08 V to 1.14 V (*vs.* RHE) at different scan rates (10 to 60 mV/s) in 0.1 M KOH. A plot of charging current density (ΔJ) at 1.105 V (*vs.* RHE) against scan rates gives a straight line with a slope equal to C_{dl} . Furthermore, the ECSA was calculated by using the equation:^{4,5}

$$ECSA = C_{dl}/C_s$$

where C_{dl} represents the double-layer capacitance, C_s is the specific capacitance of material under specific electrochemical conditions. The value of C_s used was 0.03 mF/cm², corresponding to carbon-based materials.

2.2.6 Impedance measurements

EIS measurements were performed at an open circuit potential over a frequency range between 1 kHz to 100 kHz with an AC voltage amplitude of 10 mV. The obtained data were fitted into an appropriate equivalent circuit model.

2.2.7 OER measurements

To evaluate the OER activities of the various catalysts, LSVs were recorded in the potential window from 0.9 V to 1.9 V (*vs.* RHE) in 0.1 M KOH at a scan rate of 10 mV/s and a rotation rate of 1600 rpm using GC-RDE. The OER potential was iR-corrected for ohmic losses using solution resistance determined from electrochemical impedance spectroscopy experiments.

The Tafel slope was derived from the equation:⁶

$$\eta = a + b \log |J|$$

where η is the overpotential, *J* is the measured current density, b is the Tafel slope and a is the constant. For the estimation of the tafel slope, the logarithm of current density is plotted on the x-axis, the overpotential is on the y-axis, and the linear fitting gives the value of the tafel slope. It is usually expressed in mV/decade, which means how much overpotential is required to increase the reaction rate by ten times on the respective electrode.

2.2.8 Bifunctional oxygen electrocatalysis

The electrodes where oxygen reduction reaction (ORR) and oxygen evolution reaction occur on same electrode are known as "bi-functional". Thus, the bifunctional oxygen catalysts require multi-active centres to catalyse both types of reaction *i.e.* ORR and OER. The development of bifunctional oxygen catalysts is challenging because a good ORR catalyst is not necessarily efficient for OER, and vice versa. The term used for evaluating the performance of bifunctional oxygen catalyst is ΔE , i.e potential gap between half-wave potential ($E_{1/2}$) in ORR and potential at 10 mA/cm² ($E_{10 \text{ mA/cm}}^2$) in case of OER.⁷ Figure 2.2.2 shows the typical polarization curves for ORR and OER and indicators for evaluating the performance towards bifunctional behaviour of catalyst. It tells first about the onset potential (E_{onset}) which is highest

for cathodic reaction or lowest for anodic reaction at which reaction product is produced at the electrode under specific conditions. Second, is the overpotential (η), which is required to achieve an OER current density of 10 mA/cm² and third, in the case of ORR, η is 3 mA/cm². Fourth is the half-wave potential ($E_{1/2}$) in ORR, and fifth one is a potential gap (ΔE) to measure bifunctional behaviour. The lower the potential gap between ORR and OER, the better the catalyst towards bifunctional electrocatalysis.



Figure 2.2.2 Polarization curves of ORR and OER. Reproduced with permission.⁷

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Chapter 3

Exploring facile synthesis employing cheap precursors to achieve highly efficient M-N-C for bifunctional electrocatalysis
CHAPTER 3

3.1 Introduction

3.1.1 Prelude

Electrocatalysis plays a vital role in various energy conversion and storage technologies, including fuel cells, electrolysers, and metal-air batteries.^{1–4} The development of efficient and cost-effective electrocatalysts is of paramount importance to enhance the performance and sustainability of these devices.^{5–8} In recent years, a new class of electrocatalysts known as M-N-C (Metal-Nitrogen-Carbon) catalysts has emerged as a promising solution, offering remarkable catalytic activity and stability.^{9–12} M-N-C electrocatalysts are composed of transition metal (M) nanoparticles or atomic sites coordinated with nitrogen (N) and embedded within a carbon (C) matrix. This unique structure endows M-N-C catalysts with exceptional electrocatalytic properties, making them ideal candidates for a wide range of energy conversion reactions, including oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and various organic transformations.

3.1.2 Evolution of M-N-C

In the 1964, for the first time the electrocatalytic activity of M-N₄ was reported in a cobalt chelated complex whereas in 1976 Jhanke et al. reported such electrocatalytic activities of a series of first order transition metal complexes where metal is chelated by small molecules such as dyes and Schiff bases where M-N_x acts as the active sites.^{13,14} The heterogeneous M-N-C was born in 1989 when metal binding was observed upon heating a mixture of metal salts and macromolecules.¹⁵ Later in several reports, it was found that nitrogen centers and carbon defects can act as electrocatalytic active sites in the case of bare nitrogen-doped carbon, where electrocatalytic activity can be further boosted in M-N-C when a single atom gets chelated by the pyridinic nitrogens and that M-N_x site is considered as responsible for further boosting the electrocatalytic activity when compared to N-C.¹⁶ Therefore, the abundance of pyridinic nitrogens becomes a tool to predict the electrocatalytic activity of M-N-Cs.

3.1.3 M-N-C in electrocatalysis

The high catalytic activity of M-N-C catalysts is attributed to the synergistic effects between metal active sites, nitrogen doping, and the conductive carbon matrix.^{17–19} Additionally, the nitrogen and carbon components provide excellent stability, corrosion

resistance, and resistance to poisoning by reaction intermediates. The utilization of M-N-C electrocatalysts presents several key advantages. Firstly, the metal-nitrogen-carbon structure enables enhanced catalytic activity and selectivity, leading to improved energy conversion efficiencies. Secondly, the low-cost and abundant nature of the raw materials used in M-N-C catalysts makes them economically viable and scalable for large-scale applications. Lastly, the remarkable stability and resistance to degradation allow for prolonged catalytic performance, reducing the need for frequent catalyst replacement.

3.1.4 Recent progress in M-N-Cs

The synthesis of M-N-C electrocatalysts involves a combination of bottom-up and topdown approaches. Common methods include pyrolysis of metal precursors with carbon and nitrogen sources, followed by subsequent treatments to optimize the catalyst's surface chemistry and structure. The resulting M-N-C catalysts possess a well-defined nanoscale morphology, with metal active sites surrounded by carbon and nitrogen moieties. The precise control of the composition and structure allows tailoring the catalyst's properties for specific electrochemical reactions. However, despite several advances in electrocatalysis by M-N-Cs, challenges remain in optimizing the synthesis methods and understanding the precise mechanisms governing the catalytic behaviour of M-N-C electrocatalysts.^{10,20–23}

3.1.5 Further research scope in M-N-C electrocatalysis

Further research efforts are focused on tailoring the composition and structure to achieve even higher activity, understanding the reaction kinetics at the atomic level, and exploring the scalability and durability of M-N-C catalysts in practical energy devices. However, in recent attempts, for realizing the full potential of M-N-Cs, COFs and MOF have been pyrolyzed to get highly efficient M-N-Cs because of their high surface area. But those synthesis takes a long time, sometimes several days, to achieve the final catalyst. Therefore, a crucial research scope in M-N-C is to achieve a facile and scalable synthetic strategy.

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CHAPTER 3.2

Single-step insertion of $M-N_x$ moieties in commercial carbon for sustainable bifunctional electrocatalysis: mapping insertion capacity, mass loss, and carbon reconstruction



Summary

Atomically dispersed earth-abundant metals in N-doped carbon (M-N-Cs) have emerged as a new class of electroactive materials that can match not only the performance of the precious metals but can catalyze both the cathodic and the anodic reactions due to their bifunctional behaviour. This inspires the development of simpler strategies for scale-up production since the existing ones rely on precursors whose commercial viability is not yet ascertained. Herein, we demonstrate the insertion prospects of $M-N_x$ (M= Fe, Co, Ni) moieties, the electrocatalytic centers in the M-N-Cs, into commercial carbon to establish that a single-step heating of the inexpensive precursors is sufficient to generate bifunctional electrocatalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) with efficiencies that bypass the majority of the known catalysts. Further importantly, we quantify both the ORR and OER trends and the metal insertion limits for each metal while maintaining an atomic dispersion, without the formation of surface migration-induced clustering, because such clustering is inevitable in the existing processes to necessitate an extra acid-leaching step to remove them. We further quantify and explain for each metal a negative mass balance originating from anomalous mass loss of both metal and carbon content, and a massive reconstruction of the carbon backbone catalyzed by the very metal, an event documented for the first time though it ought to be associated with other M-N-C syntheses too.

‡ Manuscript based on this work has appeared in Carbon, **2022**, 196, 1001-1011.

3.2.1 Introduction

The growing global energy demand requires the development of affordable and clean energy conversion devices like metal-air batteries or fuel cells that involve two of the most important electrochemical reactions of converting molecular oxygen to water and the reverse.^{1–5} These sluggish reactions *viz*. oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) occur via multi-electron transfer pathways forming several reaction intermediates, limiting their usefulness in the devices.^{6–10} The Pt- and Ru-/Ir- based phases are the most efficient family of catalysts for ORR and OER respectively, though neither of them, in addition to their high cost and poor durability, demonstrates a bifunctional behaviour.^{11–13} In general, designing a bifunctional oxygen electrocatalyst is challenging because materials having a high ORR activity need not be suitable for OER and vice-versa,¹⁴ leading to tremendous efforts in designing such materials that are precious-metal-free, and exhibit a low Δ E value (the difference between ORR half-wave potential and OER overpotential).^{15–17} Among the earth-abundant materials, a few like nitrogen-doped carbon (N-C), phosphides, metal oxides, carbides, sulfides, chalcogenides, etc. have been found to be sufficiently active for ORR or OER separately, but observation of a bifunctional behaviour has been scarce.^{16,18–21}

Recently, atomically dispersed single-atom metal-nitrogen-carbon (M-N-C, M=Fe, Co, Ni, Mn, Cu, etc.) catalysts have been shown as a promising alternative to noble metal-based ORR catalysts due to the presence of intrinsic active moieties (M-N_x) in the carbon matrix.^{17,22–} ²⁶ Therein, the coordination between metal and nitrogen in the carbon network can be engineered with atomic precision within a nanoscale host that regulates the local electronic structure of the active sites and the binding energy of intermediate species, leading to superior electrocatalytic activity.^{25–28} There are several methodologies adopted to synthesize M-N-Cs, most commonly the high-temperature pyrolysis of metal-organic frameworks (MOFs) or organometallic compounds containing pre-embedded atomic metal sites linked to N-containing organic linkers. However, the ligands used for such precursors as 2-methylimidiazole and 2,2bipyridine are costly and toxic.^{25,26,29,30} Besides the scalable production of such MOFs has not yet been established to limit their practical application.³⁰ In addition, precursors having a rigid crystal structure requires specific metal-ligand interaction, limiting their scope of being a universal host for all metal active sites.^{29–31} The carbon materials having porous structures have been shown to improve the oxygen mass transfer during electrocatalysis leading to enhancement in the catalytic performance.²⁴ Templating approaches have been used to make such porous structures and improve the surface area of the carbon materials prior to the incorporation of metal atoms into the carbon network.^{32,33} Yet the procedure for the preparation and removal of the template is again complicated and energy demanding.³⁴ Finally, the abovementioned processes inevitably give rise to metal nanoparticles because of a high metal to carbon ratio, which are removed by an additional acid-leaching step that is not industry-friendly.^{35,36}

3.2.2 Scope of the present investigation

In contrast to the above-mentioned difficulties in realizing bifunctional M-N-Cs that stem from the generation of an adequate carbon framework first, commercially available electroactive carbon materials such as Vulcan Carbon or Ketjen Black can be considered extremely attractive since they are cheap and scale-up production is well-established, provided the metal-binding sites (usually N)^{37–39} and the earth-abundant metals in an appropriate geometry can be incorporated in a simple process. However, the same cannot be envisioned to succeed yet due to the lack of sufficient knowledge of the process such as how commercial carbon will behave during N- and M- incorporation (noting that the metals are known to strongly interact with C, evidenced by their catalytic roles in the high-temperature synthesis of CNT and single-layer graphene),^{40,41} the extent of carbon retention,⁴² partial carbon oxidation, redistribution of the sp² and sp³ carbon fractions, ^{43,44} the extent of metal incorporation as single atoms,⁴⁵ the extent of surface migration of metals to form active-site blocking nanoparticles,⁴⁶ the distribution of single metal atoms in active sites vs. elsewhere in the framework, etc. And also, since corrosive ammonia is widely used as precursor for N, the use of melamine as a source for *in-situ* generation of ammonia at high temperatures, and avoiding large quantities of ammonia gas flow would be highly desirable for sustainable design strategies.⁴⁷

Herein, we establish a low cost, single-step approach to obtain highly electroactive M-N-C (M= Fe, Co & Ni) utilizing solid-state thermal treatment at a moderately high temperature of 700 °C of a mixture of Vulcan-C and melamine with respective metal salts, unnecessitating the use of expensive, low yield precursors and an additional leaching step. Due to the easy availability of the precursors, large-scale production is also favourable. We show that an 'optimal' loading of metal precursors can arrest surface migration induced atom-aggregation and result in atomically dispersed metals anchored on nitrogen-doped carbon matrix. However, the 'optimal' loading varies from one metal to another. Besides, and rather interestingly, a metal-catalyzed anomalous loss of carbon, and reconstruction of the residual carbon have also

been observed for the first time, which has been thoroughly investigated and quantified. Amidst all these, a cobalt catalyst (Co_{1.4wt%} -N-C) shows the highest bifunctional activity towards ORR ($E_{1/2} = 0.855$ V vs. RHE) and OER ($E_{10 \text{ mA/cm}}^2 = 1.65$ V vs. RHE) in alkaline media, which is better than that of commercial Pt/C, IrO₂ and many other noble metal-free electrocatalysts, attributed to the presence of Co-N_x active sites. The findings offer a simplified, single-step strategy to realize electroactive M-N-Cs with scale-up prospects and a deep insight for engineering of multiple factors for practical implementation that are metal-specific.

3.2.3 METHODS

3.2.3.1 Pre-treatment of Vulcan XC72 carbon

Commercially available Vulcan carbon was pre-treated by following an acid treatment method. Briefly,1 g of carbon was taken in a 250 ml beaker and mixed with 100 ml of 5 M HCl. The mixture was heated at 50 °C for 12 h under continuous magnetic stirring and then cooled to room temperature. An adequate amount of NaHCO₃ was added into the above mixture to neutralize the excess acid until the effervescence stops. The pre-treated carbon was separated by centrifugation at 10500 rpm and washed several times with water to remove excess salt formed during the neutralization process. Finally, the obtained carbon was washed with ethanol and dried overnight in a hot-air oven at 60 °C.⁴⁸

3.2.3.2 Synthesis of Co-N-C

For the synthesis of Co-N-C catalyst, cobalt chloride, melamine, and pre-treated Vulcan carbon were used as the sources of cobalt, nitrogen, and carbon respectively. In a typical synthesis procedure, 0.17 mmol (40 mg) of CoCl₂.6H₂O, 1.4g of melamine, and 400 mg of pre-treated Vulcan carbon were thoroughly mixed by grinding for ~1 h using a mortar and pestle. The resulting powder was transferred into a silica boat and placed inside the tube furnace. The sample was heated under Ar atmosphere at 350 °C for 20 min (with a heating rate of 16 °C min⁻¹) followed by heating at 600 °C for 60 min (with a heating rate of 4 °C min⁻¹) and subsequently heating at 700 °C for 120 min (with a heating rate of 1°C min⁻¹). Finally, the tube furnace was allowed to cool naturally to room temperature. The obtained sample was stored under ambient conditions for further use. The cobalt loading was estimated to be 1.4 wt.% from atomic absorption spectroscopy (AAS). Therefore, the sample was labeled as Co_{1.4}-N-C-700. The effect of Co content in the sample on electrocatalytic properties was investigated by synthesizing a series of samples with different amounts of cobalt precursors (8 mg, 200 mg,

and 400 mg of CoCl₂.6H₂O) in the sample mixture. The samples were heated inside the tube furnace under exactly the same conditions and the resulting samples were denoted as $Co_{0.4}$ -N-C-700 (8 mg), $Co_{5.6}$ -N-C-700 (200 mg) and Co_{12} -N-C-700 (400 mg) according to the estimated Co wt.% loading from AAS analysis. Further, the effect of carbonization temperature for the formation of Co-N-C was studied by performing the reactions at different pyrolysis temperatures. Similar to the synthesis of Co_{1.4}-N-C mentioned above, all precursors were mixed and kept inside the tube furnace at different target temperatures 600, 800, and 900 °C with similar heating rates. The obtained samples were denoted as Co_{1.2}-N-C-600, Co_{1.5}-N-C-800, and Co_{1.6}-N-C-900 according to the heating temperature.

3.2.3.3 Synthesis of Fe-N-C and Ni-N-C

For comparison, the synthesis of Fe_x -N-C and Ni_x -N-C were undertaken similarly by using 0.148 mmol (40 mg) of FeCl₃.6H₂O and 0.168 mmol (40 mg) of NiCl₂.6H₂O respectively with 1.4 g melamine and 400 mg of pre-treated Vulcan carbon. The heating procedure followed was similar to that of Co_{1.4}-N-C-700 sample. The Fe and Ni contents were estimated to be 2.6% and 2.5 % from AAS respectively. Therefore, the obtained products were denoted as Fe_{2.6}-N-C-700 and Ni_{2.5}-N-C-700.

3.2.3.4 Synthesis of N-C

Nitrogen-doped carbon was synthesized similarly without the addition of metal precursors. Typically, 1.4 g of melamine was mixed with 400 mg of pre-treated Vulcan carbon by using a mortar and pestle and placed inside the tube furnace. The resulting sample was labeled as N-C-700.

3.2.3.5 Characterization

All characterization techniques have been discussed in detail in chapter 2.

3.2.3.6 Determination of carbon loss and metal retention

The amount of carbon loss was determined by estimating the difference between initial weight of carbon & metal and weight of the product after completion of the reaction. Since metal content was estimated from AAS measurement, carbon mass was estimated by neglecting the error induced by N insertion since it is merely $\sim 1-2$ % while losses are much larger. Metal retention in the catalyst was measured from the difference between theoretical metal loading and metal loading determined by atomic absorption spectroscopy (AAS).

3.2.3.7 Evaluation of catalytic activity

3.2.3.7.1 Preparation of working electrode

The catalyst ink was prepared by dispersing 1 mg of the sample in 100 µl of Nafion solution (Nafion:isopropanol:water = 0.05:1:4 (v/v/v)) by ultra-sonication for 30 min. 5 µl of the catalyst ink was drop-casted on a clean and polished GC-RDE and was allowed to dry overnight at room temperature prior to the electrochemical measurements. The corresponding catalyst loading on GC is 0.707mg/cm^2 (with cobalt loading only10 µg/cm² for Co_{1.4}-N-C-700 sample). For comparison, Pt/C catalyst dispersion was prepared by dissolving 1.39 mg in 1 ml of the above prepared Nafion solution, and 3 µl of dispersion was drop-casted on GC-RDE. A 20 µg/cm² Pt loading was maintained thus on the electrode.

3.2.3.7.2 Electrocatalytic performance evaluation

The general procedure for the evaluation of ORR and OER activities are provided in section 2.2 of chapter 2.

3.2.4 RESULTS AND DISCUSSION

3.2.4.1 Structural characterization of Co-N-Cs: Atomically dispersed Cobalt on N-doped carbon was prepared by a program-controlled high-temperature pyrolysis method using pretreated commercial Vulcan carbon, cobalt chloride, and melamine as sources of C, Co, and N respectively. The same method was extended for the synthesis of the atomically dispersed Fe and Ni samples too. The structural features of the samples were studied using transmission electron microscopy (TEM) and X-ray diffraction (XRD). Figure 3.2.1a, b shows the low magnification TEM images of a Co-N-C sample with a Co content of 1.4 wt.% prepared at 700° C (Co_{1.4}-N-C-700) showing a homogeneous contrast with no obvious metal clusters decorated on their surfaces. The high-resolution TEM (HRTEM) images recorded on the sample contains disordered graphitic domains randomly oriented within the sample, but no lattice fringes corresponding to cobalt nanoparticles (NPs) or clusters on the entire carbon network. The lattice fringes with a *d* spacing of 0.36 nm in Figure 3.2.1c correspond to the (002) planes of graphitic carbon. In the selected area electron diffraction (SAED) pattern, only diffuse diffraction rings but no bright spots were observed to indicate the highly disordered state of carbon again. We confirmed the homogenous distribution of Co, N, and C atoms on the sample from the high spatial resolution elemental mapping using energy-dispersive X-ray analysis (EDS) in the high angle annular dark-field scanning tunneling microscopy (HAADF-STEM) mode (**Figure 3.2.1d**). The corresponding EDS spectrum is shown in **Figure 3.2.1e**.



Figure 3.2.1 (a) A low magnification TEM image of $Co_{1.4}$ -N-C-700. (b) TEM image consisting of the three regions labelled as 1, 2 & 3 where FFT analysis was carried out as shown in the magnified images in the inset (i), (ii) & (iii). The corresponding FFT patterns for these regions are shown in (ia), (iia) & (iiia) showing the absence of sharp ring or spot patterns, dispelling the possible presence of Co nanoparticles in the sample. (c) High-resolution TEM image showing the graphitic layers; inset is the corresponding SAED pattern. (d) STEM-EDS mapping revealing the uniform distribution of Co and N on carbon network. (e) Three typical EDS spectra recorded in regions 1, 2, 3 in (b) showing an equal intensity of the Co peak and its concentration throughout the sample.

However, such analysis can be misleading regarding the presence of metal clusters since the HRTEM images can be inadvertently selective, and also, diffraction spots with tiny intensities may get lost against an intense background in the SAED patterns. Therefore, we further carried out a detailed analysis of the sample by recording the Fast Fourier Transform (FFT) patterns obtained from several TEM images. The insets in **Figure 3.2.1b** show a few typical FFT patterns recorded on various regions of the sample, showing that not even faint diffraction spots or rings corresponding to Co were observed. Therefore, alongside the XRD and X-ray photoelectron spectroscopy (XPS) analysis, as described later, we conclusively ascertain the

presence of atomically dispersed cobalt moieties in the carbon network. This is further corroborated by the fact that metal nanoparticle based electrocatalysts contain a much larger weight fraction of the metal (**Table 3.2.1**), while the same here, at best, could be a fraction of 1.4 wt.%. The XRD pattern of the sample (**Figure 3.2.2**) contains only two broad diffraction peaks at 24.8° and 43.1° which can be assigned to (002) and (101) planes of carbon which is similar to the N doped carbon material prepared similarly but having no cobalt loading.

S.No.	Catalyst consists of	Loading of metal	References
	metal nanoparticles	(wt%)	
1.	Co@N-C/PCNF	13.81	Adv. Sci. 2021, 2101438
2.	Co@NPC	35	Nanoscale Adv., 2019,1, 2293-2302
3.	Co-N-C	11.09	ACS Appl. Mater. Interfaces 2019, 11, 43,
			39809–39819
4.	NdC-CoNPs-NdC	6	Nanoscale, 2020,12, 3750-3762
5.	Co@N-C	6.2	J. Mater. Chem. A, 2014,2, 20067-20074
6.	Co@NPC-H	17	Carbon, 2018, 13756
7.	HP-Co-NCNFs	34.6	Chem. Eur. J. 2014, 20, 1–9

 Table 3.2.1 Literature reports on metal nanoparticle loaded electrocatalysts.

3.2.4.2 Evaluation of single metal atom insertion capacity amidst anomalous metal and carbon losses: We systematically examined the maximal single atom load capacity in our process that led to several intriguing revelations unnoticed in the previous investigations on various other M-N-C systems: the process is accompanied by (i) a significant loss of carbon, and metal contents, and (ii) a massive reconstruction of the carbon content catalyzed by the respective metal atoms. First, we varied the amount of Co precursor in the reaction mixture (8 mg, 40 mg, 200 mg to 400 mg) during the synthesis at 700 [°]C and the samples were labelled as Co_x-N-C-700, where x=0.4, 1.4, 5.6, 12 represents the experimentally estimated Co content in the sample. The XRD patterns (**Figure 3.2.3a**) of the samples prepared with 8 mg (Co to C ratio ~ 1: 200) and 40 mg (Co to C ratio ~1: 40) of Co-precursors showed no discernible changes from that of the N-C sample prepared at the same T. However, when the Co-precursor of 200 mg (Co to C ratio ~ 1: 8) and 400 mg (Co to C ratio ~1: 4) were used, new diffraction peaks appeared at $2\theta = 44.2^{\circ}$, 51.4° and 75.8° that correspond to (111), (200) and (220) planes of metallic cobalt (JCPDS # 15-0806). The Co diffraction peaks intensity increases from Co_{5.6}-N-C-700 to Co₁₂- N-C-700 due to higher Co loading.



Figure 3.2.2 XRD pattern of $Co_{1.4}$ -N-C-700. Two broad peaks located at 24.8° and 43.1° correspond to (002) and (101) planes of graphitic carbon, respectively.

Past investigations have established that the catalytic activities of M_x -N-Cs are greatly influenced by the pyrolysis T due to the incorporation of different quantities of N and M.⁴⁹ Therefore, we further synthesized one of the Co_x-N-Cs (where the Co to C precursor ratio ~1: 40) at different T (600-900 °C) to check its effect on the metal-load. The sample prepared at 600 and 700 °C did not show any changes in the XRD pattern (**Figure 3.2.3b**), while the samples prepared at 800 and 900 °C contained Co NPs as indicated by the diffraction peak at 2 θ = 44.2° and confirmed by TEM (**Figure 3.2.4**). Additionally, the presence of Co NPs was confirmed from TEM images of the samples with a high Co load (**Figure 3.2.5**). The lattice fringes with a spacing of 0.204 nm in the HRTEM images match the (111) planes of cobalt. Thus, we confirm that for optimal Co loading at 700 °C maintaining atomic dispersion, the Co to C ratio should be between 0.025 to 0.125.

3.2.4.3 Anomalous loss of Carbon and metal mass: We observed that a fraction of carbon from the precursor was lost during the high-T treatment that, rather interestingly, seems to be influenced by the inserted metal atoms. It was first confirmed that melamine does not contribute significantly to the carbon mass as it evaporates completely at 600 °C or above.⁵⁰ As shown in **Figure 3.2.6a**, at 700 °C, the mass loss during N insertion in the absence of Co (N-C-700) is only 5.5%. The loss, however, increases to 7.68% in the presence of Co in Co_{1.4}-N-C-700. Overall, in the presence of Co, the mass loss increases monotonously with T i. e. it is only 4.91% at 600 °C but becomes 7.68%, 10.24%, and 12.07% at 700 °C, 800 °C, and 900 °C respectively.



Figure 3.2.3 (a) XRD patterns of the various Co_x -N-C-700 samples with different Co contents. (b) Effect of temperature on metal load in Co_x -N-C samples prepared with the same precursor concentrations.



Figure 3.2.4 (*a*, *b*) Low magnification TEM images and (*c*) HRTEM image of $Co_{1.6}$ -N-C-900. Lattice fringes corresponding to Co nanoparticles were observed when pyrolysis temperature was maintained at 900 °C.



Figure 3.2.5 TEM and HRTEM images of $(a-c) Co_{0.4}$ -N-C-700, $(d-f) Co_{5.6}$ -N-C-700, and $(g-i) Co_{12}$ -N-C-700. Lattice fringes with d-spacing corresponding to Co nanoparticles were observed with increase in the metal precursor load in the reaction mixture, as seen in (f) and (i).

Besides, we observed a more significant loss of metal content in the finally obtained samples compared to the intended metal load, which is dependent on both (i) the process T and (ii) the metal precursor load. The ratios of the obtained *vs*. the expected metal loads at different T are plotted in **Figure 3.2.6a** showing that the metal retention is only ~48% at 600 °C, but increases to 57%, 62%, and 66% at 700 °C, 800 °C, and 900 °C respectively. The loss of >50% metal content at 600 °C (in midst of some loss of carbon too) indicates that the metals escape the samples either in the form of metal clusters or as metal carbide vapor (since the metal salts

need a much higher T to evaporate).⁵¹ On the other hand, the metal content retained in carbon hastily decreases as compared to the expected load with the increase in the amount of metal precursor up to Co-precursor load of 200 mg (Co to C ratio ~ 1: 8, **Figure 3.2.6b**). At 700 °C, Co retention is 80%, 57% and 49% when the Co to C ratio is 1:200, 1:40 and 1:8 respectively. The retention increases thereafter when the Co to C ratio is \sim 1:4 due to the formation of Co NPs that cannot easily evaporate.



Figure 3.2.6 (a) Temperature dependence on anomalous metal loss and carbon loss in Co_x -N-C samples prepared using same precursor concentrations. (b) Variation in the estimated metal loading of metal in the final samples as a function of metal precursor concentration.

The enhanced carbon loss in the presence of Co and increasing loss of Co at higher Coprecursor loading indicates a strong metal-carbon interaction which is believed to be critical to attaining high metal load in such samples that can significantly alter the electrocatalytic activities.⁵² As we will discuss later during surface analysis, the mass-losses are also accompanied by a noticeable change in the compositions of carbon (such as $sp^2 vs. sp^3 C$, etc.) and N in the samples. Thus, we suggest that the carbon mass interacts with the metal to undergo reconstruction, and this leads to a loss of both carbon and metal from the sample, which we believe has not been noticed so far.

3.2.4.4 Synthesis of other M-N-C (M= Fe & Ni): Fe-N-C and Ni-N-C were also prepared by the same synthesis approach at 700 °C using 40 mg of either Fe-precursor or Ni-precursor and 400 mg of C. This led to the insertion of the metal atoms and N in carbon, albeit in different amounts than in Co-N-C to further support our hypothesis that the nature of the metal atoms is instrumental in deciding the quantity of the metal and N inserted in the sample as well as in the reconstruction of the carbon network. First, the metal contents are quantified to be 2.6 wt.%

(expected 1.96 wt.%) and 2.5 wt.% (expected 2.43 wt.%) for Fe-N-C and Ni-N-C respectively as compared to 1.4 wt.% (expected 2.43 wt.%) for Co-N-C (**Figure 3.2.7a**).



Figure 3.2.7 (*a*) *Variations in the estimated (vs. intended) loading of metal contents in Fe*_{2.6-}*N-C-700, Co*_{1.4}*-N-C-700 & Ni*_{2.5}*-N-C-700. (b) the XRD patterns of Co*_{1.4}*-N-C-700, Fe*_{2.6}*-N-C-700 & Ni*_{2.5}*-N-C-700.*

Second, the XRD pattern of the Fe_{2.6}-N-C-700 sample is similar to Co_{1.4}-N-C-700 but different for Ni_{2.5}-N-C-700 (Figure 3.2.7b). TEM images of Fe_{2.6}-N-C-700 do not show the formation of iron NPs while the EDS mapping confirms the uniform distribution of Fe, C, N in the sample (Figure 3.2.8a, 3.2.8b). However, the XRD pattern of Ni_{2.5}-N-C-700, despite having a similar metal load, shows sharp peaks at 44.4°, 51.8°, and 76.4° corresponding to the (111), (200), and (220) planes of nickel (JCPDS #04-0850). TEM and EDS mapping analysis confirmed the presence of nickel NPs on carbon (Figure 3.2.9). Third, Raman spectra of Co_{1.4}-N-C-700, Fe_{2.6}-N-C-700, and Ni_{2.5}-N-C-700 exhibit two peaks at 1348 cm⁻¹ and 1590 cm⁻¹. assigned as the D and G bands of carbon respectively (Figure 3.2.10a). The G band is related to graphitic carbon (sp^2) while the D band is associated with the disordered carbon (sp^3) , and the ratio of their intensities (I_D/I_G) was used as an indicator of ordering in carbon. The quantity of disordered domains influences the conductivity of the carbon as well as the number of active sites for oxygen electrolysis.⁵³ The Co-sample showed a relatively higher I_D/I_G value of 0.99 in comparison to the Fe-sample (0.95) and the Ni-sample (0.96) respectively, potentially beneficial for enhanced electrocatalytic activity. Fourth, the surface areas of the different samples were estimated using Brunauer-Emmett-Teller (BET) method (Figure 3.2.10b & **3.2.11**). Co_{1.4}-N-C-700 has a higher surface area of 230 m²/g than that of Fe_{2.6}-N-C-700 (160 m^2/g) and Ni_{2.5}-N-C-700 (215 m^2/g). N-C-700 has a lower surface area of 170 m^2/g only, clearly exemplifying the pivotal role of the metal in carbon reconstruction.



Figure 3.2.8a (*a-c*) *TEM images of* $Fe_{2.6}$ -*N-C-700 at various magnifications.* (*d-h*) A *STEM image and the corresponding EDS elemental mapping images (same scale bar in all = 30 nm).*



Fig. 3.2.8b (a, b) HAADF-STEM images of Fe_{2.6}-N-C-700 showing the absence of metal nanocrystals.



Figure 3.2.9 (*a-b*) *TEM* images of Ni_{2.5}-N-C-700. (*c*) High resolution *TEM* image which shows the presence of nickel nanoparticles on carbon network. (*d*) HAADF-STEM image with corresponding EDS mapping images of Ni_{2.5}-N-C-700.

Finally, detailed X-ray photoelectron spectroscopy (XPS) analysis was conducted to determine the influence of metals on the chemical nature of each element in the different samples. The XPS survey spectra of the M-N-C-700 samples showed the presence of C, N, O, M (= Fe, Co, Ni) only and no other impurities. **Figure 3.2.12a** shows the high-resolution XPS spectrum of C 1s orbital of Co_{1.4}-N-C-700, Fe_{2.6}-N-C-700, Ni_{2.5}-N-C-700, and N-C-700. The deconvolution of the C1s spectrum of Co_{1.4}-N-C-700 shows a prominent peak around 284.4 eV corresponding to sp^2 C. The other two peaks at 285.9 and 287.3 eV are attributed to sp^3 C and C=N respectively.^{23,26,54} The contents of the sp^2 C, sp^3 C and C from C=N are 86.84%, 10.65% and 2.49% respectively. Interestingly, in C 1s spectra of Fe_{2.6}-N-C-700 and Ni_{2.5}-N-C-700, an additional peak appears at a binding energy of 289.0 eV corresponding to O-C=O (**Figure 3.2.12a**).⁵⁴ Besides, unexpectedly, the ratio of the various types of C atoms exhibited a marked change in the samples with different metals (**Figure 3.2.12b**). The Co sample has the highest sp^2 C and the lowest sp^3 C content while the same are the lowest and the highest (80.86% and

12.75%) respectively in the Fe-sample. The O-C=O groups are in higher abundance in the Fe sample (2.85%) than in the Ni sample (1.35%), which is absent in the Co-sample.



Figure 3.2.10 (a) Raman spectra, and (b) BET surface area estimated from N₂ adsorptiondesorption isotherms of Co_{1.4}-N-C-700, Fe_{2.6}-N-C-700 & Ni_{2.5}-N-C-700.

We correlated the O-C=O and mass loss to find that the higher C losses in the Fe and the Ni samples are accompanied by the appearance of the O-C=O peak in the XPS spectra. Therefore, we postulate that the C loss is contributed by its oxidation, catalyzed by the inserted metal atoms, and induced by the trace O_2 present in Ar used during the synthesis, and some of the residual O-C=O groups remain attached to the sample. However, such oxidation is less in the Co-inserted and N-C-700 samples where the O-C=O peak is not observable, leading to a lower C loss.

Additionally, the catalytic reconstruction was also confirmed from the XPS analysis of the N in the samples, which vary in the 0.6-1.0% range in the different samples. **Figure 3.2.12c** shows the deconvolution of the N-1s spectrum of Co_{1.4}-N-C-700. The presence of four different components at 398.4 eV, 400.3 eV, 401.1 eV and 402.5 eV were observed corresponding to pyridinic-N (46.98%), pyrrolic-N (28.87%), graphitic-N (4.06%) and oxidized–N (11.45%) respectively. An additional peak at 399.2 eV is attributed to the Co-N_x species (8.61%).^{54,55}

The corresponding ratios of the various N species in all the samples are summarized in **Figure 3.2.12d** to show that the abundance of the pyridinic-N remains nearly the same in all. However, the pyrrolic-N and graphitic-N contents significantly redistribute. The pyrrolic fraction is minimum in the Fe-sample (24.20%) and maximum in the Ni sample (34.33%), but still lesser than in the N-C-700 (39.95%). Graphitic-N is maximum in the Fe-sample (15.43%) and minimum in the Ni-sample. The metal-bound N (M-N_x) is highly abundant in the Ni sample (10.18%) and least in the Fe-sample (7.5%).



Figure 3.2.11 (*a-d*) N_2 adsorption isotherms of N-C-700, $Co_{1.4}$ -N-C-700, $Fe_{2.6}$ -N-C-700 and $Ni_{2.5}$ -N-C-700 respectively

The analysis of the C and N XPS signals shows that the various C and N components in the samples are quite different, but either higher or lower than that in the N-C-700 sample. This, in conjunction with the Raman spectral analysis, surface area analysis, and anomalous mass loss observations, is a definitive indication of a fascinating reconstruction of the carbon framework in these samples catalyzed by the metal atoms, which we believe have remained unnoticed so far. In addition, since N-content is ~1% of carbon *i.e.* the metal-bound N is barely 0.1%, while the metal% in M-Nx configuration is in the range of 0.2-0.5 in each sample, a large fraction of the metal-atoms ought to be surrounded by to carbon atoms only, rather than forming the M-N_x moieties.



Figure 3.2.12 (a) High-resolution C1s XPS spectra of N-C-700, $Fe_{2.6}$ -N-C-700, $Co_{1.4}$ -N-C-700 and $Ni_{2.5}$ -N-C-700; insets show the magnified region in particular range for all samples. (b) Relative abundance of various carbon species in different samples estimated from C1s XPS spectra. (c) High-resolution N1s XPS spectrum of $Co_{1.4}$ -N-C-700. (d) Abundance of various nitrogen species in the samples observed from the respective XPS spectra. (e) High-resolution Co-2p XPS spectrum of $Co_{1.4}$ -N-C-700.

Figure 3.2.12e shows the Co-2p spectrum for Co_{1.4}-N-C-700. Its deconvolution contains two peaks at 780.5 eV (for Co $2p_{3/2}$) and 795.7 eV (for Co $2p_{1/2}$) which are at higher binding energy than the same for metallic Co²³ (which appear at 779.2 and 794.7 eV) suggesting charge-transfer from Co to carbon.^{54,56,57} The two other peaks at 787.6 and 802.5 eV are shake-up satellite peaks of Co $2p_{3/2}$ and Co $2p_{1/2}$ respectively. The peak at 780.3 eV corresponds to the Co-N_x component with ~12% abundance. This accounts for, per mole of C, 0.025 moles of Co attached to 0.10 moles of N (from N XPS peak deconvolution) conforming to ~Co-N_x configuration.

3.2.4.5 *Bifunctional Electrocatalytic Activities of the various M-N-Cs:* The electrochemical measurements were performed on a rotating disk electrode in 0.1 M KOH solution. The evaluation of the ORR and OER activities of the different samples showed that the Co insertion leads to the best overall bifunctional activity. However, the different metals demonstrated trends in the ORR and OER activities that are quite independent of each other.



Figure 3.2.13 (a) Linear sweep voltammetry (LSV) curves of various Co_x -N-C-700 recorded at a rotation rate of 1600 rpm in O_2 saturated 0.1 M KOH. (b) Comparison of I_k (at 0.8 V vs. RHE) and $E_{1/2}$ of the various Co_x -N-C-700 samples. (c) Effect of sample preparation temperature on the $E_{1/2}$ and I_k at 0.8 V vs. RHE for Co_x -N-C samples obtained using the same precursor concentrations.

Figure 3.2.13a shows the ORR polarization curves for the Co_x-N-C-700 (x= 0.4 1.4, 5.6, and 12) samples recorded under O₂ saturation at a scan rate of 10 mV/s. It can be observed that while Co insertion improved the ORR properties significantly as compared to the Co-free sample, the onset potential of Co_{1.4}-N-C-700 is more positive than the other Co_x-N-C-700 samples. Furthermore, the ORR currents were compared in the intermittent potential range from the half-wave potential (E_{1/2}) values. The E_{1/2} values (**Figure 3.2.13b**) follow the order Co_{1.4}-N-C-700 (0.855 V) > Co₁₂-N-C-700 (0.844 V) > Co_{5.6}-N-C-700 (0.845 V) > Co_{0.4}-N-C-700 (0.829 V). The lower E_{1/2} value of Co_{0.4}-N-C-700 than Co_{1.4}-N-C-700 is attributed to a much lower density of cobalt sites. The E_{1/2} value improves with increasing the Co loading on NC to 1.4 wt.% but deteriorates with a further increase to 5.6 and 12 wt.% due to the formation of cobalt NPs, suggesting that the NPs block the active Co-N₄ sites.⁵⁸ Notably, the higher metal load might have changed the carbon framework to a larger extent as well. The kinetic currents

(I_{kinetic}) for the different samples are plotted in **Figure 3.2.13b**, showing that Co_{1.4}-N-C-700 has the highest I_{kinetic} value. The effect of heat treatment temperature on ORR activities of the Co_x-N-C catalysts was also investigated (**Figure 3.2.13c**, **Figure 3.2.14a**) to find that the Co_{1.4}-NC-700 sample outperforms the other samples prepared at 600, 800, 900 °C. The not so obvious trends in the kinetic current values and performances of the samples prepared at different T indicate that not only the metal load, but the reconstruction of the carbon network that can alter the oxygen diffusion near the active sites have a significant role in affecting the overall ORR kinetics.⁵⁹



Figure 3.2.14 (a) ORR LSV curves of Co_x-N-C samples prepared at different temperatures using the same precursor concentrations, recorded in O₂ saturated 0.1 M KOH solution with a rotation rate of 1600 rpm. (b) ORR polarization curves of N-C-700, Fe_{2.6}-N-C-700, Co_{1.4}-N-C-700, Ni_{2.5}-N-C-700 and Pt/C in 0.1 M KOH solution.

We have further compared the ORR performance of Co_{1.4}-N-C-700 with that of N-C-700, Fe_{2.6}-N-C-700, Ni_{2.5}-N-C-700, and commercial Pt/C (**Figure 3.2.14b**). Co_{1.4}-N-C-700's onset potential of 0.99 V and E_{1/2} of 0.855 V *vs*. RHE is significantly superior to commercial Pt/C (onset-1.02 V, E_{1/2}-0.869 V), Fe_{2.6}-N-C-700 (onset-0.97 V, E_{1/2}-0.82 V), and Ni_{2.5}-N-C-700 (onset-0.94 V, E_{1/2}-0.78 V). The Co_{1.4}-N-C-700 also demonstrated a better limiting current density (-5.3 mA/cm²) than that of commercial Pt/C (-4.8 mA/cm²). The superior performance of Co_{1.4}-N-C-700 indicates the presence of highly active atomically dispersed cobalt atoms on

carbon. The number of electrons (n) transferred during ORR was estimated using Koutecky– Levich (K-L) equation (**Figure 3.2.15**). The average n for Co_{1.4}-N-C-700 is 3.9 confirming the desired four-electron ORR pathway. The n values were also calculated for other materials under identical conditions (**Figure 3.2.16**) as 4.0, 3.85, and 3.01 for commercial Pt/C, Fe_{2.6}-N-C-700, Ni_{2.5}-N-C-700 respectively. Due to variations in the *n* values, we further estimated the H₂O₂ production at different potentials. As seen in **Figure 3.2.17a**, Co_{1.4}-N-C-700 has extremely high ORR catalytic efficiency with only 10-15% H₂O₂ production in the 0.2 to 0.8 V range as compared to the other samples. The electron transfer property of these samples was characterized by electrochemical impedance spectroscopy⁶⁰ (EIS, **Figure 3.2.17b**). The plots show a well-defined semicircle in the high frequency region followed by a straight line in the low frequency region. The data can be fitted into an equivalent circuit consisting of solution resistance (R_s), charge transfer resistance (R_{ct}), constant phase element (CPE), Warburg impedance (W) and double layer capacitance (Cdl), comparable to other carbon based electrocatalysts^{61,62}, shown in **Figure 3.2.18**. The result demonstrates that Co_{1.4}-N-C-700 exhibits the lowest charge transfer resistance, attributed to the highest *sp*² carbon content.



Figure 3.2.15 (a) ORR LSV curves of $Co_{1.4}$ -N-C-700 at various rotation rates in O_2 saturated 0.1 M KOH solution at a scan rate of 10 mV/s, and (b) corresponding K-L plots at different potentials (vs. RHE).



Figure 3.2.16 ORR LSV curves at various rotation rates in O₂ saturated 0.1 M KOH solution and the corresponding K-L plots of Pt/C, Fe_{2.6}-N-C-700 and Ni_{2.5}-N-C-700 respectively.



Figure 3.2.17 (a) the H_2O_2 yield of different samples in the 0.2-0.8 V range (vs. RHE). (b) Nyquist plots of the samples in 0.1 M KOH.



Figure 3.2.18 The equivalent circuit used for fitting the experimental impedance measurement data for the Nyquist plot. The circuit consists of solution resistance (R_s), charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}), constant phase element (CPE) relating to the non-ideal characteristics of the double layer, and W indicates the Warburg impedance.

The durability of $Co_{1.4}$ -N-C-700 was tested by performing chronoamperometry measurement in O_2 saturated 0.1 M KOH solution, (**Figure 3.2.19a**) and found to exhibit high stability by retaining 65% of its initial activity even after 72000 s. The current loss was more rapid in the beginning, reaching 75% of the initial value within 20000 s. However, in the case

of commercial Pt/C, 50% of current loss occurs after only 36000s. The resistance to methanol crossover was tested by injecting methanol into the electrolyte (final concentration = 1 M) after 100 s of the measurements. This led to a slight change in the ORR current of $Co_{1.4}$ -N-C-700, but a sharp drop in the case of commercial Pt/C (**Figure 3.2.19b**).



Figure 3.2.19 (a) Chronoamperometric responses and (b) methanol tolerance test for $Co_{1.4}$ -N-C-700 and Pt/C (arrows indicates the injection of 3.25 ml of methanol).

In addition to ORR test, we have evaluated the OER activities of the materials in the same electrolyte solution to assess the overall oxygen redox behaviour. **Figure 3.2.20a** shows the iR-corrected linear sweep voltammogram (LSV) of Co_x -N-C-700 (x= 0.4, 1.4, 5.6, 12) at a scan rate of 10 mV/s. $Co_{1.4}$ -N-C-700 shows a smaller onset potential (1.55 V) and a higher current density (54 mA/cm²) compared to the other Co_x -N-C. Activities of the catalysts towards OER were evaluated by comparing the overpotential (η) required to achieve a current density of 10 mA/cm². The η of $Co_{1.4}$ -N-C-700 (420 mV) was much lower than that of $Co_{0.4}$ -N-C-700 (470 mV), Co_{12} -N-C-700 (480 mV), and $Co_{5.6}$ -N-C-700 (520 mV). The OER kinetics was revealed by Tafel plots,¹³ (**Figure 3.2.20b**) in which $Co_{1.4}$ -N-C-700 possesses a much lower temperatures (**Figure 3.2.21**).



Figure 3.2.20 (a) OER polarization curves of the various Co_x -N-C-700 samples prepared by using different amounts of cobalt precursors in 0.1 M KOH solution recorded at rotation speed of 1600 rpm compared with N-C-700 and (b) the corresponding Tafel plots.



Figure 3.2.21 OER LSV curves of various Co_x -*N*-*C*-700 *prepared at different temperatures* (600, 700, 800 & 900 °C) using the same precursor concentrations, and (b) the corresponding Tafel plots.

We have then compared the OER activity Co_{1.4}-N-C-700 with Fe_{2.6}-N-C-700, Ni_{2.5}-N-C-700, N-C-700, and commercial IrO₂ under similar reaction conditions. The Ni_{2.5}-N-C-700 exhibited a slightly better OER activity with lower overpotential (390 mV) and Tafel slope (71 mV/dec) as compared to Co_{1.4}-N-C-700. On the other hand, both these samples demonstrated much higher OER activities and faster OER kinetics (**Figure 3.2.22a, b**) than IrO₂ ($\eta = 480$ mV, Tafel slope = 112 mV/dec) and Fe_{2.6}-N-C ($\eta = 500$ mV, Tafel slope = 93 mV/dec). The high OER activity of Ni_{2.5}-N-C-700 is attributed to the presence of nickel NPs on the surface of carbon,^{63,64} even though the same NPs may not be useful for ORR, as discussed in the previous section.



Figure 3.2.22 (a) OER LSV curves of $Fe_{2.6}$ -N-C-700, $Co_{1.4}$ -N-C-700, $Ni_{2.5}$ -N-C-700 and commercial IrO_2 in 0.1 M KOH solution and (b) the corresponding Tafel plots.

Overall bifunctional oxygen electrocatalytic performance of the catalysts was evaluated from the ORR E_{1/2}, OER E_{10 mA/cm}², and the potential difference ($\Delta E = E_{10mA/cm}^2$, OER - E_{1/2,ORR}) values of oxygen electrode activity parameters (**Figure 3.2.23a, b**). While the best ORR and OER performances were observed in the Co and Ni samples respectively, Co_{1.4}-N-C-700 exhibited the least ΔE of 0.795 V which is much smaller than Fe_{2.6}-N-C-700 (0.910 V) and Ni_{2.5}-N-C-700 (0.840). The ΔE of Co_{1.4}-N-C-700 surpasses many other recently reported bifunctional catalysts such as Co@Co₃O₄/NC (0.85V), Fe/Ni-N-CNFs (0.81V), B, N dual – doped porous carbon (1.06V) as shown in **Table 3.2.2**, suggesting that Co-N-C catalyst can be served as a highly efficient electrocatalyst in rechargeable metal-air batteries or alkaline fuel cells.



Figure 3.2.23 (a) Overall oxygen activity, ΔE (= $E_{10mA/cm}$, $_{OER}$ - $E_{1/2, ORR}$) comparison of $Co_{1.4}$ -N-C-700 with Fe_{2.6}-N-C-700 and Ni_{2.5}-N-C-700 within the ORR and OER potential window in O₂ saturated 0.1 M KOH solution. (b) Comparison of half-wave potential, OER overpotential and ΔE values of Co_{1.4}-N-C-700, Fe_{2.6}-N-C-700 and Ni_{2.5}-N-C-700.

S.No.	Electrocatalysts	ORR E1/2 (V vs. RHE)	OER E10 mA/cm ² (V vs. RHE)	ΔE (Eoer - Eorr) (V vs. RHE)	Reference
1.	Co1.4-N-C-700	0.855	1.65	0.795	This work
2.	Ni _{2.5} -N-C-700	0.780	1.62	0.840	This work
3.	Fe _{2.6} -N-C-700	0.820	1.73	0.910	This work
4.	CoSAs-NGST	0.89	1.79	0.9	65
5.	Co-POC	0.83	1.70	0.87	66
6.	Fe-NC SAC	0.88	1.68	0.8	67
7.	Fe-N/P-C	0.867	1.66	0.793	23
8.	Co-N,B-CSs	0.83	1.66	0.83	68
9.	Co-N _x -C	0.79	1.74	0.95	69
10.	Fe-N _x -PNC	0.86	1.64	0.78	70
11.	Co-N-PDEB	0.82	1.90	1.08	71
12.	CoNi-SAs/NC	0.76	1.57	0.81	72
13.	Fe-NSDC	0.84	1.64	0.8	73
14.	Co-Co ₃ O ₄ @NAC	0.795	1.61	0.815	74
15.	NdC-CoNP-NdC	0.80	1.63	0.83	75
16.	CoNPC-71	0.81	1.63	0.82	76

Table 3.2.2 Comparison of the ORR/OER activities of $Co_{1.4}$ -N-C-700 with recent reported data.

17.	Co-N/PC@CNT-700	0.77	1.63	0.86	77
18.	Ni-BTB-BPE/C	0.74	1.64	0.9	78
19.	Co-N-PCN	0.82	1.63	0.81	79
20.	N-Co ₉ S ₈ /G	0.77	1.64	0.88	80
21.	NiCo@NC	0.76	1.78	1.02	81
22.	Fe@N-C	0.83	1.71	0.88	82
23.	Co@NC-3	0.904	1.72	0.816	83
24.	CoO/Co@N–C	0.850	1.672	0.822	18
25.	Fe/N-CNT	0.81	1.75	0.94	84
26.	Co ₃ Fe ₇ -PCNF-850	0.85	1.61	0.80	85
27.	FeCo-CNT	0.87	1.72	0.85	86
28.	Fe/Fe-N-C	0.88	1.80	0.92	87
29.	Fe ₃ C@FeN@CNF- 900	0.84	1.67	0.83	88
30.	Fe-NCNTs/NG	0.871	1.865	0.994	89
31.	Ni _{0.25} Cu _{0.75} -C	0.80	1.63	0.83	90
32.	Co ₂ FeO ₄ -NCNTs	0.8	1.65	0.85	91
33.	CoFe-N-GCT	0.79	1.67	0.88	92
34.	Co ₂ Fe ₁ @NC	0.85	1.65	0.80	93
35.	Co-SAs@ NC	0.82	1.8	0.98	94

3.2.5 CONCLUSIONS

In summary, we present for the first time an enticing one-step approach to implant atomically dispersed transition metals and N into commercial nanostructured carbon and impart superior bifunctional electrocatalytic behaviour towards ORR and OER. Besides offering significantly easier scale-up production prospects for M-N-Cs than the state-of-the-art approaches due to affordability of the precursors, the process has several other advantages including being a generic approach for the insertion of diverse metals, a ridiculously simple handle to control the metal to carbon ratio that enables the metals to retain an atomic dispersion rather than forming clusters or nanoparticles and in doing so, makes it possible to avoid the acid-mediated nanoparticle leaching step which is industry-unfriendly but pertinent to most other existing approaches. A detailed analysis of the process sets the boundaries for singlemetal insertion vs. cluster formation and lays out a roadmap to overcome further challenges that we show to be very specific to the transition metal in consideration. This is also the first account of the observation that M-N-C formation is accompanied by a negative mass-balance, originating from carbon and significant metal loss, and a massive reconstruction of carbon backbone catalyzed to a different extent by different metals. Finally, only a fraction of the atomically dispersed metals reside in the vicinity of N, and yet remarkably improve catalytic behaviour. Therefore, by improving M-N_x content, or by increasing the metal load while maintaining an atomic dispersion and by converting carbon reconstruction into an advantage (of generating a superior carbon backbone)⁴³ can lead to even higher bifunctional efficiency in commercial carbon while keeping affordability of mass-production in mind.

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CHAPTER 3.3

Conclusions and future prospects

Conclusions

Electrocatalysis stands as a pivotal technology in the seamless integration of renewable energy sources into grid. This process involves the acceleration of electrochemical reactions, crucial for the efficient conversion and storage of energy. The key to bringing fuel cell and energy storage battery technology into the commercial sphere lies in the creation of materials that are economically viable, highly efficient, and durable. However, Widespread adoption of electrocatalytic systems faces a bottleneck due to heavy reliance on toxic and costly metals like Palladium (Pd) and Platinum (Pt). Despite their effectiveness, these metals pose economic and environmental challenges due to scarcity and toxicity, inflating production expenses and hindering scalability for large renewable energy projects. To overcome this, there's an urgent need for electrocatalysts with more abundant elements. Embracing such materials can reduce economic and environmental burdens associated with precious metal mining and refining. Elements like iron, nickel, and cobalt show great potential for sustainable energy applications. M-N-C catalysts hold promise in achieving performance comparable or even superior to noble metal counterparts. Unlocking the potential of earth-abundant elements in electrocatalysis paves the way for a more accessible, cost-effective, and environmentally sustainable renewable energy landscape, advancing efforts towards a greener future. Considering the potential of significant efficiency of M-N-Cs the first part of this thesis is focused on bringing sustainability in scalable M-N-C synthesis. The key findings of this part of this thesis are discussed below.

Chapter 3.1 depicts the evolution of M-N-C-based electrocatalysts representing a significant stride towards harnessing the potential of earth-abundant elements for sustainable energy solutions. M-N-Cs, comprised of first-row transition metals (M), nitrogen (N), and carbon (C), have emerged as promising alternatives to noble metal catalysts. The electrocatalytic activity of M-N-Cs stems from their unique electronic structure and the synergistic interactions between metal centers and adjacent nitrogen-doped carbon supports. This configuration facilitates the rapid charge transfer processes essential for efficient electrochemical reactions. However, the current synthetic protocols for high-performing M-N-Cs are intricate and heavily dependent on metal-organic frameworks (MOFs) and covalent

organic frameworks (COFs) as precursors. The synthesis of MOFs and COFs, though integral to this process, presents its own set of challenges. These precursor materials often involve complex and multistep procedures, which not only increase the overall synthetic complexity but also hinder scalability. Moreover, the production of MOFs and COFs can be resource-intensive, and their precise control during synthesis can be troublesome. Consequently, the reliance on these frameworks poses a significant obstacle in achieving widespread application of M-N-Cs in electrocatalytic systems. Finally, in this chapter a research scope is established to streamline and optimize the synthetic methodologies, with the aim of developing more efficient and scalable routes to M-N-C-based electrocatalysts, ultimately advancing the transition towards sustainable and accessible energy solutions.

Chapter 3.2 demonstrates a facile way to achieve an efficient M-N-C towards electrocatalytic ORR and OER using cheap carbon and nitrogen precursor (Vulcan carbon and melamine respectively), and commercially viable cobalt salt. This process not only offers a more cost-effective precursor, making scaled-up production of M-N-Cs much more feasible compared to current state-of-the-art techniques, but it also boasts additional benefits. It serves as a versatile approach for incorporating various metals, provides a straightforward means to regulate the metal-to-carbon ratio, ensuring metals remain dispersed at an atomic level rather than forming clusters or nanoparticles. Consequently, it eliminates the need for the acidmediated nanoparticle leaching step, a process often incompatible with industry practices but prevalent in other existing methodologies. Furthermore, a comprehensive analysis of the procedure delineates the boundary between single-metal integration and cluster formation, outlining a pathway to address specific challenges associated with the particular transition metal under consideration. Our study reveals a previously undocumented phenomenon: the formation of M-N-C leads to a negative mass balance, originating from carbon and substantial metal loss, accompanied by a significant restructuring of the carbon framework catalyzed to varying degrees by different metals. Surprisingly, only a fraction of the atomically dispersed metals is found in close proximity to nitrogen, yet they remarkably enhance catalytic performance. Hence, enhancing the M-N_x content or increasing the metal loading while maintaining atomic dispersion, coupled with leveraging carbon restructuring to create a superior backbone, holds the potential for even greater bifunctional efficiency in commercial carbon, all while considering cost-effective mass production.

Future prospects

The urgent need for sustainable energy solutions in the face of environmental challenges has led to a surge in research focused on electrocatalysis. Among the promising materials, earth-abundant elements-based M-N-C electrocatalysts have emerged as a frontrunner due to their cost-effectiveness and potential to replace precious metal-based catalysts. However, for these catalysts to play a pivotal role in future energy systems, it is crucial to address their durability issues and further enhance their electrocatalytic efficiency. The potential of bimetallic compositions, dual-atom sites, and atomic-scale alloying as strategies are crucial to explore to augment the performance and stability of M-N-C electrocatalysts.

Bimetallic electrocatalysts offer a promising avenue for enhancing the durability of M-N-C catalysts. By combining two different metals, synergistic effects can be harnessed, leading to improved stability and catalytic performance. For instance, a combination of iron (Fe) and cobalt (Co) has shown remarkable promise in enhancing the oxygen reduction reaction (ORR) activity of M-N-C catalysts, while also promising to resist the metal dissolution and corrosion.^{1,2} The controlled integration of these metals at the atomic level allows for the precise tuning of catalytic properties, resulting in a more robust and long-lasting electrocatalyst.

The manipulation of electronic structure plays a pivotal role in dictating the catalytic activity of M-N-C electrocatalysts. Dual-atom sites, characterized by the presence of two different metal atoms within close proximity, provide an avenue for fine-tuning the electronic structure of the catalyst. This leads to an optimized adsorption and desorption process, crucial for enhancing the efficiency of the electrocatalytic reactions.³ This strategy not only boosts the activity but also ensures the stability of the catalyst under harsh operating conditions.

Atomic-scale alloying offers a powerful tool to further enhance the electrocatalytic efficiency of M-N-C catalysts. By precisely controlling the composition and arrangement of metal atoms, it is possible to create alloys with tailored electronic properties. For example, the incorporation of transition metals like manganese (Mn) into the catalyst structure can lead to the formation of active sites with unique electronic configurations, thus boosting the catalytic performance.^{4,5} Moreover, atomic-scale alloying can help overcome challenges related to metal dissolution and leaching, ensuring the long-term stability of the catalyst.

The future of sustainable energy systems hinges on the development of efficient and durable electrocatalysts. Earth-abundant elements-based M-N-C electrocatalysts have shown

immense promise in this regard. Through strategic approaches such as bimetallic compositions, dual-atom sites, and atomic-scale alloying, researchers can significantly enhance the performance and stability of these catalysts. As we continue to unravel the intricate interplay of these strategies, we move closer to a future where renewable energy sources are harnessed with unprecedented efficiency, ushering in a new era of sustainable development.

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Chapter 4

Advancing durability of M-N-C based electrocatalysts by incorporating noble metal (Pd) at minimal metal-loading

CHAPTER 4.1

4.1 Prelude

Pd nanoparticles have gained significant attention in various fields, particularly in catalysis and electrocatalysis, as Pd nanoparticles are known for their durability and stability, especially in comparison to other noble metals like Pt.^{1–5} This makes them attractive candidates for long-term applications in electrocatalysis. Due to their remarkable electrocatalytic activity and stability, the utilization of Pd nanoparticles in processes like fuel cells and water electrolysis holds great potential for advancing clean energy technologies.^{6–8} Recent studies have revealed that by employing inventive design approaches, adjusting their surfaces through facet engineering or alloy creation, and fine-tuning the interactions between the substrate and catalyst, it is possible to enhance the electrocatalytic effectiveness of Pd-based catalysts in a systematic and substantial manner, bringing them on par with those of Pt.^{9–13}

4.2 Existing synthetic strategies for loading Pd Nanoparticles

Synthetic pathway often determines the catalytic efficiency of nanoparticles as the size, shape, and composition of the nanostructures dictate the catalytic efficiency of the nanomaterials.¹⁴ The significant enhancement in catalytic activity achieved by reducing the size of nanoparticles is primarily attributed to the increased available surface area.¹⁵ However, the inherent tendency of these nanoparticles to randomly clump together results in a reduction of their effective surface area, leading to a gradual decline in catalytic performance over time.^{16–18} In an effort to prevent nanoparticle agglomeration, researchers have explored the use of anchoring sites on the support material, where the nanoparticles graft to the support surface and thereby prevent coalescence.^{19,20} This approach generally suffers from several drawbacks, including the random attachment of nanoparticles, unintended binding to active sites, reduced material stability, and impaired selectivity due to hindered accessibility. Additionally, for achieving small size and tuning the shape of nanoparticles, many capping agents are often utilized to synthesize Pd nanoparticles.^{21–24} However, those capping agents hindered the diffusion of reactant molecules significantly, leading to sluggish reaction kinetics.²⁵ Therefore, it is very crucial to achieve a sustainable strategy for loading Pd nanoparticles on the support.

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CHAPTER 4.2

Origin and the invoking of photoactive Co-N₄ centers in Co-N-C for loss-less infusion of highly ORR active palladium in ambient conditions

Summary

The sluggish oxygen reduction reaction (ORR) kinetics remains a bottleneck in the utilization of palladium in alkaline fuel cells, which can potentially be improved by compositing with low-cost M-N-Cs. Realizing such Pd-electrocatalysts under mild conditions is an equally important challenge for industries. Herein, we introduce atomically dispersed Co-containing N-doped carbon (Co-N-C) as a catalyst-support for Pd with multiple benefits. Theory and experiments establish that the Co-N₄ moieties in the carbon-matrix act as semiconducting centers to generate excitons under sunlight, which are capable of reducing Pd-salts to deposit Pd nanoparticles (NPs) on Co-N-C at room temperature. The size of Pd-NPs is comparable to those used in commercial catalysts due to anchoring to the support, despite not using any capping agents, resulting in improved mass transfer on its surface. Importantly, we find that the Co atom mediates a superior charge transfer between the Pd-NPs and support, leading to a very high ORR efficiency (E_{1/2} of 0.915 V *vs*. RHE) and stability (8mV shift in E_{1/2} after 20,000 cycles) of Pd NPs photodeposited on Co-N-C. These findings should inspire the use of transition metal (M) based M-N-Cs as a new class of support for electrocatalysts with improved activities and also, their use in photocatalysis.

‡Manuscript based on this work is under revision.

4.2.1 Introduction

Alkaline fuel cells (AFCs) are promising as efficient energy conversion devices due to many advantages such as a less corrosive alkaline environment, reduced alcohol fuel-crossover effect, and also, the highly active nature of palladium as a catalyst.¹⁻¹² In contrast, Pt nanoparticles dispersed on carbon (Pt/C) are used in commercial proton exchange membrane fuel cells where the high cost of Pt, as well as high alcohol cross-over, limits their prospects.^{13–} ¹⁷ However, the overall efficiency of AFCs is hindered by several factors including the sluggish kinetics of oxygen reduction reaction (ORR) on the cathode.

Recent investigations have established that Pd-based nanomaterials can exhibit high ORR activities that can surpass the performance of benchmark catalysts in alkaline media by adopting various strategies such as facet engineering of its nanocrystals and surface modulation.^{8,18–20} In addition, the ORR activities can be majorly attuned by the suitable design of the catalyst-support because significant energy loss of the device occurs in the form of electrical resistance while the electrons move across the metal-support interface.^{21–23} That apart, metal–support interaction plays an important role in enhancing the efficiency of an active center by modulating its electronic charge density by means of the orbital rehybridization that can favourably alter the strength of ORR intermediate binding to the catalyst surface.^{24–26} Finally, supports also improve the electrochemical stability of metal nanoparticles against corrosion^{27,28} and prohibit agglomeration of metal nanoparticles due to superior heat dissipation from the metal-support interface²⁹. Therefore, choosing a support with commercial viability that induces a high conductivity across this interface can be deemed to be integral to a rational design of an electrocatalyst.

As another class of electrocatalyst, atomically dispersed non-precious first-row transition metals on nitrogen-doped carbon (M-N-Cs, M= Co, Fe, etc.) have attracted significant recent interest due to their high atom economy and increasingly improved activity in alkaline media.^{30–37} M-N-C can accelerate oxygen adsorption and its activation during ORR due to the presence of the M-N_x sites and is deemed a promising alternative to precious metal catalysts. However, the benefits of their inexpensive nature are diluted by a lower ORR efficiency in comparison to Pd.^{38–42} Another severe detriment, often neglected, is that even though M-N-Cs appear inexpensive, the highly active ones are usually obtained by pyrolysis and further (multi-step) processing of high-valued precursors such as metal-organic-

frameworks, where the pyrolysis yields can be extremely low, and demotivating for industrial scale utilization.⁴³

4.2.2 Scope of the present investigation

In such a scenario, it occurs that by combining M-N-Cs with Pd can be beneficial from the following considerations: (i) since, the activity of a catalytically active center is governed by the conductivity of the metal-support interface, introducing a metal atom such as those in M-N-Cs as a contact between a Pd nanoparticle (Pd NP) and carbon support should significantly reduce the metal-support contact resistance.²² (ii) Recently, we demonstrated the utilization of commercial electroactive C to produce efficient M-N-C electrocatalysts with many industry-relevant benefits,⁴³ and therefore, (iii) if we can develop a strategy to decorate these M-N-Cs with Pd NPs in a rational way to ensure intimate M-Pd interaction, at the same time taking care that the process is renewable energy based and with high Pd atom economy, the process will be high on merit for sustainability.

Herein, we investigate the electronic structure of the N₄ and Co-N₄ moieties in N-doped carbon (N-C) and Co-N-C respectively to establish that these centers act as semiconducting moieties engraved within a conducting carbon matrix that can absorb sunlight, albeit from different origins of electronic transitions. We then demonstrate, for the first time, the possibility of a benign, room-temperature Pd photodeposition process on N-C and Co-N-C. Importantly, we show that introducing a Co atom in the semiconducting N₄ photoactive center lowers the charge-transfer (CT) resistance between a Pd particle and N-C due to an in-built charge gradient between Co and N, and that the same can lead to efficient ORR activities in PdCo-NC exceeding that of commercial Pd and Pt catalysts. We present the photodeposition kinetics of Pd.

We also outline the potential drawbacks of the photodeposition process that one will need to work on. However, such a catalyst prepared by photodeposition of Pd NPs on atomically dispersed Co-N-C exhibits outstanding ORR activity with a $E_{1/2}$ of 0.915 V vs. RHE in alkaline electrolyte and durability with less than 8 mV shift in $E_{1/2}$ after 20,000 cycles. A key feature of this process is achieving sub-8-nm Pd NPs that are capping agent free. Usually capping agents or ligands are employed to control the growth of metal nanoparticles where the 'shell' of ligands around the 'core' NP can inhibit the rate of electron transfer and lowers the inherent activity of NPs.⁴⁴⁻⁴⁶ We believe that elucidation of the detailed nature of photoactive centers in M-N-Cs will inspire many new studies in sustainable post-modifications of M-N-Cs, besides exploration of M-N-Cs in photocatalysis, *etc*.

4.2.3 METHODS

4.2.3.1 Synthesis of Co-N-C

Atomically dispersed Co-N-C was synthesized by following our previous method.⁴³ Typically, stoichiometric quantities of melamine, cobalt chloride, and pre-treated Vulcan carbon were mixed by grinding. The resulting mixture was heated in a tube furnace at 350 °C for 20 min followed by 600 °C (1 h) and finally at 700 °C (2 h) under Ar atmosphere before cooling naturally to room temperature. The obtained sample is labelled as Co-N-C. The cobalt loading was estimated to be 1.4 wt.% from atomic absorption spectroscopy (AAS).

4.2.3.2. Synthesis of Co-N-C catalyst loaded with Pd NPs (via photodeposition)

Co-N-C was used as a substrate for the deposition of Pd NPs. Photodeposition was done by dispersing the as-synthesized Co-N-C powder in 100 ml of distilled water containing 400 μ l of methanol as a scavenger at room temperature. The solution was degassed with Ar purging for about 1 h. After that, a certain amount of H₂PdCl₄ was added to it and the mixture was subjected to irradiation with a 400 W Xe lamp for 2 h without using any cut-off filter. Finally, the resulting solid powder was collected by centrifugation and washed with water and ethanol, and then dried in an oven at 60 ^oC. The sample was marked as Pd_pCo-N-C. The weight percentage of Pd was estimated by atomic absorption spectroscopy (AAS) measurements. The Pd loading on Co-N-C (Pd_pCo-N-C) in this method was found to be 4.1 wt.% indicating a near complete deposition of the Pd salt (expected 5 wt.%).

4.2.3.3 Characterization

All characterization techniques have been discussed in detail in chapter 2.

4.2.3.4 Evaluation of catalytic activity

4.2.3.4.1 Preparation of working electrode

Before dropcasting, glassy carbon (GC) rotating disk electrode (RDE) was polished with 0.05 μ m alumina powder and cleaned by water and isopropyl alcohol. The electrocatalyst ink was prepared by dispersing the 1 mg of the catalyst in 120 μ l of Nafion : isopropanol : water (in ratio of 0.05:1:4 (v/v/v) by ultrasonication for about 30 minutes. After that, 4ul of catalyst ink was drop-casted on clean and polished glassy carbon (GC) rotating disk electrode (RDE) having geometric surface area of 0.0707 cm² and allowed to dried overnight at room temperature. The loading of Pd was calculated to be 19.56 μ g/cm² on the electrode surface for Pd_pCo-N-C. Similarly, metal loadings for other samples like Pt/C, Pd-N-C were maintained at 20 μ g/cm² on electrode surface.

4.2.3.4.2 Electrocatalytic performance evaluation

The general procedure for the evaluation of ORR activities is provided in section 2.2 of chapter 2.

4.2.3.5 Computation details

The density functional theory (DFT) based calculations are performed with the help of Vienna Ab Initio Simulations Package (VASP).^{47,48} VASP implements DFT using projector augmented-wave (PAW) potentials. To incorporate the electronic exchange and correlation effects, we use generalized gradient approximation (GGA) exchange and correlation functional with Perdew-Burke-Ernzerhof (PBE) parametrization.⁴⁹ The plane wave basis set, that is chosen for all the calculations has a kinetic energy cut off of 520 eV. To model the Co–N₄ cluster in the two dimensional (2D) graphene sheet, we first consider a 7 × 7 graphene supercell and then in that supercell we incorporate pyridinic nitrogen moiety (N₄) and Cobalt (Co) embedded N₄ (Co – N₄) cluster. A structural relaxation is performed with electronic self consistency cut-off of 10⁻⁶ eV for graphene and N₄-graphene (N-C system) and of 10⁻⁷ eV for Co – N₄ - graphene (Co-N-C system). The force tolerance of 0.01 eV/ A^o is used. Since the supercell is significantly large, calculations are performed centered at Γ point. For Co-N-C system spin polarized calculation is done. The absorption coefficient is calculated from the dielectric tensor, as obtained using VASP. The imaginary part of the dielectric tensor is given by,

$$\varepsilon_{\alpha\beta}^{(I)}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{c,v,\mathbf{k}} 2\omega_{\mathbf{k}} \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega) \times \langle u_{c\mathbf{k} + e_{\alpha q}} | u_{v\mathbf{k}} \rangle \langle u_{c\mathbf{k} + e_{\beta q}} | u_{v\mathbf{k}} \rangle^*$$

where c and v refer to the conduction and valence band, respectively and u_{ck} is the cell periodic part of the orbitals at the wave vector k. The real part of the dielectric tensor is obtained by Kramer-Kronig relation,

$$\varepsilon_{\alpha\beta}^{(R)}(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon_{\alpha\beta}^{(I)}(\omega')\omega'}{{\omega'}^2 - \omega^2 + i\eta} d\omega'$$

where P indicates the principle value. From these information, the absorption coefficient is calculated as,

$$\alpha_{\alpha\beta}(\omega) = \frac{\sqrt{2}\omega}{c} \left[\sqrt{(\varepsilon_{\alpha\beta}^{(I)})^2 + (\varepsilon_{\alpha\beta}^{(R)})^2} - \varepsilon_{\alpha\beta}^{(I)} \right]^{\frac{1}{2}}$$

The position of conduction band minima and valence band maxima are first calculated by taking vacuum as reference. A correspondence with Normal Hydrogen Electrode (NHE) is established by noting that H^+/H_2 reduction level (zero of NHE) is -4.44 V at pH 0 with respect to vacuum.⁵⁰ VASPKIT is used for post processing.⁵¹

Before proceeding with investigating opto-electronic properties and ORR ability of the systems, the system structures were optimized first. **Fig. 4.2.1** shows the relaxed supercells for graphene, N-C system and Co-N-C system, which were considered for further calculations. All the structures are completely planer (2D). The relaxed lattice vectors for 7×7 supercell, a and b are both equal and is of 17.28 A° with an angle of 60° between them. Upon incorporation of N moiety, a and b become 17.32 A° and 17.23 A°, respectively, with an angle of 59.8° between them. In the Co-N-C system a and b is changed to 17.34 A° and 17.20 A°, respectively and the lattice angle becomes 59.7°. With this slight modification the overall rhombus nature of the supercell is approximately preserved and hence the first Brillouin zone remains as hexagonal.



Figure 4.2.1 The optimized geometries of 7 X 7 supercell of (i) graphene, (ii) N-C and (iii) Co-N-C systems.

4.2.4 RESULTS AND DISCUSSION

Previous works on N-C centers have indicated that N-doped carbon can behave as an *n*-type semiconductor due to the contribution of the lone pairs of electrons of nitrogen to π conjugation, resulting in a charge separation and consequent band gap opening at Fermi
energy.⁵² Here, we first investigated the electronic structure of Co-N-C in detail and compared
with that of N-C system. We observe that, upon inclusion of Co in the cavity, the Fermi energy
shows an overall upshift due to the charge transfer from the Co atom to the N-C system and
therefore the conduction bands of N-C system, that are arising from C atoms (as evident from
the fat-band analysis) gets partially filled. This makes the Co-N-C system metallic. However,
we observe that the Co-N-C system behaves as optically gapped system owing to the optical
selection rule that allows the optical transition between the Co bands with explicit conservation
of spins. Therefore, the Co-N-C system provides a unique platform of semiconducting Co
centers embedded in a metallic matrix of honeycomb carbon network. Moreover, this system
can respond to UV-visible light irradiation such as those of natural sunlight._This prompted the
exploration of photodeposition of Pd NPs on Co-N-C achievable at the room temperature.

Pristine graphene is semimetallic with conduction and valence band touching at highsymmetric 'K' point as shown in Figure 4.2.2a. Therein, the introduction of N-moieties induces electron localization due to carbon-nitrogen electronegativity difference and presence of vacancy center. It leads to a direct band gap of 0.35 eV, making the N-C system semiconducting (Figure 4.2.2b). The flat blue bands show the signature of highly localized electrons of nitrogen. Even though the electronic band gap is in the infrared range, from the calculated absorption spectrum, it is clear that N-C system is capable of absorbing UV and visible photons due to electronic transitions to orbitals at higher energies, as evident from Figure 4.2.2c. However, when Co is introduced at the centre of the N moieties, the valence band crosses the Fermi energy and the system becomes metallic (Figure 4.2.2d). Besides, due to presence of unpaired 3d electron in Co, the system becomes magnetic with a net magnetic moment of 0.9998 µB, suggesting that the electronic bands are non-degenerate for up and down spin of the Co-N-C system. Analysis of the contributions of each spin originating from each element showed that the metallic bands are contributed from the C atoms. However, the metallic bands (the ones that crosses Fermi energy) are contributed only by C matrix and does not have any Co contribution. The Co contributed bands are nearly dispersion less and appear away from Fermi energy. The Co contributed valence and conduction bands are wide apart by an energy of approximately 3 eV. The absorption spectra (**Figure 4.2.2e**) reveal that even though the Co-N-C system is overall metallic, the photon harvest takes significant value only after 3 eV, which essentially corresponds to the optical transition between Co bands. Therefore, the Co-N₄ moiety can effectively act as optically gapped centres, as if engraved within a metallic matrix of C and can be used to harvest photons. This property intrigued us to further investigate whether the electrons and holes that are generated due to optical transition between Co bands, are potent enough to reduce Pd^{2+}/Pd and deposit Pd NPs on Co-N-C. In **Figure 4.2.2f**, we observe that the Co contributed conduction band minimum (CBM) for Co–N₄ system is at 2.89 eV (for up spin) and 3.41 eV (for down spin) lower potentials than the Pd^{2+}/Pd reduction level, which affirms the possibility of photo-reductive deposition of Pd on top of Co-N-C with large thermodynamic drive. This creates the platform to explore Co-N₄ centers present in the Co-N-C as light-harvesting centers and opens up possibilities of sustainable surface modification of M-N-Cs in photochemical pathways.



Figure 4.2.2 Electronic band structure of (a) graphene 7 X 7 supercell, (b) N-C and (c) Co-N-C systems. The blue and grey bands in (b) indicate the contributions from nitrogen and graphene, respectively. (c) Absorption spectra of N-C system In figure (d) the red (green) bands correspond to cobalt up spin (down spin) contribution, grey (yellow) bands correspond to carbon up spin (down spin), respectively. The radii of the circular dots are signifying the extent of elemental contribution. Nitrogen has negligible contributions and appear just as dots. The horizontal and vertical dotted lines indicate the high-symmetric points and Fermi energy,

respectively. (e) The absorption spectra of Co-N-C system. (f) The position of the conduction and the valence band edges of Co up (red dotted line) and down (green dotted line) spins with respect to the vacuum (left axis) and Normal Hydrogen Electrode (NHE) (right axis). The maroon solid line indicates the Fermi energy of Co-N-C system. The purple dotted line shows the Pd^{2+}/Pd reduction level.

Therefore, we attempted exploit the semiconducting nature of the Co-N-C to photodeposit Pd salts in the form of nanoparticles, keeping in mind that the Pd NPs thus formed will be capping agent free and should exhibit a superior electrocatalytic behaviour owing to facile mass-transfer at the catalyst-electrolyte interface. We emphasize that capping agent free preparation of electroactive Pd is otherwise difficult to achieved in industry friendly aqueous synthesis because of uncontrolled and highly facile precipitation of solid Pd NPs.^{44-46,53}

The Co-N-C substrate was prepared by one-step calcination of a mixture of commercially viable, cheap sources of C, N, and Co at 700^{0} C under inert atmosphere following our previous work.⁴³ Furthermore, we have also prepared N-doped carbon (N-C) without Co in a similar way to elucidate the superior effect of Co in charge transport. The synthetic protocols for generating Pd nanoparticles on Co-N-C is discussed in detail in the experimental section. Briefly, the deposition of the nanoparticles on the Co-N-C was achieved employing a complete reduction of a H₂PdCl₄ salt solution wherein the powder of Co-N-C was dispersed, under the irradiation a 400 W Xe lamp for 2h.

The semiconductor behaviour of N-doped carbon was verified from Mott-Schottky (MS) analysis by plotting $1/C^2 vs V$ as shown in **Figure 4.2.3a**. The distinct positive slope observed in MS plot of N-C indicates the *n*-type semiconducting behaviour of the sample. This further establishes the potential of N₄ centers to photochemical deposition of Pd, in accordance with our density functional theory (DFT) findings.

Powder X-ray diffraction (XRD) analysis confirms the successful deposition of Pd nanoparticles on the Co-N-C as seen in **Figure 4.2.3b**. The appearance of broad peak around 24.8° corresponds to the (002) plane of graphitic carbon. The peaks at 39.9°, 46.5° and 67.9° can be assigned to (111), (200) and (220) planes of palladium with an FCC crystal structure (JCPDS no. 88-2335). A Transmission electron microscope (TEM) image and a scanning TEM (STEM) image of the Pd NPs on the support are seen in **Figure 4.2.3c**, **3d** respectively. The lattice fringes corresponding to the (111) plane of Pd and (002) plane of carbon of Co-N-C were found in the high-resolution TEM (HRTEM) image (**Figure 4.2.3e**) with interplanar

spacing of 0.23 nm and 0.36 nm respectively (inset of **Figure 4.2.3e**). The diffraction rings in the selected area electron diffraction (SAED) pattern (**Figure 4.2.3f**) can be indexed to the (111), (200), (220) planes of Pd. A careful observation of a large number of TEM images revealed that the average size of the Pd particles is ~5 nm and are rather monodisperse (inset of **Figure 4.2.3d and Figure 4.2.4**). Similarly, Pd NPs were also successfully photodeposited on N-C, and confirmed by the TEM images and PXRD pattern of the sample (**Figure 4.2.5**), as predicted by DFT.



Figure 4.2.3 (a) Mott-Schottky plot of N-C at different frequencies (500, 1000 and 1500 Hz). The arrow indicates the flat band potential of N-C. (b) Powder XRD pattern of Pd_pCo -N-C. (c) Low magnification TEM image. (d) A STEM image; inset is the corresponding particle size distribution. (e) High-resolution TEM image of the sample showing the graphitic layers; inset is the lattice fringes with d-spacing corresponding to Pd NPs, and (f) the corresponding SAED pattern of the sample.

The kinetics of photodeposition was studied by tracking the absorbance originating from Pd^{2+} ion ($\lambda_{max} = 425$ nm) present in the reaction mixture at different time intervals under illumination during the photodeposition process. As seen in **Figure 4.2.6a** and **Figure 4.2.7a**, photodeposition of Pd occurs rapidly on Co-N-C as absorbance drops by 80% of its initial value within 1 h. On the contrary, absorbance decreases relatively slowly when N-C was used as the substrate (**Figure 4.2.7b**). On the other hand, there was no change in absorbance (inset in **Figure 4.2.6 and Figure 4.2.7c**) when the reaction mixture was kept in the dark for over 2 h.

Figure 4.2.6b and Figure 4.2.7d depict that Co-N-C can complete 50% of photodeposition within just 30 minutes whereas N-C takes ~50 minutes to deposit the same amount of Pd. Analysis of the deposition kinetics revealed that the process follows a first order kinetics. The faster deposition of Pd on Co-N-C when compared with N-C is evident from ~1.4 times higher rate constant observed for the formation of Pd_pCo-N-C than that of Pd-N-C (**Figure 4.2.6b and Figure 4.2.7e, f**). This also indicate the highly facile transfer of photogenerated charge carriers on Co-N-C due to the presence of Co, as compared to N-C, and a probable stronger Pd-support interaction in Pd_pCo-N-C compared to that in Pd-N-C.



Figure 4.2.4 (*a-e*) *TEM images at various magnifications of Pd_pCo-N-C*.



Figure 4.2.5 (a-e) TEM images and (f) XRD pattern of Pd-N-C.



Figure 4.2.6 (a) UV-Vis absorption spectra recorded during the deposition of Pd on Co-N-C in light; inset is recorded under dark. (b) Pd deposition kinetics in case of Co-N-C (red dots indicate the amount of Pd deposited at given time and blue dots show the corresponding rate constant plot).



Figure 4.2.7 (*a*, *b*) UV-Vis absorption spectra recorded during the deposition of Pd on Co-N-C and N-C, respectively. (c) Absorption spectra recorded at certain intervals over 2 h after addition of Pd precursor into the aqueous dispersion of Co-N-C in the dark. (d) Pd deposition kinetics in case of Co-N-C and N-C. (e, f) The first order rate constant plots corresponding to the kinetics of Pd deposition on Co-N-C and N-C, respectively.

As discussed later, detailed electrochemical measurements have demonstrated that the performance of the photodeposited Pd NPs were good in terms of outperforming benchmark catalysts Pt/C and Pd/C, and yet poorer than our expectation of very high efficiency, considering their tiny and capping agent free nature. A careful look at the microscopic images showed that the deposition of the NPs on the substrate is far from uniform and concentrated on the edges of the substrate only. Subsequently, we have attempted several times to achieve the uniform distribution of Pd nanoparticles throughout the surface of Co-N-C on the photochemical pathway alone. We indeed could observe the desired dispersion of Pd NPs over the Co-N-C surface at two specific reaction conditions. However, the successful attempts were found to be inappropriate in terms of scalability, essential for a synthetic protocol to reach industrial standard. Firstly, when a diluted (2.5 times) dispersion of Co-N-C was used to photodeposit Pd on Co-N-C, the Pd NPs were found to distributed all over the Co-N-C surface as shown in Figure 4.2.8a, b. A similar scenario was observed even when the concentrated dispersion of Co-N-C was first subjected to ultrasonication for 1 hr before light-irradiation (corresponding TEM images are shown in Figure 4.2.8c, d. The energy consumed in such a prolonged ultrasonication becomes bottleneck in keeping the overall synthetic strategy sustainable. Hence, it can be concluded from these controlled experiments that the spatial distribution of the photodeposited Pd NPs reaches a desirable distribution only either by using a significant diluted precursor strength and when Co-N-C dispersion is subjected to prolonged ultrasonication prior to photodeposition. Therefore, we infer that this phenomenon originates due to temporal Co-N-C agglomeration in the reaction setup and thus poor light penetration to the photoactive centers.⁵⁴ Only those portions exposed to light can yield Pd NPs. However, both the use of dilute precursor and prolonged sonication may severely limit the scalability of this synthetic strategy from an industrial perspective.

To track the changes in lattice structure of Co-N-C as a result of Pd loading, the Raman spectra were recorded before and after Pd deposition as shown in **Figure 4.2.9a.** Two distinct peaks corresponding to the D and the G bands were found around 1350 and 1590 cm⁻¹ respectively in all samples. Upon Pd loading, a red-shift in both the bands (**Figure 4.2.9b, c**) were observed when compared to that of N-C and Co-N-C, indicating strain on carbon networks induced by Pd NPs.⁵⁵⁻⁵⁷ and electron doping into carbon lattice probably due to the Pd-N charge transfer X-ray photoelectron spectroscopy (XPS) was further employed to study the surface functionalities of the samples. As the high-resolution N-1*s* XPS spectrum of Co-N-C depicts, in accordance with our earlier study there are 4 different N-species corresponding to

pyridinic (398.4 eV), pyrolic (400.3 eV), graphitic (401.1 eV) and oxidised nitrogen (402.5 eV).⁴³ After photodeposition of Pd NPs on Co-N-C, a negative shift in binding energy is observed corresponding to pyrolic nitrogen compared to Co-N-C (**Figure 4.2.10a**), which further suggests a charge-transfer from Pd to N.⁵⁵ Additionally, a significant positive shift of ~0.13 eV in binding energies corresponding to both Pd 3d_{3/2} and Pd 3d_{5/2} in Pd_pCo-N-C (**Figure 4.2.10b**) compared to the binding energy of Pd(0) suggests a facile charge-transfer of Pd *d*-electrons to support, giving rise to a positive charge accumulation on Pd accelerating the ORR reaction kinetics.^{58,59} Pd_pCo-N-C possesses a specific surface area of 165 m²/g which slightly lower than the that of Co-N-C and N-C, as expected and the corresponding N₂ adsorption-desorption isotherms are shown in **Figure 4.2.11**.



Figure 4.2.8 TEM images of (a-b) $Pd_pCo-N-C$ *synthesized using diluted precursor strength, and (c-d) prolonged ultrasonication before photodeposition.*



Figure 4.2.9 (*a-c*) *Raman spectra of the* $Pd_pCo-N-C$, Pd-N-C, Co-N-C and N-C samples in different frequency ranges.



Figure 4.2.10 High resolution (a) N-1s XPS and (b) Pd-3d XPS spectra of Pd_pCo-N-C.



Figure 4.2.11 (a-c) N_2 adsorption-desorption isotherms of N-C, Co-N-C and $Pd_pCo-N-C$ respectively.

The electrocatalytic efficiencies towards ORR were examined under alkaline conditions using a rotating disk electrode (RDE) at room temperature and compared with commercial Pt/C. Linear sweep voltammetry (LSV) was recorded in O₂ saturated electrolyte at rotation rate of 1600 rpm to study the ORR activities. For the judgement of optimized loading of Pd, evaluation of ORR activities was done on the samples having different wt.% of Pd on Co-N-C. The ORR polarization curves of samples having different loading of Pd NPs on Co-N-C shown in Figure 4.2.12a and 5wt.% was found to be an optimized loading. Figure 4.2.12a summarizes the corresponding half wave potential ($E_{1/2}$) and kinetic current density (j_k) of various samples. As Figure 4.2.13a depicts, Pd decorated sample with optimized amount of Pd (Pd_pCo-N-C) exhibits a superior activity with a more positive onset potential and a half wave potential ($E_{1/2}$) of 0.915 V which is 55 mV positive than commercial Pt/C under identical loading. The PdpCo-N-C sample also outperforms Pd-N-C having 34 mV lower E_{1/2} value and bare Co-N-C. It suggests that performance of Pd NPs got enhanced towards ORR after coupling with atomically dispersed Co in the support matrix. Besides this, the effect of Pd incorporation was found to be highly beneficial since the electrocatalytic performance got enhanced significantly from that we reported previously for bare Co-N-C.⁴³ The $E_{1/2}$ of the various catalysts is summarized in Figure 4.2.13b.



Figure 4.2.12 (a) The ORR polarization curves of $Pd_pCo-N-C$, Pd-N-C, Co-N-C and Pt/C recorded in O_2 saturated 0.1 M KOH at 1600 rpm, (b) Comparison of $E_{1/2}$ and kinetic current density (I_k) of samples at 0.85 V vs. RHE.



Figure 4.2.13 (a) The ORR polarization curves of $Pd_pCo-N-C$, Pd-N-C, Co-N-C and Pt/C recorded in O_2 saturated 0.1 M KOH at 1600 rpm, (b) Comparison of $E_{1/2}$ and (c) mass activities of samples.

Mass activities (I_k) were estimated by normalizing the kinetic currents with the respective noble metal loads (**Figure 4.2.13c and Figure 4.2.14 -4.2.16**), demonstrating the highest value by the Pd_pCo-N-C (0.42 A/mg). As suggested by Raman and XPS spectral analysis this enhanced electrocatalytic activity of Pd_pCo-N-C can be attributed to the positive charge accumulation on Pd as a result of metal-support interaction.



Figure 4.2.14 (a) ORR polarization curves of $Pd_pCo-N-C$ recorded at different rotation rates in O₂ saturated 0.1 M KOH with a scan-rate of 10 mV/s, (b) the corresponding K-L plots at different potentials (vs. RHE).



Figure 4.2.15 (a) ORR polarization curves of Pd-N-C recorded at different rotation rates in O_2 saturated 0.1 M KOH with a scan-rate of 10 mV/s, (b) the corresponding K-L plots at different potentials w.r.t. RHE.



Figure 4.2.16 (a) ORR polarization curves of Pt/C recorded at different rotation rates in O_2 saturated 0.1 M KOH with a scan-rate of 10 mV/s, (b) the corresponding K-L plots at different potentials vs. RHE.

To further rationalize the enhanced activity the charge transfer ability of the samples was studied by electrochemical impedance spectroscopy (EIS).⁶⁰ As suggested by the trend in radius of semicircle as found in Nyquist plot, Pd_pCo-N-C exhibits the lowest charge transfer resistance compared to N-C, Co-N-C and Pd-N-C (**Figure 4.2.17a**). Besides, The Pd_pCo-N-C

catalyst demonstrated excellent stability and methanol tolerance. The durability of catalysts was examined with an accelerated durability test (ADT) through CV cycling in the potential range of 0.6-1.1 V *vs*. RHE at a scan rate of 100 mV/s in an O₂ saturated electrolyte. **Figure 4.2.17b** shows the ORR polarization curves of Pd_pCo-N-C before and after the stability test where the $E_{1/2}$ decreases by only 8mV after 20000 cycles. For the evaluation of fuel crossover effect, 1 M methanol was injected into the O₂ saturated electrolyte during the chronoamperometric measurements. As shown in **Figure 4.2.17c**, there is very minute change in the ORR current of Pd_pCo-N-C while the commercial Pt/C suffers from drastic current drop (35 % loss) indicating that the catalyst shows significant stability under methanol crossover.



Figure 4.2.17 (a) Nyquist plots of samples in alkaline electrolyte (b) The ORR polarization curves of $Pd_pCo-N-C$ before and after durability tests recorded at rotation rate of 1600 rpm in O_2 saturated 0.1 M KOH, respectively. (d) chronoamperometry plots of samples before and after adding methanol with concentration of 1 M after 100 s.

4.2.5 CONCLUSIONS

In conclusion, we establish using DFT studies that N4 and MN4 (M=Co) moieties in Ndoped carbon (N-C), and Co-N-C (where Co is atomically dispersed) respectively are semiconducting in nature and act like semiconductor centers engraved within a conducting framework of carbon that is capable of harvesting natural sunlight. DFT studies have also shown that the alignment of the valance band and the conduction bands of these semiconducting centers are suitable for the photoreduction of noble metal salts such as Pd^{2+} . This was experimentally verified by the photodeposition of Pd²⁺ following an expected firstorder kinetics at room temperature in the form of crystalline NPs. The anchoring of these NPs to the N-C and Co-N-C supports arrests their growth to generate nanocrystalline sizes that are similar to commercial electrocatalysts, but advantageous because deposition occurs at room temperature using renewable sunlight energy. Besides, there is no need for using capping agents as is often the case when NPs are preformed and loaded on a catalyst support, making mass transfer across the catalyst solution interface facile. Using DFT studies and experiments, we also demonstrate that charge transfer between carbon and Pd NP can become extremely facile when the Co atom is positioned between the N-doped carbon support and Pd NP which helps in generating facile electrocatalytic activities of the deposited Pd NPs. Pd_pCo-N-C shows efficient ORR activity in alkaline media with a very high $E_{1/2}$ of 0.915 V vs. RHE. In addition, it also exhibits very high methanol tolerance and durability with less than 8 mV shift in $E_{1/2}$ after 20000 cycles due to a stronger binding from Co-mediated-charge transfer from Pd to the support. Our findings should establish M-N-Cs as a new class of catalyst-support for noble metal electrocatalysts and also the exploration of their utility in photocatalysis.
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CHAPTER 4.3

Overcoming the limitation of photochemical incorporation of Pd nanoparticles on M-N-C and tuning the metal-support interaction towards oxygen reduction reaction



Summary

The highly stable and electrocatalytically active Pd nanoparticles (NPs) limits its largescale realization because of its high cost, giving rise to an urge to utilize at its minimal dependence by compositing with low-cost electrocatalyst. Incorporation of highly active Pd NPs on support under mild conditions was achieved by employing photochemical pathway but realized with no-uniform deposition. Herein, we evolve a sequential Pd loading strategy where both uniform distribution of Pd nanoparticles and a strong interaction with its support, atomically dispersed Co-containing N-doped carbon (Co-N-C) was achieved. Several spectroscopic techniques and DFT calculation suggest that formal positive charge was accumulated on Pd as a result of strong metal-support interaction brought by the photochemical pathway whereas uniform distribution was achieved by a prior dry-impregnation process. Consequently, a very high ORR efficiency ($E_{1/2}$ of 0.94 V *vs*. RHE) and stability (< 3 mV shift in $E_{1/2}$ after 20,000 cycles) was shown by sequentially decorated Pd NPs on Co-N-C. This study demonstrates the dominating effect of tuning metal-support interaction in determining both the catalytic efficiencies as well as durability of Pd NPs decorated on Co-N-C surface.

‡Manuscript based on this work is under preparation.

4.3.1 Introduction

Palladium (Pd) nanoparticles are known for their remarkable stability and excellent electrocatalytic properties.^{1–5} However, their high cost can be a limiting factor for large-scale applications, giving rise to an urge to utilize at its minimal dependence by compositing with low-cost electrocatalyst. Combining Pd nanoparticles at minute loading with other electrocatalytically active cost-effective materials can bring synergistic effect towards boosted catalytic performance compared to each component individually. The choice of the low-cost electrocatalyst is critical. It should possess certain desirable properties, such as good electrical conductivity, stability, and preferably, some intrinsic catalytic activity. Common low-cost materials that are considered for compositing with Pd include transition metal oxides, carbon-based materials, and even certain polymers.^{6–10}

Achieving these composite materials involves specific synthesis techniques. For instance, one might employ methods like chemical deposition, co-precipitation, or electrochemical deposition to combine Pd nanoparticles with the chosen low-cost material.^{11–15} But, the most crucial part towards realizing such synergy is economically viable and scalable composite formation. Recent research in this field aims to refine the synthesis techniques, optimize composite compositions, and explore new low-cost materials for compositing with Pd. In summary, the approach of compositing highly stable and electrocatalytically active Pd nanoparticles with low-cost electrocatalysts holds promise for overcoming the economic challenges associated with Pd's high cost, paving the way towards sustainable energy conversion.

Furthermore, it is noteworthy that there is a critical role of metal-support interaction in determining the catalytic efficiency of composite materials.^{16–19} This interaction is crucial for both the performance as well as the durability of electrocatalysts to facilitate electrochemical reactions, such as those occurring in fuel cells or storage batteries. The catalytic efficiency of composite materials relies on how effectively the charge carriers can transport through the catalyst from the electrode to reactant.^{20,21} Therefore, a strong metal-support interaction helps in reducing the resistance at the interface between the metal and the supporting material.^{22–24} In electrochemical processes, particularly at the nanoscale, resistance at this interface can impede the flow of charge carriers (such as electrons or ions).^{25–27} By minimizing this resistance, the composite material can facilitate smoother and more efficient electrochemical reactions.

Additionally, a strong metal-support interaction contributes to the mechanical and chemical stability of the composite material.^{28–30} This means that the electrocatalyst remains structurally sound and chemically active over an extended period, even in the harsh conditions typically encountered during electrochemical reactions. This durability is crucial for the practical application of electrocatalysts in real-world scenarios. The degree of metal-support interaction varies based on the synthetic strategies employed in creating the composite material.^{31,32} Hence, a rational designing and engineering composite materials for electrocatalysis should also be aimed at bringing high metal-support interaction along with achieving sustainability in the synthetic strategy.

4.3.2 Scope of the present investigation

Incorporation of highly active Pd NPs on support under mild conditions was achieved in our previous study by employing photochemical pathway but realized with no-uniform deposition, elaborately nanoparticles were loaded in certain areas and distributed unevenly across the surface of the support. A non-uniform deposition of Pd nanoparticles is inevitably counter-productive for the performance of the resulting composite material. Controlled experiments showed in the earlier chapter that uniform deposition can be achieved by photochemical strategy only for very low-scale execution or employing a prior energyintensive prolonged sonication.

Herein, a sequential Pd loading strategy was realized where both uniform distribution of Pd nanoparticles and a strong interaction with its support, atomically dispersed Cocontaining N-doped carbon (Co-N-C) was achieved. Sequentially decorated Pd NPs on Co-N-C exhibited a very high ORR efficiency ($E_{1/2}$ of 0.94 V *vs*. RHE) and stability (<3 mV shift in $E_{1/2}$ after 20,000 cycles). Therefore, this study showcases how adjusting the interaction between the metal and the supporting material significantly influences both the catalytic performance and the long-term stability of palladium nanoparticles placed on a Co-N-C surface.

4.3.3 METHODS

4.3.3.1 Synthesis of Co-N-C

We prepared atomically dispersed Co-N-C using a procedure described in our previous work.³³ In summary, melamine, cobalt chloride, and pre-treated Vulcan carbon were combined in precise proportions and ground together. The resulting mixture was then subjected to heating in a tube furnace, starting at 350°C for 20 minutes, followed by 600°C for 1 hour, and finally

at 700°C for 2 hours, all under an argon (Ar) atmosphere. After the heating steps, the sample was allowed to cool naturally to room temperature and is denoted as Co-N-C. The cobalt content was determined to be 1.4 wt.% using atomic absorption spectroscopy (AAS).

4.3.3.2. Synthesis of Co-N-C catalyst loaded with Pd NPs

Co-N-C was used as a substrate for the deposition of Pd NPs by single and two-step methods. The single-step method is the same as the two-step method except for the introduction of the dry impregnation method.

4.3.3.2.1 Single-step method (photodeposition)

Photodeposition was done in similar manner described in section 4.2.3.2 in Chapter 4.2.

4.3.3.2.2 Two-step method (dry-impregnation followed by photodeposition)

First, dry-impregnation treatment was used to decorate Co-N-C by Pd NPs.³⁴ For this, the Co-N-C catalyst was dispersed in an aqueous solution containing the desired amount of H₂PdCl₄ as a Pd precursor. In a typical synthesis, aqueous dispersion of Co-N-C was ultrasonicated for 1 hr, followed by another 1 hr of ultrasonication after the addition of Pd precursor. Then, the dispersion was stirred overnight. After that, the sample was gently dried in an oven and the resulting powder mixture was put into an alumina boat and placed in a tube furnace. The sample was heated under 5% H₂/Ar atmosphere at 350 °C for 2 h (with a heating rate of 2 °C min⁻¹). Finally, the furnace was allowed to cool down naturally and the obtained sample was stored for further use after washing with water and ethanol and overnight drying. Subsequently, the additional amount of Pd was loaded on the Pd-impregnated sample by the photo-deposition process discussed above to yield $Pd_{i+p}Co-N-C$. Total Pd loading was estimated to be 4.20 wt.% in $Pd_{i+p}Co-N-C$. For comparison, certain amount of Pd was loaded on Co-N-C catalyst by only dry-impregnation method alone, maintaining the same reaction conditions to yield $Pd_iCo-N-C$. Total Pd loading achieved in this process was estimated to be 4.52 wt.% for Pd_iCo-N-C.

4.3.3.3 Characterization

All characterization techniques have been discussed in detail in chapter 2.

4.3.3.4 Evaluation of catalytic activity

4.3.3.4.1 Preparation of working electrode

A glassy carbon (GC) rotating disk electrode with a 3mm diameter and a working area of 0.0707 cm² was polished using 0.5 μ m alumina powder until achieving a smooth, mirrorlike surface. This polished GC electrode was utilized as the working electrode. A mercury/mercuric oxide (Hg/HgO) electrode (0.1 M NaOH) served as the reference electrode, while a platinum wire acted as the counter electrode. To create the catalyst ink, 1 mg of the catalyst was dispersed in 120 μ l of a nafion solution (consisting of 5 wt% nafion, isopropanol, and water in a ratio of 0.05:1:4, v/v/v). The dispersion was sonicated for approximately 15 minutes. Next, 4 μ l of this dispersion was dropcasted onto the clean GC-RDE and left to dry under ambient conditions. The estimated amount of Pd loaded onto the GC electrode was approximately 19.8 μ g/cm². For consistency, the metal loadings on the electrode surface for other samples, such as Pt/C were maintained at 20 μ g/cm².

4.3.3.4.2 Electrocatalytic performance evaluation

The general procedure for the evaluation of ORR activities is provided in section 2.2 of chapter 2.

4.3.4 RESULTS AND DISCUSSION

In accordance with our previous study as a potential pitfall was encountered in photochemical Pd deposition on Co-N-C. Alternatively, and for comparison while still keeping the synthesis approach a capping agent free one, dry-impregnation method was chosen to load 5 wt.% Pd NPs (same as that of photodeposition) on Co-N-C (hereafter called as Pd_iCo-N-C) under 5% Ar/H₂ atmosphere at 350 °C. This approach was adopted by keeping in mind several benefits that will be clear from the subsequent experiments. The dry-impregnation method resulted in uniform distribution of Pd NPs throughout the Co-N-C sheets as shown in (Figure 4.3.1a, b) as expected, due to the absence of factors like non-uniform light exposure. However, statistical size distribution analysis of the sample depicted that as compared to Pd_pCo-N-C (avg. size ~5 nm), a larger average particle size (~11.5 nm) and a much broader distribution of particle size (±10 nm) was achieved in case of Pd_iCo-N-C (Figure 4.3.1c), suggesting significant agglomeration between the Pd NPs. Also, note that the particle size in our case should not be compared with other studies due to the presence of Co in the sample, which can catalyze carbon reconstruction and effect Pd deposition process.³³ We, therefore, conclude that although dry-impregnation can lead to uniform distribution of particles over the entire support, it eventually results in deposition of larger particles than the photodeposition process which is not desirable for high electrochemical performance.



Figure 4.3.1 (*a-b*) *TEM images and* (*c*) *average particle size distribution of Pd_iCo-N-C*.

To overcome the shortcomings of both the individual processes, *i.e.* the non-uniform deposition under photocatalytic conditions and the formation deposition of larger Pd NPs under dry-impregnation conditions, the synthetic strategy was further modified by a prior loading of a fraction of Pd NPs on Co-N-C by dry-impregnation treatment followed by photodeposition of the remaining fraction of Pd. It was hypothesized that loading of a smaller fraction of Pd will lead to uniform distribution of smaller particles due to limited availability of Pd precursors. In that scenario, loading the remaining fraction of Pd by photodeposition will remain uniform due to (i) a slower precursor-controlled kinetics of the deposition process and (ii) the presence of pre-formed Pd NPs that should enable a more efficient separation of photo-excitons, leading to Pd deposition even in those corners of the carbon mass where light penetration is minimal.³⁵ And therefore, the sample made by the sequential decoration method ($Pd_{i+p}Co-N-C$) delivered a higher and more stable electrocatalytic activity as discussed later. The microstructural features Pd_{i+p}Co-N-C were examined by TEM and HAADF-STEM imaging as seen in Figure 4.3.2a, b. The low magnification TEM images clearly show that Pd NPs are successfully loaded with uniform distribution throughout Co-N-C. The average diameter of Pd NPs is ~7.5 nm with a standard deviation of ± 3 nm. (Figure 4.3.2c). The lattice fringes with interplanar spacing of 0.23 nm and 0.36 nm observed in the HRTEM images (Figure 4.3.2d) correspond to the (111) plane of Pd and (002) plane of carbon of Co-N-C respectively. We point out that powder XRD patterns were recorded for the Pd_iCo-N-C and the Pd_{i+p}Co-N-C samples (Figure 4.3.3) and no appreciable differences were noticed between the peak positions.

A comparative Raman and XPS spectral analysis of the various samples revealed that not only the dimension and size-distribution of the Pd NPs got varied as a result of changes in synthetic strategy, but the materials properties also got altered significantly despite incorporating a similar wt.% of Pd NPs, due to the ability of metal nanoparticles to reconstruct carbon materials.³³ From the Raman spectra shown in **Figure 4.3.4a**, two characteristics peaks centred around 1350 and 1590 cm⁻¹ were detected in all samples corresponding to the D and the G bands respectively. The relative intensity ratio of D-band to G-band is a key indicator of the defects present in carbon materials. The ratio of the two peak intensities (I_D/I_G) of Pd_iCo-N-C and Pd_pCo-N-C are found to be 0.94 and 1.03 respectively, suggesting a similar amount of Pd NPs loaded in different synthetic strategy brings dissimilarity in defects incorporated into the carbon framework in both the samples. Besides, a red-shift in G-band is more pronounced (Figure 4.3.4b) in case of Pd_pCo-N-C & Pd_{i+p}Co-N-C and even in Pd-N-C when compared with Pd_iCo-N-C, a clear indication of more strain on carbon networks induced by Pd NPs.³⁶⁻³⁸ This also suggests that a more intimate interaction of the Pd NPs with the N-C support can be achieved when photodeposition is involved. On the other hand, another red-shift of ~ 15 cm⁻¹ in D-band (Figure 4.3.4c) can be attributed to higher electron doping of carbon and confirms a facile charge transfer from Pd NPs to nitrogen, making Pd relatively more electropositive which is beneficial for oxygen adsorption.^{39,40} Therefore, Pd_{i+p}Co-N-C possesses both favourable metal-support interaction like PdpCo-N-C as well as uniform distribution of catalytic centers like in Pd_iCo-N-C.



Figure 4.3.2 Microscopic characterization of $Pd_{i+p}Co-N-C$, (a) Low magnification TEM, (b) A STEM image, (c) the corresponding particle size distribution histogram of Pd NPs and (d) high-resolution TEM; inset showing the (111) planes of Pd NPs.



Figure 4.3.3 (a) *Powder XRD patterns of Pd*_{i+p}*Co-N-C*.



Figure 4.3.4 (*a*-*c*) *Raman spectra of the* $Pd_{i+p}Co-N-C$, $Pd_pCo-N-C$, $Pd_iCo-N-C$ and Pd-N-C samples in different frequency ranges.

To support the Raman spectroscopic analysis (and also bader charge analysis and EIS data discussed *vide infra*), the surface functionalities of the samples were investigated by X-ray photoelectron spectroscopy (XPS). From the N-1*s* XPS spectrum of Co-N-C, we have earlier showed the presence of 4 different N-species corresponding to pyridinic (398.4 eV), pyrolic (400.3 eV), graphitic (401.1 eV) and oxidised nitrogen (402.5 eV).³³ Now, upon Pd loading on Co-N-C by the three different strategies, there appears to be negative shift in binding energy corresponding to pyrolic nitrogen in the samples (**Figure 4.3.5a**), which further

suggests a charge-transfer from Pd to N.⁴⁰ The larger shift in $Pd_{i+p}Co-N-C$ (0.24 eV) and $Pd_pCo-N-C$ (0.22 eV) compared to $Pd_iCo-N-C$ (0.1 eV) on the best fit values indicate a superior contact between Pd NPs and support obtained by photodeposition, consistent with Raman spectral analysis. This observation was further confirmed by analysing high resolution Pd-3d spectra obtained for the three samples (**Figure 4.3.5b**). A significant positive shift of ~0.13 eV in binding energies corresponding to both Pd 3d_{3/2} and Pd 3d_{5/2} in Pd_pCo-N-C and Pd_{i+p}Co-N-C compared to Pd_iCo-N-C suggests a facile charge-transfer of Pd *d*-electrons to support, which is expected to lead to a reduction in Pd electron density that favours the acceleration of ORR reaction kinetics.⁴⁰ Such positive charge accumulation on Pd agrees with the computational results based on DFT. We have calculated the charge density profile of Pd_{i+p}Co-N-C system with respect to Co-N-C and bare Pd tetrahedra. **Figure 4.3.6** shows that Pd cluster is partially positive and it is consistent with experimental observation. From Bader charge analysis, we find the Pd cluster to possess a net positive charge of +0.102|e|.



Figure 4.3.5 High resolution (a) N-1s XPS spectra and (b) Pd-3d XPS spectra of $Pd_{i+p}Co-N-C$, $Pd_pCo-N-C$ and $Pd_iCo-N-C$. The green dotted lines indicate the highest peak positions corresponding to $Pd_iCo-N-C$ sample for reference.



Figure 4.3.6 The top and side view of charge density profile on $Pd_{i+p}Co-N-C$ *system.*



Figure 4.3.7 (*a-e*) N_2 adsorption- desorption isotherms of N-C, Co-N-C, $Pd_{i+p}Co$ -N-C, Pd_pCo -N-C and Pd_iCo -N-C respectively.

The specific surface area of the samples was determined by nitrogen adsorptiondesorption isotherm analysis. Upon loading Pd NPs on Co-N-C surface, there is a decline in the specific surface area as compared to bare Co-N-C and N-C, as expected (**Figure 4.3.7a, b**). Pd_iCo-N-C possesses a surface area of 125 m²/g which is less than the one Pd_pCo-N-C (165 m²/g), which we attribute to the larger average size of NPs in Pd_iCo-N-C (**Figure 4.3.7d, e**). Pd_{i+p}Co-N-C shows (**Figure 4.3.7c**) an intermediated surface area of 145 m²/g, as expected. Thus, tuning the Pd incorporation strategy not only improves Pd-support interaction but also enhances the availability of active sites and should further boosts the overall catalytic efficiency.



Figure 4.3.8 (a) The ORR polarization curves of $Pd_{i+p}Co-N-C$, $Pd_pCo-N-C$, $Pd_iCo-N-C$, Pd_i N-C and Pt/C recorded in O₂ saturated 0.1 M KOH at 1600 rpm, (b) Comparison of $E_{1/2}$ and j_k of various samples.

To experimentally evaluate the ORR performance and the possible influence of interaction between Pd NPs on Co-N-C, the electrocatalytic activities of the various catalysts were examined under alkaline conditions using a rotating disk electrode (RDE) at room temperature and compared with commercial Pt/C. The ORR activities were measured by recording linear sweep voltammetry (LSV) in O₂ saturated electrolyte at rotation rate of 1600 rpm. As shown in Figure 4.3.8a, all samples exhibit reasonably good oxygen reduction capacity, among which Pd_{i+p}Co-N-C demonstrates an excellent activity with a more positive onset potential and a half wave potential $(E_{1/2})$ of 0.943 V which is 83 mV positive than commercial Pt/C under identical loading. The performance of PdpCo-N-C and PdiCo-N-C are also better than commercial Pt/C, but having 28 and 53 mV lower $E_{1/2}$ values respectively than the Pd_{i+p}Co-N-C. Pd-N-C, on the other hand, showed a comparable activity with Pt/C revealing the enhanced performance of Pd towards ORR after coupling with atomically dispersed Co in the support matrix. Besides this, the effect of Pd incorporation was found to be highly beneficial since the electrocatalytic performance got enhanced significantly from that we reported previously for bare Co-N-C.³³ The $E_{1/2}$ and kinetic current densities (j_k) of the various catalysts is summarized in Figure 4.3.8b.

For the evaluation of intrinsic ORR activity, mass activities (I_k) were estimated by normalizing the kinetic currents with the respective noble metal loads (Figure 4.3.9 - 4.3.13). The Pd_{i+p}Co-N-C delivers a higher I_k of 0.64 A/mg which is 1.2, 2, 2.9 and 4 higher than that of Pd_pCo-N-C (0.53 A/mg), Pd_iCo-N-C (0.33 A/mg), Pd-N-C (0.22 A/mg) and commercial Pt/C (0.16 A/mg) respectively (Figure 4.3.14).



Figure 4.3.9 (a) ORR polarization curves of $Pd_{i+p}Co$ -N-C recorded at various rotation rates in O_2 saturated 0.1 M KOH with a scan-rate of 10 mV/s, (b) the corresponding K-L plots at different potentials (vs. RHE).



Figure 4.3.10 (a) ORR polarization curves of $Pd_pCo-N-C$ recorded at different rotation rates in O₂ saturated 0.1 M KOH with a scan-rate of 10 mV/s, (b) the corresponding K-L plots at different potentials (vs. RHE).



Figure 4.3.11 (a) ORR polarization curves of Pd_iCo -N-C recorded at different rotation rates in O₂ saturated 0.1 M KOH with a scan-rate of 10 mV/s, (b) the corresponding K-L plots at different potentials w.r.t. RHE.



Figure 4.3.12 (a) ORR polarization curves of Pd-N-C recorded at different rotation rates in O_2 saturated 0.1 M KOH with a scan-rate of 10 mV/s, (b) the corresponding K-L plots at different potentials w.r.t. RHE.



Figure 4.3.13 (a) ORR polarization curves of Pt/C recorded at different rotation rates in O² saturated 0.1 M KOH with a scan-rate of 10 mV/s, (b) the corresponding K-L plots at different potentials vs. RHE.



Figure 4.3.14 Comparison of mass activities of various PdCo-N-C samples, respectively.

Generally stated, the ORR performance of $Pd_{i+p}Co-N-C$ is superior or comparable to those of the state-of-the-art catalysts also (**Table 4.3.1**). The superior performance of $Pd_{i+p}Co-N-C$ further affirms the intimate contact of Pd NPs with Co-N-C achieved via sequential deposition of Pd NPs by dry-impregnation method followed by photo-deposition, as revealed by Raman and XPS analysis, and later using impedance spectroscopy.

S.No.	Electrocatalysts	ORR E1/2 (V vs. RHE)	Electrolyte	Mass activity (A/mg)	Reference
1.	Pd _{i+p} Co-N-C	0.943	0.1 M KOH	0.64	This work
2.	PdpCo-N-C	0.915	0.1 M KOH	0.41	This work
3.	Pd _i Co-N-C	0.890	0.1 M KOH	0.31	This work
4.	Pd/FeCoNC	0.88	0.1 M KOH	-	41
5.	Pd/N–HsGY	0.849	0.1 M KOH	0.38	42
6.	Pd ₇₂ Cu ₂₈ mesoporous nanospheres	0.89	0.1 M KOH	0.19	43
7.	Fe-N ₄ /Pt-N ₄ @NC	0.93	0.1 M KOH	-	44
8.	Pd ₅₉ Cu ₃₀ Co ₁₁	0.91	0.1 M KOH	0.38	45
9.	Pd-Co nanocrystals on N-C	0.845	0.1 M KOH	0.45	46
10.	Ni@Pd ₃ NCs	0.86	0.1 M KOH	0.035	47
11.	Pd-Ru@NG	0.8	0.1 M KOH	-	48
12.	Dealloyed PdNi/C	0.87	0.1 M KOH	0.37	49
13.	Ordered PdCuCo/C Nanoparticle	0.872	0.1 M NaOH	0.13	50
14.	Ni-Sas-Pd@NC	0.84	0.1 M KOH	-	51
15.	FeN ₃ -Pd@NC NBs	0.926	0.1 M KOH	0.0092	52

 $\label{eq:table 4.3.1 Comparison of ORR performance of $Pd_{i+p}Co-N-C$ with recently reported literature data}$

The ORR kinetics was further explored by recording the polarization curves at different rotation rates from 400 to 2400 rpm (**Figure 4.3.9-4.3.13**) and evaluating the corresponding electron transfer numbers (*n*) by using Koutecky-Levich (KL) equation. The average *n* value for Pd_{i+p}Co-N-C was calculated to be 3.91 indicating the desired 4 electron ORR pathway. The other values of *n* were also calculated as 3.84, 3.82, 3.58 and 3.91 for Pd_pCo-N-C, Pd_iCo-N-C, Pd-N-C and commercial Pt/C respectively under identical conditions. Subsequently, the rotating ring disk electrode (RRDE) experiments were performed to further support the near ideal n values by determining the percentage of H₂O₂ formed by the 2 electron pathways (**Figure 4.3.15a**). The average percentage peroxide yields for Pd_{i+p}Co-N-C is very low (<5 %). Pd-N-C on the other hand yielded 20% peroxides, which is quite higher but less than N-C (40%) confirming that metal strongly induces the 4 electron pathways. However, due to localized photodeposition of Pd in Pd-N-C that leaves major fraction of the catalyst surface similar to pure N-C, the peroxide yields are as much high. The n value determined from RRDE experiments (**Figure 4.3.15b**) also in agreement with the RDE results and confirming again the 4 electron ORR process.



Figure 4.3.15 (a) the corresponding H_2O_2 yield of samples and (b) Plot of electron transfer number vs. potential w.r.t RHE derived from RRDE measurements.

The feasibility of ORR on PdCo-N-C was also checked using density functional theory (DFT) based calculations, revealing the fourth electron transfer step (OH* to H₂O conversion) as the rate determining step. The free energies of the intermediates with respect to reversible hydrogen electrode (RHE) at zero electrode potential (U = 0 V) shown in **Figure 4.3.16**. We note that the formation of OOH* is followed by a free energy change (Δ G1) of -2.586 eV. The free energy change associated with formation of OH* (Δ G2) and formation of OH*

from 0^* ($\Delta G3$) are -1.052 eV and -1.352 eV, respectively. The last step of OH^{*} to H₂O formation occurs with free energy change of +0.07 eV and hence is the potential rate determining step.

We have incorporated this simplistic model to get qualitative idea about the reaction mechanism and the rate determining step. However, since in the experimental set up the number of Pd atoms are of the order of five thousand, simulating the experimental set up with quantitative match is not achievable computationally in this case. Since catalytic activity is highly dependent on Pd cluster shape and size,⁵³ we do not consider the exact values for our analysis.



Figure 4.3.16 The free energy profile of $Pd_{i+p}Co$ *-N-C system for ORR at* U = 0 *V.*

The Nyquist plots obtained from the electrochemical impedance spectroscopy (EIS) measurements, shown in **Figure 4.3.17**, were used to examine the charge transfer behaviour of the samples.⁵⁴ The semicircle in the high frequency region is a measure of the charge-transfer resistance followed by a straight line in the low frequency region representing the diffusion characteristics near the electrode surface. The data can be fitted into Randles equivalent circuit model (**Figure 4.3.18**) consisting of solution resistance (R_s), charge transfer resistance (R_{ct}), constant phase element (CPE, Q) and double layer capacitance (C_{dl}) which showed that $Pd_{i+p}Co-N-C$ exhibits the lowest charge transfer resistance compared to other samples. This observation was further supported by our theoretical investigations.



Figure 4.3.17 Nyquist plots of samples in alkaline electrolyte.



Figure 4.3.18 Randles equivalent circuit used for fitting the experimental impedance measurement data for the Nyquist plot. The circuit consists of solution resistance (R_s), charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}), and a constant phase element (Q).

We have analyzed the charge transfer process in Co-N-C system by calculating the differential charge density $\Delta \rho(\vec{r})$ using the following equation:

$$\Delta \rho(\vec{r}) = \rho_{Co-N-C}(\vec{r}) - \rho_{N-C}(\vec{r}) - \rho_{Co}(\vec{r})$$

where $\Delta \rho_{Co-N-C}(\vec{r})$, $\Delta \rho_{N-C}(\vec{r})$ and $\Delta \rho_{Co}(\vec{r})$ are the charge densities of Co-N-C system, N-C system, and Co atom, respectively as a function of the position vectors. **Figure 4.3.19** shows the differential charge density plot (both the top and the side views), where the yellow region depicts the accumulation of charge and cyan region depicts depletion of charge.

We found that the presence of Co-N-C moieties significantly influences the charge distribution in the system. Nitrogen pulls the electrons from both N-C and N-Co bonding due to its relatively higher electronegativity. To get a quantitative estimate of this process, we performed Bader charge analysis, which is in well accordance with differential charge density results. We note that the accumulation of electron on nitrogen is in the range of -1.15 to -1.25e, whereas cobalt becomes +0.924e by transferring charge towards neighbouring nitrogen moieties. As a consequence, when external electrons enter the Co-N-C system from the electrode, the Co atom facilitates charge transfer to Pd and hence contributes to reduce the charge-transfer resistance in Pd decorated Co-N-C samples, thereby boosting the efficiency of ORR process. The enhanced performance can thus be attributed to the optimised effect of higher metal-support interaction and uniform distribution of Pd NPs over the catalyst surface. As suggested by Bader charge analysis, the photo generated electrons get transferred through Co atoms and further reduce the Pd²⁺ for *in-situ* Pd NPs deposition, connecting the Pd NPs on the support through the Co atoms. Overall, Pd NPs contribute as the major active sites possibly along with some of the Co atoms which remain exposed at the catalyst surface.



Figure 4.3.19 Top and side view of differential charge density in Co-N-C system. The yellow and cyan region indicate accumulation and depletion, respectively.

The $Pd_{i+p}Co-N-C$ catalyst demonstrated excellent stability and methanol tolerance, when compared with $Pd_pCo-N-C$ and $Pd_iCo-N-C$. The durability of catalysts was examined with an accelerated durability test (ADT) through CV cycling in the potential range of 0.6-1.1 V vs. RHE at a scan rate of 100 mV/s in an O₂ saturated electrolyte. **Figure 4.3.20a** shows the ORR polarization curves of $Pd_{i+p}Co-N-C$ before and after the stability test where the $E_{1/2}$ decreases by only 3 mV after 20,000 cycles. In comparison, Pd_iCo-N-C experienced a decrease of 36 mV only after 10,000 cycles (**Figure 4.3.20b**). The stability of Pd_pCo-N-C was relatively poor with more than 8 mV negative shift in $E_{1/2}$ after 20,000 cycles (**Figure 4.3.20c**). The enhanced durability can be ascribed to the unique choice of substrate to anchor the Pd NPs strongly due to prolific charge transfer that imparts high electrochemical stability compared to other carbon frameworks. For the evaluation of fuel crossover effect, 1 M methanol was injected into the O₂ saturated electrolyte during the chronoamperometric measurements. As shown in **Figure 4.3.20d**, there is very minute change in the ORR current of Pd_{i+p}Co-N-C while the commercial Pt/C suffers from drastic current drop (35 % loss) indicating that the catalyst shows significant stability under methanol crossover.



Figure 4.3.20 (a, b and c) The ORR polarization curves of $Pd_{i+p}Co-N-C$, $Pd_iCo-N-C$, $Pd_pCo-N-C$ before and after durability tests recorded at rotation rate of 1600 rpm in O_2 saturated 0.1 *M* KOH, respectively. (d) chronoamperometry plots of samples before and after adding methanol with concentration of 1 M after 100 s.

4.3.5 CONCLUSIONS

In this work we demonstrate a sequential Pd loading strategy bringing both uniform distribution of Pd nanoparticles and a strong metal-support interaction together. As confirmed by several spectroscopic techniques and DFT calculation the formal positive charge was accumulated on Pd, responsible for accelerating the ORR kinetics, can be attributed to the strong metal-support interaction brought by the photochemical pathway while the prior dry-impregnation step brings the uniform distribution Pd NPs throughout the Co-N-C surface. Consequently, a very high ORR efficiency ($E_{1/2}$ of 0.94 V vs. RHE) and stability (<3 mV shift in $E_{1/2}$ after 20,000 cycles) was achieved by sequentially decorated Pd NPs on Co-N-C. Finally, along with achieving prolonged durability of Pd NPs decorated on Co-N-C surface the electrocatalytic efficiencies were depicted in this study as a major function of metal-support interaction.

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CHAPTER 4.4

Conclusions and future prospects

Conclusions

The integration of low-cost electrocatalysts with highly active yet expensive noble metals at minimal loading represents a pivotal advancement in the realm of electrocatalysis, holding immense promise for sustainable energy applications. This amalgamation addresses the critical challenge of cost-effectiveness without compromising performance, a paramount consideration in the pursuit of widespread renewable energy adoption. By strategically combining these materials, researchers endeavor to unlock the full potential of electrocatalysts, rendering them more accessible to a broader spectrum of applications. Moreover, the exploration of sustainable composite formation pathways is crucial as it not only reduces the environmental footprint of these technologies but also ensures a reliable and reproducible manufacturing process. This research frontier heralds a new era in materials science, pioneering methods to harness the synergistic effects between low-cost substrates and noble metals, culminating in highly efficient composite electrocatalysts. The concept of strong metal-support interaction further amplifies the catalytic potential of these composites, enhancing their stability and longevity in demanding electrochemical environments. This groundbreaking approach not only represents a triumph of innovation but also underscores the urgency of transitioning towards more sustainable energy paradigms. As the world grapples with the imperatives of climate change and energy security, these composite electrocatalysts stand poised at the forefront, poised to revolutionize how we generate, store, and utilize energy. Their far-reaching impact transcends the confines of the laboratory, offering a tangible pathway towards a more sustainable and resilient energy future. The seamless integration of costeffectiveness, high performance, and environmental consciousness embodied by these composite electrocatalysts exemplifies a paradigm shift in materials science, setting the stage for a new era of renewable energy technologies. This part of thesis can be concluded in the following way:

Chapter 4.1 describes the importance of highly electrocatalytically active and stable palladium nanoparticles, the traditional procedures of Pd loading on carbon supports and its hazards. Highly electrocatalytically active and stable palladium nanoparticles play a pivotal role in catalysis, particularly in energy conversion technologies like fuel cells and hydrogen

production. These nanoparticles offer a high surface area-to-volume ratio, providing abundant active sites for crucial chemical reactions. However, conventional procedures for loading palladium onto carbon supports entail the use of hazardous substances, such as strong acids or organic chemicals (capping agents) under high temperature and pressure, presenting risks to both the environment and human health. Additionally, these methods can lead to non-uniform distribution and clustering of palladium nanoparticles on the support, diminishing their catalytic efficiency and long-term stability. Thus, this chapter concludes that it is important to explore safer and more efficient techniques for palladium loading on carbon supports. By doing so, it is possible to significantly enhance the performance and reliability of electrochemical systems, propelling us towards a more sustainable materials production.

Chapter 4.2 identifies the photoactive centers in M-N-Cs and utilizes those for a sustainable Pd incorporation by the photochemical pathway. Our DFT investigations confirm that N₄ and MN₄ (M=Co) units within nitrogen-doped carbon (N-C), and atomically dispersed cobalt in Co-N-C, exhibit semiconductor-like properties. These act as embedded semiconductor centers within a conductive carbon framework, capable of harnessing natural sunlight. Furthermore, our DFT analyses reveal that the alignment of valence and conduction bands in these semiconducting centers is conducive to the photoreduction of noble metal salts like Pd²⁺. Experimental verification was achieved through the photodeposition of Pd NPs, exhibiting anticipated first-order kinetics at room temperature, resulting in crystalline nanoparticles. Anchoring these nanoparticles to N-C and Co-N-C supports limits their growth, yielding nanocrystals akin to commercial electrocatalysts. This method offers a distinct advantage, as deposition transpires at room temperature, utilizing renewable solar energy. Additionally, the absence of capping agents, often required with preformed nanoparticles on a catalyst support, facilitates mass transfer across the catalyst solution interface. Through both DFT analyses and experiments, we demonstrate that the presence of a Co atom between the Ndoped carbon support and Pd nanoparticle greatly facilitates charge transfer, leading to enhanced electrocatalytic activity of the deposited Pd nanoparticles. PdCo-N-C showcases proficient oxygen reduction reaction (ORR) activity in alkaline conditions, exhibiting an impressively high $E_{1/2}$. Moreover, it displays exceptional methanol tolerance and durability, with only a marginal shift in $E_{1/2}$ after prolonged catalytic cycles, owing to a more robust binding facilitated by Co-mediated charge transfer from Pd to the support. These discoveries solidify M-N-Cs as a promising catalyst-support class for noble metal electrocatalysts, opening up new avenues for their application in photocatalysis.

Chapter 4.3 depicts a unique synthetic protocol for scalable, uniform loading of Pd NPs on M-N-C with fine tuning of metal-support interaction. In this study, we present a method for loading Pd in a step-by-step fashion, resulting in both a uniform dispersion of Pd nanoparticles and a robust metal-support interaction. Through various spectroscopic techniques and DFT calculations, we observed a formal positive charge accumulation on Pd, which significantly enhances the kinetics of the oxygen reduction reaction (ORR). This effect is primarily attributed to the potent metal-support interaction facilitated by the photochemical process, while the initial dry-impregnation step ensures even distribution of Pd nanoparticles across the Co-N-C surface. Consequently, this sequential Pd decoration on Co-N-C yields exceptionally high ORR efficiency and remarkable stability. Furthermore, our study underscores that the prolonged durability of Pd nanoparticles on the Co-N-C surface is directly correlated with the strength of the metal-support interaction, highlighting its pivotal role in dictating electrocatalytic performance.

Future prospects

The recent breakthrough in the study of photodeposited Pd loading on M-N-Cs (Metal-Nitrogen-Carbon) have unveiled a remarkable potential for their application in various fields, particularly in the realm of photoactivity. This research has paved the way for a new era in renewable energy technologies, offering promising avenues in photoelectrochemical cells, solar batteries, and solar hydrogen peroxide (H_2O_2) production.

One of the most prominent applications of M-N-Cs' photoactivity lies in the development of efficient photoelectrochemical cells. By harnessing the power of sunlight, these cells convert solar energy directly into chemical energy, holding immense promise for sustainable energy generation.^{1,2} The unique electronic properties of M-N-Cs, characterized by their semiconducting nature, make them ideal candidates for photoanodes and photocathodes. These materials can significantly enhance the charge separation and transport within the cell, leading to higher overall conversion efficiencies. Additionally, the strong metal-support interaction in M-N-Cs may further enhance their stability, ensuring prolonged and reliable operation of photoelectrochemical cells.

The research on M-N-Cs photoactivity has also opened up exciting prospects in the development of advanced solar batteries. These batteries utilize sunlight to generate electrical energy, offering a clean and renewable alternative to conventional energy storage systems.³ M-N-Cs, with their exceptional semiconducting properties, can serve as photoactive components

within the battery structure. This enables them to efficiently capture and convert solar energy, which is then stored in the battery for later use. The integration of M-N-Cs in solar batteries has the potential to revolutionize energy storage technologies, making them more sustainable and environmentally friendly.

Another groundbreaking application of M-N-Cs photoactivity may be in the production of solar hydrogen peroxide (H₂O₂). H₂O₂ is a versatile chemical compound with numerous industrial applications, including water treatment, disinfection, and chemical synthesis. Conventionally, its production involves energy-intensive processes, making it a costly and environmentally taxing endeavour. However, the utilization of M-N-Cs as photocatalysts in H₂O₂ production offers a sustainable and energy-efficient alternative.^{4,5} These materials, with their unique electronic properties, facilitate the selective reduction of oxygen, leading to the synthesis of H₂O₂ under solar irradiation. This development holds immense potential for revolutionizing the H₂O₂ industry, making it more accessible and environmentally sustainable.

The current research work on M-N-Cs photoactivity in this part of thesis has illuminated a path towards a more sustainable and efficient future in renewable energy and chemical synthesis. The diverse applications discussed - in photoelectrochemical cells, solar batteries, and solar H_2O_2 production - showcase the versatility and transformative potential of these materials. As we continue to harness the power of sunlight, M-N-Cs stand as key players in driving the transition towards a cleaner, greener, and more sustainable energy landscape. Their incorporation in these technologies represents a significant step forward in our collective pursuit of a more sustainable and environmentally conscious future.

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Chapter 5

Carbon nanotube mediated completely noblemetal-free electrocatalysis
CHAPTER 5

5.1 Introduction

5.1.1 Prelude

Carbon nanotubes (CNTs) are a unique and important allotrope of carbon.¹ They are cylindrical structures with diameters on the nanometer scale and lengths that can reach several centimeters.² CNTs can be either single-walled or multi-walled, depending on the number of concentric cylinders they contain.³ The discovery and subsequent research on carbon nanotubes have had a significant impact on various fields, making it an important invention as CNTs possess high mechanical strength, excellent electrical and thermal conductivity, large surface area and remarkable flexibility.⁴

5.1.2 Synthetic strategies for CNTs

The synthesis of carbon nanotubes (CNTs) has evolved significantly over time, leading to various synthetic procedures.^{5,6} Among them arc discharge is the one of the earliest methods used for producing MWCNTs only.⁷ It involves applying vaporization of graphite while a high current is applied between two graphite electrodes in an inert atmosphere. Later, a process involving heat energy driven vaporization of graphite and subsequent condensation of carbon vapor was found to be effective for the formation of both MWCNTs and SWCNTs, known as laser ablation method. Both of these methods were limited to low scale and high cost. ⁸The most widely used procedure for large-scale production of CNTs at comparatively lower temperature is Chemical Vapor Deposition (CVD).⁹ While carbon precursors are incorporated into reactor in vapor form at controlled flow rate in CVD method, another process involving the vaporization of solid carbon precursor in the presence of a catalyst precursor, such as iron or cobalt was evolved as floating catalyst technique.^{10,11} The most sophisticated method for producing high quality CNT is template-assisted Growth where CNTs are grown within the pores of a template material, such as anodized aluminum oxide (AAO).¹²

5.1.3 Growth mechanism of CNTs

Carbon nanotubes (CNTs) exhibit diverse growth mechanisms, with two prominent modes: base-growth and tip-growth.^{13–15} These mechanisms govern how carbon atoms assemble into the cylindrical nanostructures. The interaction between catalyst and support substate decides the mechanism. In case of strong catalyst-support interaction CNTs grow in

base-growth mechanism. This process involves mainly two steps: nucleation of catalyst particles and carbon precipitation. Subsequently, carbon accumulates beneath this cap, forcing it to rise, similar to the growth rings of a tree. This process generally gives rise to single-walled carbon nanotubes (SWCNTs) with a consistent diameter. Contrarily, tip-growth involves the continuous elongation of a carbon nanotube from its apex where support-catalyst interaction is weak. This mechanism is notably observed in multi-walled carbon nanotubes (MWCNTs).

Furthermore, the Vapor-Liquid-Solid (VLS) mechanism is a vital to understand the CNT growth, especially in the base-growth mode.^{16,17} It involves the following stages: 1) Catalyst melting: Under high-temperature conditions, the metal catalyst particle melts and forms a liquid alloy with carbon. 2) Carbon dissolution: Carbon atoms from the feedstock gas dissolve into the molten catalyst. This supersaturated solution becomes enriched with carbon. 3) Nanotube precipitation: As the carbon concentration reaches a critical level, carbon starts to precipitate out of the catalyst, forming graphene layers. These layers stack to create the nanotube structure. The VLS mechanism significantly influences the diameter and chirality of the resulting nanotubes. The size and composition of the catalyst, as well as the growth temperature, play pivotal roles in determining the properties of the CNTs.

5.1.4 Diverse application of CNTs

Carbon nanotubes (CNTs) have garnered significant attention due to their extraordinary properties, making them a versatile material with diverse applications across various industries.¹⁸ CNTs are used as reinforcing agents in composites to enhance mechanical, thermal, and electrical properties. They are incorporated into polymers, ceramics, and metals, resulting in stronger and more lightweight materials. These nanocomposites find applications in aerospace, automotive, and sports equipment industries.¹⁹ CNTs possess excellent electrical conductivity, making them promising candidates for next-generation electronic devices like energy storage applications.^{20–22} The high surface area of carbon nanotubes (CNTs) plays a crucial role in their application in water purification and environmental remediation as they can adsorb contaminants like heavy metals, organic pollutants, and oils.²³ Besides, CNTs have garnered attention in biomedicine for drug delivery, imaging, and tissue engineering. Functionalized CNTs can serve as carriers for targeted drug delivery due to their high surface area and ability to encapsulate drugs.²⁴ Additionally, CNTs are also employed in various sensing technologies due to their high sensitivity to changes in the surrounding environment.

5.1.5 CNTs in electrocatalysis

Electrocatalysis holds immense potential to be a common global solution be integrating several geographically specific and often intermittent renewable energy resources throughout the world by means of fuel cells and storage batteries.^{25–27} But, currently effective electrocatalytic systems mainly involves costly, toxic, less-abundant noble metals like Pt and Pd.^{28–31} In this regard CNT can be a promising alternative as a metal-free electrocatalyst and it possess several potential properties to meet the desired efficiency.^{32–35} While graphene is known for its highest electrical conductivity, this inherent conductivity is preserved when rolled into a cylindrical form to create a nanotube.³⁶

5.1.6 Further research scopes in CNTs

As we venture into further research on CNTs, the field of carbon nanotubes (CNTs) presents an exciting frontier in materials science. Tailoring the properties of CNTs through controlled functionalization and doping processes opens up opportunities for customizing their behaviour for specific applications, from flexible electronics to reinforced composites. While fine-tuning of catalytic properties can be achieved through diverse synthetic strategies, understanding the governing factors behind these manipulations is paramount for unlocking their full potential. This precision not only augments their performance in a range of applications but also holds the promise of significantly enhancing the electrocatalytic activity of low-cost, first-row transition metal-based catalysts. New findings in this field can revolutionize electrocatalysis, offering a more economically viable and sustainable alternative for a wide array of energy conversion and storage technologies.

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CHAPTER 5.2

Mapping the effect of reaction atmosphere, catalyst dose and scalability in bamboo-like CNT synthesis for efficient electrocatalysis



Summary

Carbon nanotubes (CNTs) play vital role in electrocatalysis due to large surface area and unique one-dimensional conductivity, reducing electron scattering. The abundance of the defect sites in CNTs, the catalytically active sites vary based on synthesis methodology. While chemical vapor deposition (CVD) technique has been widely studied, a detailed correlation of the synthetic parameters in the floating catalyst method, with activity is missing. Scalability is also crucial to study as in CVD technique carbon vapor is injected into the furnace but floating catalyst method relies on in-situ vapor generation from solid carbon precursors. We have mapped catalyst dosage and reaction atmosphere's impact on electrocatalytic efficiency for various **CNTs** produced under different conditions towards the oxygen reduction reaction (ORR) and rationalised the variation in activity by spectroscopic evidences. Optimized CNTs exhibit a high electrocatalytic ORR efficiency with prolonged durability, highlighting the role of the interaction between CNTs and encapsulated iron nanoparticles in response to reaction atmosphere.

‡Manuscript based on this work is under revision.

5.2.1 Introduction

Electrocatalysis facilitates the direct conversion of chemical energy from fuels into electricity without combustion resulting in minimal emissions, crucial for achieving renewable energy generation.¹⁻⁶ The conventional efficient electrocatalytic systems often rely on highly expensive and rare noble metals such as Pt, Pd etc.⁷⁻¹⁴ In such electrodes, high surface area conducting carbon is used as a catalyst support in order to arrest their agglomeration on the electrode surface which can tremendously increase contact resistance and reduce catalytic efficiencies.¹⁵⁻¹⁹ Considering such electrode configurations, CNTs are deemed as advantageous because of the large surface area, high conductivity, and absence of grain boundaries, promoting better conduction.²⁰⁻²⁴ In addition, CNTs exhibit other important features such as one-dimensional conductivity minimizing scattering of electrons and suitable for long-range electron transport along the length of the nanotube with minimum lateral current spreading or leakage.²⁵⁻²⁷

For large-scale implementation of CNTs in electrocatalysis, there is a crucial role of rational choice of production conditions towards achieving scalable, sustainable production. The synthesis of carbon nanotubes (CNTs) has evolved significantly over time, leading to various synthetic procedures.^{28,29} Among them, arc discharge is one of the earliest methods used for producing MWCNTs only.³⁰ Later, a process known as laser ablation method was evolved to effectively forming both MWCNTs and SWCNTs.³¹ The most widely used procedure for large-scale production of CNTs at comparatively lower temperatures is Chemical Vapor Deposition (CVD).^{32,33} While carbon precursors are incorporated into the reactor in vapor form at controlled flow rate in CVD method, another process involving the vaporization of solid carbon precursor in the presence of a catalyst precursor, such as iron or cobalt was evolved as floating catalyst technique.^{34,35}

The active sites of carbon nanotubes (CNTs) responsible for electrocatalysis can vary depending on the structure of CNT synthesized in a particular synthetic strategy. Some of the active sites of CNT, often attributed for the electrocatalysis are tube ends and edge defects, which can interact with reactants and facilitate catalytic processes.³⁶ Besides, doped nitrogen centers, encapsulated iron nanoparticles, single atom Fe-N_x sites are also responsible for tuning electronic structure and adsorbing reactant on CNTs.³⁷⁻³⁹ The abundance of these various catalytically active sites may vary depending on the synthetic strategies.⁴⁰ Factors contributing to variation in all these parameters include the catalyst's chemical environment and the reaction

atmosphere. In this regard, a thorough study on the oxidation state of catalyst as a function of reaction atmosphere is of utmost important.

5.2.2 Scope of the present investigation

Along with the optimization of the reaction conditions, the scalability of a process for achieving a highly efficient CNTs should be explored in order to understand the potential of a particular synthetic strategy in the perspective of high-scale implementation. For example, although high scalability is achieved by CVD technique as carbon vapor is injected but in case of floating catalyst pathway there is a need of optimization in the carbon precursor loading to achieve highly efficient CNTs as here carbon vapor gets in-situ generated from solid carbon precursor.⁴¹ Despite several reports on optimizing the reaction conditions in CVD technique,^{42–46} detailed documentation and experimental evidence supported rationalization of the role of different synthetic parameters for the floating catalyst technique has so far been overlooked in the literature.

Herein, we report on a thorough study on the effect of different factors involved affecting the electrocatalytic activity of bamboo-like multi-walled CNTs synthesized in a floating catalyst technique. First, we optimized the catalyst load for growth of CNTs and rationalised the optimized result by analysing Raman spectra of different CNTs produced which revealed that catalyst dose is efficacious towards the conductivity of CNTs obtained. Second, we have evaluated the limit of scalability while achieving high quality CNTs by varying the amount of carbon precursor at a fixed catalyst load. Third, to know the effect of the reaction atmosphere for synthesis of CNTs, keeping the optimized catalyst dose intact, the reaction atmosphere was varied from completely inert argon and nitrogen to extreme reducing environment of 5% H₂/Ar at an optimum reaction scale and analysed by x-ray photoelectron spectroscopy (XPS). This indicated that the metallic iron content increases in more reducing environment which facilitates the electrocatalysis. Benefitting from these observations, the optimized catalyst Fe_{0.5}CNT₄(H₂/Ar) exhibits superior catalytic activity towards ORR with E_{1/2} = 0.85 V *vs.* RHE. Thus, this study provides a thorough guideline towards rational choice of reaction parameters for producing highly efficient CNTs for electrocatalysis.

5.2.3 METHODS

5.2.3.1 Synthesis of bamboo-like CNTs

8 ml ethanolic solution of x millimole iron nitrate (FeNO₃. 9H₂O) were drop casted evenly on a silica boat placed in a dry air oven at 60° C.⁴⁷ The boat was kept undisturbed for 2 h so that ethanol was completely evaporated. After that the boat was placed inverted at the top of another boat containing y g of melamine powder. Then that assembly of two boat was placed inside an alumina tube furnace and subjected to heating at 800 °C for 3 h at 5 °C min⁻¹. After the completion of reaction, the tube furnace was allowed to cool down naturally and sample on the inverted boat was scratched by a spatula and labelled as Fe_xCNT_y(atmosphere).

5.2.3.2 Characterization

All characterization techniques have been discussed in detail in chapter 2.

5.2.3.3 Evaluation of catalytic activity

5.2.3.3.1 Preparation of working electrode

Firstly, the glassy carbon (GC) rotating disk electrode (RDE) was polished using 0.05 μ m alumina powder and cleaned thoroughly with water and isopropyl alcohol. Subsequently, an electrocatalyst ink was prepared by dispersing 1 mg of the catalyst in a solution comprising 100 μ l of Nafion, isopropanol, and water in a 0.05:1:4 (v/v/v) ratio. This mixture was ultrasonicated for approximately 30 minutes. Next, 5 μ l of the catalyst ink was carefully drop-casted onto a clean and polished glassy carbon (GC) rotating disk electrode (RDE), which possessed a geometric surface area of 0.0707 cm². The electrode was allowed to air dry overnight at room temperature. The calculated loading of catalyst on the electrode surface was 0.707 mg/cm².

5.2.3.3.2 Electrocatalytic performance evaluation

The general procedure for the evaluation of ORR and OER activities are outlined in section 2.2 of chapter 2.

5.2.4 RESULTS AND DISCUSSION

Bamboo-like multi-walled carbon nanotubes were synthesized following a facile synthetic strategy reported previously.⁴⁷A cheap carbon precursor, melamine was subjected to heating in an inert atmosphere while exposing it to commercially viable iron salt as a catalyst immobilized on an alumina crucible for growing a CNT network at its surface. As

shown in **Fig. 5.2.1**, the CNTs were produced in a novel synthetic arrangement. Melamine was kept in an alumina crucible put at the bottom of an inverted alumina where ethanolic solution of a definite concentration of iron nitrate was drop casted at its inner surface. At first, CNT was produced with 4 g of melamine and using 0.5 mmol iron nitrate under nitrogen



Figure 5.2.1 Schematic representation of the synthetic approach for FeCNT.

atmosphere and as-synthesized black sample was collected by scratching the inner surface of inverted boat and marked as $Fe_{0.5}$ CNT₄(N₂). The tubular morphology of as-synthesized $Fe_{0.5}$ CNT₄(N₂) was first confirmed by scanning electron microscopy (SEM) (**Figure 5.2.2a**). **Figure 5.2.2b** depicts the bamboo-like CNTs where iron nanoparticles are confined within the diameter of CNTs as found in its low-magnification transmission electron microscopic (TEM) images. A high- resolution TEM image (**Figure 5.2.2c**) of CNT demonstrates the highly crystalline feature of the Fe NPs along with the lattice fringes observed for the carbon walls of CNTs. The fringe lines observed in inset of **Figure 5.2.2c** with d-space = 0.21 nm were attributed to the presence of Fe (110) lattice.⁴⁸ The presence of iron nanoparticle confined inside the bamboo-like CNTs was further visualised by the distinct contrast observed for metal nanoparticle in STEM image as shown in **Figure 5.2.2d**. The confinement of iron nanoparticle inside the CNT wall and homogeneity of *in-situ* doped nitrogen arising from vaporisation of melamine was depicted by the elemental mapping recorded using energy dispersive X-ray spectroscopy (EDS) as shown in **Figure 5.2.2e**.

After successfully producing the CNTs as confirmed from the morphological analysis, same synthetic strategy was repeated involving three different iron nitrate solution by varying the iron catalyst dose (0.1, 0.5, 1 mmol). Transmission electron microscopic (TEM) images (**Figure 5.2.3**) confirmed the growth of tubular carbon nanostructures in each case. The powder X-ray diffraction (PXRD) patterns (**Figure 5.2.4**) of all those CNTs confirmed the (002) planes of graphitic carbon from the carbon support are reflected at $2\theta = 24.8^{\circ}.4^{9}$ In those

diffraction patterns the peaks at $2\theta = 44.6^{\circ}$ and 65° respectively indicate the presence of (110) and (200) planes of Fe in Fe-NPs confined inside the CNTs as also confirmed before by their microscopic images (JCPDS No. 65-4899).⁵⁰⁻⁵² Along with the Fe diffraction peak corresponding to $2\theta = 44.6^{\circ}$, an additional peak can also be observed at $2\theta = 43.4^{\circ}$ in all the samples, indicating the presence of Fe₃C lattice (JCPDS No. 89-2867).^{53,54} Carbon dissolution in the Fe lattice during the initiation of CNT growth can be attributed to the existence of such Fe₃C lattices.⁵⁵ The intensity of the peak corresponding to both Fe and Fe₃C gradually increases with the increase in the molarity of iron nitrate solution. To correlate this enhanced peak intensity in PXRD pattern with increase in iron catalyst dose, the obtained iron content in all the samples was determined by performing thermogravimetric analysis (TGA) (Figure 5.2.5a) in air with temperature elevated from 25 °C to 850 °C. As suggested by the PXRD pattern of residues collected after all the TGA experiments it was found that the aerobic heat treatment of the sample led to formation of Fe₃O₄ as residue (Figure 5.2.5b).⁵⁶ Therefore, with respect to the theoretical wt.% of Fe in Fe₃O₄ the iron contents in those samples were calculated as 8.84%, 9.96% and 11.4% for Fe_{0.1} CNT₄(N₂), Fe_{0.5} CNT₄(N₂), and Fe_{1.0} $CNT_4(N_2)$ respectively (Fig. 5.2.6a). In line with this trend there was significant difference encountered in their performance in ORR electrocatalysis as discussed later.



Figure 5.2.2 Microscopic analysis of the $Fe_{0.5}CNT_4(N_2)$: (*a*) *SEM image*, (*b*) *low-magnification TEM image, and* (*c*) *high-resolution TEM image (inset shows the lattice fringe corresponding to Fe).* (*d*) *The corresponding STEM image and* (*e*) *elemental mapping.*



Figure 5.2.3 TEM images of $Fe_{0.1}CNT_4(N_2)$ and $Fe_{1.0}CNT_4(N_2)$.



Figure 5.2.4 PXRD patterns of CNTs synthesized in N_2 atmosphere having different iron content.



Figure 5.2.5 (*a*) *Thermal gravimetric analysis (TGA) plots of CNTs synthesised using different iron content in nitrogen atmosphere. (b) PXRD pattern of the residue collected after TGA.*



Figure 5.2.6 (a) the percentage by weight of iron present in different samples determined from TGA analysis. (b) Raman spectra of $Fe_{0.5}CNT_4(N_2)$, $Fe_{0.1}CNT_4(N_2)$, and $Fe_{1.0}CNT_4(N_2)$.

To study the effect of this variation in the iron content on both the CNT growth and the carbon lattice of the different CNTs produced by varying the iron catalyst dose, Raman spectroscopy was performed to study the extent of graphitization in different samples as the electrocatalytic performance of carbon-based materials as the conductivity of carbon nanostructure depends on the degree of graphitization the catalyst. Two distinct peaks were found in the Raman spectra of all the samples (Figure 5.2.6b) as identified at ~1328 cm⁻¹ as the D band and ~1586 cm⁻¹ as the G band.⁵⁷ The intensity of G- and D-band indicates the degree of graphitization and extent of defects in the carbon lattice respectively. The I_G/I_D ratios of different samples were calculated as 0.996, 1.09, and 1.04 for Fe_{0.1}CNT₄(N₂), $Fe_{0.5}CNT_4(N_2)$ and $Fe_{1.0}CNT_4(N_2)$ respectively (Figure 5.2.7a). The highest graphitization observed for Fe_{0.5}CNT₄(N₂) explains its best electrocatalytic activity as shown later due to improved conductivity as the conjugated pi-network is responsible for the conductivity of CNTs. ^{58,59} It is noteworthy that the defects at the wall of CNTs are potential active sites for ORR as the hydrogenation of O₂ to OOH* intermediate is known to be facilitated by these defects. ⁴⁰ The value of I_G/I_D of the optimized sample (Fe_{0.5}CNT₄(N₂)) was not much elevated from unity, indicating the presence of sufficient number of edge-defects in the sample. Hence, this optimization of iron catalyst amount results in an optimized interplay between the degree of graphitization, crucial for conductivity and abundance of defects, active sites for oxygen reduction reaction. Another crucial information about number of exposed active sites was derived from the determination of specific surface areas of the samples as estimated from BET surface area measurement, shown in Figure 5.2.7b. The CNTs with optimized iron content (Fe_{0.5} CNT₄(N₂)) possesses the specific surface area of 27 m^2/g which is comparable with previous reports. The plot of N₂ adsorption-desorption isotherms of all the samples and the corresponding multipoint BET plots are shown in Figure 5.2.8.



Figure 5.2.7 (*a*) *Plot showing the extent of graphitization in various CNTs synthesized using different amount of iron catalyst.* (*b*) N_2 *adsorption-desorption isotherms of* $Fe_{0.5}CNT_4(N_2)$ *at 77K; inset showing the BET multipoint plot of same*).



Figure 5.2.8 (a, b) N_2 adsorption-desorption isotherms, and (c, d) BET multipoint plot of $Fe_{0.1}CNT_4(N_2)$ and $Fe_{1.0}CNT_4(N_2)$, respectively.

After optimizing the catalyst dose, further attempt was made to evaluate the scalability of the process by varying the precursor dose. As shown in **Figure 5.2.9a** the highest scalable production in this process up to 4 g of melamine as a carbon precursor. Carbon nanotube growth is only initiated when the concentration of carbon vapor inside the Fe lattice exceeds carbon dissolution saturation. Therefore, initially certain amount of carbon precursor gets utilized to saturate the iron lattice before producing the CNT and with subsequent increase in carbon precursor, the excess carbon vapor contributes in the increase in the yield of CNTs. It is noteworthy that with increase in carbon precursor, vapor pressure of carbon inside the closed sandwich reactor increases which leads to enhanced molecular motion. When the kinetic energy of carbon vapor exceeds a certain limit, running away of carbon vapor from the vicinity of iron catalyst results in loss in the yield of carbon nanotube.

With these optimized reaction condition with catalyst dose as 0.5 millimole of iron nitrate and 4 g of carbon precursor, the reaction atmosphere was further varied to check the

effect of catalyst oxidation state. The presence of encapsulated iron in the different CNTs synthesized in varied reaction atmosphere was confirmed by their corresponding PXRD pattern as shown in **Figure 5.2.9b**.⁵⁰ From the TGA analysis (**Figure 5.2.10a**) as discussed before, as shown in **Figure 5.2.10b** the Fe_{0.5}CNT₄ synthesized in hydrogen-rich environment showed a little higher (10.4%) iron content whereas the same produced under argon atmosphere contains a slightly reduced (9.5%) amount of iron compared to that (9.96%) obtained in nitrogen environment. This variation can be understood by the trend in the abundance of Fe-N_x species in the corresponding samples as the metal retention during the calcination process is supposed to be higher where iron exists predominantly as strongly bound to the nitrogen, as discussed in detail below by XPS analysis.



Figure 5.2.9 (a) Plot showing the yield of CNTs synthesized using different amount of melamine. (b) PXRD patterns of $Fe_{0.5}CNT_4(N_2)$, $Fe_{0.5}CNT_4(H_2/Ar)$ and $Fe_{1.0}CNT_4(Ar)$ CNTs, respectively synthesized in different atmosphere having same iron content.



Figure 5.2.10 (a) Thermal gravimetric analysis (TGA) plots of CNTs synthesised in different atmosphere using same iron content. (b) iron content (wt.%) in various samples estimated from TGA analysis.

X-ray photoelectron spectroscopy (XPS) analysis depicts the relative compositions of different metallic species in as-synthesized materials. In all the high-resolution Fe 2p scan the peak centered at 707.3 and 720.3 eV indicate the presence of Fe (0), while those at 709.8 and 722.9eV suggest the presence of Fe (+2), and those at 712.6 and 725.7 eV are attributed to Fe (+3). In the same spectrum, the peak at 711.3 eV corresponds to those Fe atoms those (Fe-N_x) are directly attached to N in the carbon whereas the rest two peaks at 716.5 and 728.3 eV are the satellite peak (Figure 5.2.11a-c).^{16,60} The relative abundance of Fe-N_x in the different samples determines the availability of excess active sites along with the intrinsic active sites of the CNTs such as edge-defects, doped nitrogen centers etc.,⁶¹ found to be the highest in Fe0.5 CNT₄(H₂/Ar) and a slight decline was found in Fe0.5CNT₄(N₂) as displayed in Figure **5.2.11d**. However, there is a significant fall in the relative abundance of $Fe-N_x$ species in case of $Fe_{0.5}CNT_4(Ar)$. This Fe-N_x sites arises from the interaction between Fe (0) and nitrogen centers and consequently a Fe to N back electron transfer induces a formal positive charge on Fe-Nx sites, favourable for O₂ adsorption and hence responsible for accelerating ORR kinetics.⁶² The trend in relative abundance of Fe-N_x sites in different CNTs are in line with the variation observed in relative abundance of metallic iron (Fe (0)) as depicted by Figure **5.2.11e.** This observation can be understood by considering the strong reducing nature of hydrogen atmosphere and the higher thermal conductivity of nitrogen than argon.^{63,64} Furthermore, the relative ratio between the abundance of $Fe-N_x$ with respect to that of Fe (0)

as found to in same trend as shown in **Figure 5.2.11f** suggests the extent of charge-transfer between Fe and N, indicating the strength of metal-support interaction in a catalyst which is crucial for facile electrical conductivity at the electrode-electrolyte interface.⁶²



Figure 5.2.11 High-resolution Fe 2p XPS spectra of (a) $Fe_{0.5}CNT_4(Ar)$ (b) $Fe_{0.5}CNT_4(N_2)$ and (c) $Fe_{0.5}CNT_4(H_2/Ar)$. (d &e) Relative contents of metallic iron and $Fe-N_x$ moieties present in different samples synthesised under different reaction atmosphere. (f) Plot showing the relative ratio of FeN_x moieties to metallic iron in various samples estimated from XPS.

The ORR electrocatalytic performance of all the samples was examined with rotating disk electrode (RDE) measurements in 0.1 M KOH solution saturated with oxygen. From the linear sweep voltammetry (LSV) curves (**Figure 5.2.12a**), it has been found that CNTs with optimized amount of iron content $Fe_{0.5}CNT_4(N_2)$ shows good oxygen reduction capacity with more positive onset potential of 1.01 V and half wave potential ($E_{1/2}$) of 0.83 V compared. The corresponding $E_{1/2}$ and onset potential of samples having different iron content summarized in **Figure 5.2.12b**. The enhanced performance of $Fe_{0.5}CNT_4(N_2)$ is attributed to improved conductivity of catalyst due to the highest graphitization revealed from Raman analysis and lower charge transfer resistance among all other samples in the Nyquist plot.⁶⁵ (**Figure 5.2.13**).



Figure 5.2.12 (a) LSV curves of $Fe_{0.1}CNT_4(N_2)$, $Fe_{0.5}CNT_4(N_2)$, and $Fe_{1.0}CNT_4(N_2)$ recorded at 1600 rpm in O_2 saturated alkaline electrolyte with scan rate of 10 mV/sec. (b) Comparison of onset potentials and $E_{1/2}$ of the various samples having different iron content.



Figure 5.2.13 Nyquist plots of samples recorded in 0.1 M KOH.

To study the effect of reaction atmosphere, the electrocatalytic activity of FeCNT synthesised in different atmosphere was evaluated under identical reaction conditions. The corresponding ORR polarization curves shown in **Figure 5.2.14a** and the Fe_{0.5}CNT₄ synthesized in H₂/Ar atmosphere shows the highest electrocatalytic ORR efficiency with positive onset potential of 1.03 V and E_{1/2} of 0.85 V as compared to the ones made in nitrogen and argon atmosphere. As shown in **Figure 5.2.14b**, these parameters demonstrate significant enhancement in Fe_{0.5}CNT₄(H₂/Ar) over Fe_{0.5}CNT₄(Ar) (with an onset potential of 0.92 V and E_{1/2} of 0.75 V) and Fe_{0.5}CNT₄(N₂) (with an onset potential of 1.01 V and E_{1/2} of 0.83 V). The

improved electrochemical activity of $Fe_{0.5}CNT_4(H_2/Ar)$ is due to presence of high metallic iron and hence more Fe-N_x sites due to highly reductive atmosphere compared to others as discussed in XPS analysis earlier. Thus, it can be concluded that there is role of reducing environment to enhance the electrochemical activity of CNTs towards ORR. The increment in the relative abundance of Fe-N_x in Fe_{0.5}CNT₄(H₂/Ar) is expected to reduce the resistance at electrode-electrolyte junction which is reflected in the lowest charge-transfer resistance observed in the corresponding Nyquist plot (**Figure 5.2.14c**) derived by performing electrochemical impedance spectroscopy (EIS).



Figure 5.2.14 (a) ORR polarization curves of $Fe_{0.5}CNT_4(N_2)$, $Fe_{0.5}CNT_4(H2/Ar)$, and $Fe_{0.5}CNT_4(Ar)$ in 0.1 M KOH solution. (b) Comparison of $E_{1/2}$ and onset potential of various FeCNT samples. (c) Nyquist plot of samples in 0.1 M KOH.

The kinetics of the oxygen reduction reaction (ORR) were investigated by recording the polarization curves at different rotation rates, ranging from 400 to 2400 rpm (**Figure 5.2.15-5.2.17**). The electron transfer numbers (n) per oxygen molecule in ORR process was determined using the Koutecky-Levich (KL) equation. The calculated n for $Fe_{0.5}CNT_4(H_2/Ar)$

was found to be 3.91 indicating the preferred 4 electron ORR pathway. The n values were also calculated as 3.89 for $Fe_{0.5}CNT_4(N_2)$ and 3.86 for $Fe_{0.5}CNT_4(Ar)$ under similar conditions. In order to provide additional confirmation of the nearly ideal electron transfer numbers (n), rotating ring disk electrode (RRDE) experiments were conducted to evaluate the percentage of H_2O_2 formed through the 2-electron pathways. The average percentage of peroxide yield is less than 5% (**Figure 5.2.18**) again confirming that the catalytic reduction of oxygen follows 4-electron pathway.



Figure 5.2.15 (a) ORR polarization curves of $Fe_{0.5}CNT_4(H_2/Ar)$ recorded at different rotation rates in O₂ saturated 0.1 M KOH with a scan-rate of 10 mV/s, b) the corresponding K-L plots at different potentials w.r.t. RHE.



Figure 5.2.16 (a) ORR polarization curves of $Fe_{0.5}CNT_4(N_2)$ recorded at different rotation rates in O₂ saturated 0.1 M KOH with a scan-rate of 10 mV/s, b) the corresponding K-L plots at different potentials w.r.t. RHE.



Figure 5.2.17 (a) ORR polarization curves of $Fe_{0.5}CNT_4(Ar)$ recorded at different rotation rates in O₂ saturated 0.1 M KOH with a scan-rate of 10 mV/s, b) the corresponding K-L plots at different potentials w.r.t. RHE.



Figure 5.2.18 H₂O₂ yield estimated from RRDE tests in the range of 0.2-0.8 V (vs. RHE).

To evaluate the durability of the optimized catalyst $Fe_{0.5}CNT_4(H_2/Ar)$, an accelerated durability test (ADT) was carried out by subjecting the catalyst to continuous cyclic voltammetry (CV) cycles ranging from 0.6 to 1.1 V *vs*. RHE in an oxygen-saturated alkaline electrolyte. The linear sweep voltammetry (LSV) curves were compared before and after 10,000 continuous cycles (**Figure 5.2.19a**), revealing nearly identical onset potential and negligible shift in $E_{1/2}$. To assess resistance to methanol crossover, methanol (final concentration of 1 M) was injected into the electrolyte after 100 seconds of the measurements. This resulted in a minor change in the oxygen reduction reaction (ORR) current of

 $Fe_{0.5}CNT_4(H_2/Ar)$. However, for commercial Pt/C, a notable and rapid reduction in current was observed (**Figure 5.2.19b**).



Figure 5.2.19 (a) ORR polarization curves of $Fe_{0.5}CNT_4(H_2/Ar)$ before and after the durability test. (b) Chronoamperometry plot of $Fe_{0.5}CNT_4(H_2/Ar)$ and Pt/C before and after addition of methanol (1 M) after 100 s.

5.2.5 CONCLUSIONS

We have performed an extensive study on the reaction parameters involved in the CNT production by a floating catalyst method. We demonstrate and rationalize that after a certain dose of catalyst used for the growth of CNTs, the electrocatalytic activity of CNTs starts degrading. This study shows that floating catalyst technique is able to produce CNTs in a facile manner avoiding sophisticated arrangements used during CVD technique. Hence, as the source of carbon for CNT growth is supplied by *in-situ* vaporisation of solid carbon precursors, its scalability is limited up to certain level of solid carbon precursor. Furthermore, it is revealed that oxidation state of the encapsulated iron nanoparticles varies with the reaction atmosphere of the CNTs growth that is found to alter the electrocatalytic efficiencies of CNTs. In the CNTs produced under reducing hydrogen atmosphere, the relative abundance of metallic iron (Fe(0)) was found to be the highest compared to those made under inert atmospheres. Among nitrogen and argon atmospheres, nitrogen results in relatively higher metallic iron in the CNTs obtained under N₂ atmosphere compared to those synthesized under argon atmosphere. Consequently, a higher content of Fe-N_x species, which are responsible for bringing high electrocatalytic performances as reflected in our electrochemical studies. The trend in performance as 5% $H_2/Ar > N_2 > Ar$ was found as result of back electron transfer from Fe to N, resulting in a positive formal charge on Fe facilitating the oxygen adsorption and hence accelerating the kinetics of oxygen reduction reaction. Most importantly, the relative ratio of $Fe(N_x)$ to Fe(0) depicts the extent of Fe-N interaction, crucial for strong metal-support interaction. This enhanced metalsupport interaction is reflected in the trend observed in charge-transfer resistance by electrochemical impedance spectroscopy (EIS) of the optimized CNT (Fe_{0.5}CNT₄(H₂/Ar)). This study depicts a thorough investigation on the optimized reaction parameters and scalability of CNTs production by floating catalyst method and offers insight into the origin of the variation in catalytic properties.

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CHAPTER 5.3

Extending conducting channels in Fe-N-C by interfacial growth of CNT with minimal metal loss for efficient ORR electrocatalysis



Summary

Achieving high electrocatalytic performance by completely metal-free electrocatalyst, preferably based on only carbonaceous materials remains a challenge. Alternatively, an efficient composite of carbon nanostructure and non-noble metal with minimum dependence on metal holds immense potential. Although single atom catalysis brings superior performance, its complex synthetic strategy limits its large-scale implementation. Previous investigation has shown that atomic dispersion (Fe-N_x-C) is accompanied by higher metal-loss compared to nanoparticle formation (Fe-NPs-N-C). Therefore, to achieve minimum metal loss, we first incorporated iron nanoparticles (Fe NPs) on N-doped carbon (N-C) and then exposed to a cheap carbon source, melamine at high temperature, resulting in the growth of carbon nanotube (CNT) catalysed by the very Fe NPs loaded on N-C (Fe-NPs-N-C). Thermogravimetric analysis showed that the metal-retention in the composite is higher than the bare carbon nanotube and even the atomically dispersed Fe-active sites on N-C. The composite material (Fe-NPs-N-C/CNT) shows a high half-wave potential (0.89 V vs. RHE) which outperforms commercial Pt/C towards oxygen reduction reaction (ORR). The enhanced activity is attributed to the synergistic effect of high conductivity of CNT and active Fe-sites as the composite exceeds the individual electrocatalytic performance shown by Fe-CNT & Fe-NPs-N-C, even atomically dispersed Fe-active sites on N-C.

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5.3.1 Introduction

Renewable energy technologies, such as fuel cells, batteries, and water splitting hold immense potential to mitigate global energy and environmental crisis.¹⁻¹⁴ Noble-metal catalysts (e.g. Pt, Pd) are generally employed to promote the chemical transformations involved in such green energy production processes like the oxygen reduction reaction (ORR) in fuel cells.¹⁵⁻²¹ The limited resources and hence the high cost of the noble-metal-based catalysts diminish the industrial implementation prospects of such sustainable energy conversion technologies. Besides, the use of any metal is inevitably accompanied by a complex industrial sewage management process since even the first-row transition metals at higher concentration results in severe toxicity.^{22,23} Therefore, there is a high demand of completely metal-free electrocatalyst based on carbon-based materials.

But realization of such carbon-based catalytic system remains a challenge. Firstly, their catalytic efficiencies still need to be boosted enough to fulfil the commercial requirements.^{24,25} Secondly, precise elucidation of the structure of whole catalyst and identification of specific active sites is still in its infancy.²⁶ Thirdly, anisotropic behaviour of such carbon-based catalysts makes the electrode fabrication process much complex.²⁷ Therefore, it is still challenging at current stage for carbon-based catalysts to substitute metal-counterparts in commercial applications.

However, considerable attempts have been made to replace the noble-metal by making composite of transition metal and carbon-based materials.^{28,29} In this regard atomic dispersion of transition metal on nitrogen doped carbon (M-N-C) has emerged as one of the most promising alternatives.³⁰⁻³² But complex multistep synthetic protocols of M-N-C has limited its large-scale production. Furthermore, our previous investigation showed that atomic dispersion (Fe-N_x-C) leads to higher metal-loss compared to nanoparticle formation (Fe-NPs-N-C).³³ Such metal-loss occurring during a high-temperature process contributes to the uncontrolled waste which at industrial-scale will put extremely negative impact on environment.²² On the other hand, in nanoparticles there are many active-sites which remain unexposed and hence unutilized. Therefore, nanoparticle-based catalysts with extended conducting network can bring high atom-economy and minimal metal-loss together, and hence hold potential to show superior electrocatalytic performance as a sustainable substitute to the precious, toxic noble-metal based electrocatalyst.

5.3.2 Scope of the present investigation

Such extended conducting channels are possible to bring into carbon-supported transition metal nanoparticles by growing carbon nanotubes (CNTs) at its surface as CNTs exhibit high conductivity and extremely high mechanical and thermal stability.³⁴⁻³⁸ Apart from its wide use in electronics CNTs also serve a crucial role of adsorbent as it is highly used in wastewater treatment because of their large surface area, offering huge potential to enhance active surface-sites in a composite of carbon-supported nanoparticle and CNTs.³⁹⁻⁴¹ The chemical vapor deposition (CVD) process has emerged as a preferred synthesis route due to the choice of a wide variety of carbon precursors and comparatively lower synthesis temperature (~800⁰ C).^{42,43} This comparatively low-temperature synthesis of CNTs requires a metal catalyst (generally, iron) for its growth.

The growth of CNTs in CVD technique follows two mechanistic pathways namely, tipgrowth and base-growth mechanism.⁴⁴⁻⁴⁶ The base-growth mechanism is followed in the case of strong catalyst (iron)-substrate interaction whereas CNT grows following the tip-growth mechanism where the catalyst (iron)-substrate interaction is poor.⁴⁷ Therefore, there is a crucial role of iron-substrate interaction in the growth of CNT. Besides in case of unsupported bare CNT synthesis, iron catalyst is served as a naive coating (generally, evaporation-derived) placed in the vicinity of carbon precursor and hence there is a scope of potential metal-loss as the iron loosely bound to the reactor vessel is prone to vaporisation at high-temperature. Instead, a Fe-NPs anchored on a nitrogen-doped carbon can effectively grow carbon nanotube at its surface.

Herein, we firstly, incorporated Fe-NPs on the surface of nitrogen-doped carbon (N-C) sheets following a facile synthetic strategy and then, CNTs were grown at the surface of Fe NPs loaded NC (Fe-NPs-N-C) using an inexpensive carbon precursor. We observed that retention of iron-content in this composite is 3-fold higher than unsupported bare CNTs, indicating a much higher metal precursor utilization involved in the composite formation compared to bare CNT production. The conducting CNT network synergistically boosts the electrocatalytic activity of N-C supported Fe NPs by improving the charge-transfer resistance tremendously due to additional conducting CNT channels. The composite not only shows a high ORR activity ($E_{1/2} = 0.89$ V *vs.* RHE) but also outperforms the commercial Pt/C and demonstrates its recyclability with negligible decline in activity up to 10000 cycles. Besides the composite exhibits enhanced electrocatalytic activity than that showed by the Fe-NPs-N-C and Fe-CNT individually. Most interestingly, the catalytic activity of this catalyst exceeds the

performance we previously reported for atomically dispersed Fe on nitrogen-doped carbon (Fe-N-C) which was achieved with lower metal-retention as compared to Fe-NPs-N-C and hence demonstrates itself as a bridge to bring in high atom-economy and elevated metal-retention together.

5.3.3 METHODS

5.3.3.1 Synthesis of Fe-NPs-N-C

For the synthesis of iron nanoparticles encapsulated in nitrogen doped carbon iron chloride, melamine and pre-treated Vulcan carbon was used as sources of iron, nitrogen and carbon respectively.³³ Typically, 0.5 mmol (135 mg) FeCl₃.6H₂O were mixed with 1.4 g of melamine and 400 mg of pre-treated Vulcan carbon using mortar and pestle. Next, the mixture was transferred into silica boat and pyrolyzed at 350 °C for 20 min in the tube furnace under inert atmosphere (N₂) followed by 600 °C for 1 h (heating rate of 4 °C min⁻¹) and thereafter at 800 °C (heating rate of 1 °C min⁻¹) for 2 h. After cooling down naturally, the resulting black sample was labelled as Fe-NPs-N-C. Similar preparation scheme was followed to produce bare nitrogen-doped carbon (N-C) in absence of iron salts.

5.3.3.2 Synthesis of Fe-NPs-N-C/CNT

The as-synthesized Fe-NPs-N-C (10 mg) was dispersed in ethanol (8 ml) by sonication for 5 min followed by stirring for 12 h. The resulting solution was then dropcasted evenly on a silica boat placed in an oven. The boat was kept undisturbed for 2 h so that ethanol was completely evaporated. Then this boat was placed inverted at the top of another boat containing 4 g melamine. Thereafter sample was heated at 800 °C in a tube furnace for 3 h with heating rate of 5 °C/min in N₂ atmosphere. After the reaction was completed, the tube furnace was allowed to cool down naturally and sample on the inverted boat was scraped off and resulting sample was named as Fe-NPs-N-C/CNT. For comparison, similar synthetic strategy was adopted to produce iron nanoparticle encapsulated carbon nanotube (Fe-CNT) by drop casting iron salt on the silica boat.

5.3.3.3 Characterization

All characterization techniques have been discussed in detail in chapter 2.

5.3.3.4 Evaluation of catalytic activity

5.3.3.4.1 Preparation of working electrode

A glassy carbon (GC) rotating disk electrode (3mm in diameter, working area = 0.0707 cm^2) was polished with 0.5 µm alumina powder until mirror finish surface was obtained and used as working electrode. An Hg/HgO (0.1 M NaOH) as reference and Pt wire as counter electrode. The catalyst ink was prepared by dispersing 1 mg of the catalyst in 100 µl of nafion solution (5 wt% nafion : isopropanol : water (= 0.05:1:4 (v/v/v))) and ultrasonicate it for about 15 min. 5 µl of the dispersion was then dropcasted on the clean GC-RDE and allowed to dried under ambient condition. The amount of catalyst loading on GC electrode was estimated to be 0.707 mg/cm².

5.3.3.4.2 Electrocatalytic performance evaluation

The general procedure for the evaluation of ORR activities are provided in section 2.2 of chapter 2.



Figure 5.3.1 Schematic representation of the synthetic strategy for Fe-NPs-N-C/CNT.

5.3.4 RESULTS AND DISCUSSION

5.3.4.1 Synthetic strategy of Fe-NPs-N-C/CNT

Iron nanoparticles (Fe NPs) were at first incorporated on nitrogen-doped carbon (N-C) following a facile synthetic strategy reported previously.³³ Fe-NPs-N-C was subjected to heating in an inert atmosphere while exposing it to commercially inexpensive melamine as a carbon precursor for growing a CNT network at its surface. **Figure 5.3.1** describes the arrangements made to produce extended conducting channels by networking the surface of Fe NPs-N-C with *in-situ* grown CNTs to achieve the composite material (Fe-NPs-N-C/CNT).

Herein, CNTs grew following a chemical vapor deposition (CVD) mechanism catalysed by the Fe-NPs anchored at the surface of N-C.

5.3.4.2 Microscopic characterization of Fe-NPs-N-C

As seen in **Figure 5.3.2a**, low-magnification transmission electron microscopic (TEM) images of N-C was captured to visualize the nanosheet morphology of the bare support. **Figure 5.3.2b & c** are low-magnification TEM and STEM images of Fe-NPs-N-C demonstrating the well decorated surface of N-C by Fe-NPs where presence of iron nanoparticles was distinguished by the sharp contrast with respect to the N-C nanosheet under the electron beam. **Figure 5.3.2d** shows a high- resolution TEM image of Fe-NPs-N-C, displaying highly crystalline feature of the Fe NPs. The fringe lines observed in inset of **Figure 5.3.2d** were found to be originated from Fe (110) lattice whereas SAED pattern (inset of **Figure 5.3.2d**) shows all three crystallographic planes ((110), (200), (211)) corresponding to the Fe-NPs.⁴⁸ The distribution of iron nanoparticle over the N-C surface and homogeneity of doped nitrogen throughout the carbon lattice is depicted by the elemental mapping recorded using energy dispersive X-ray spectroscopy (EDS) as shown in **Figure 5.3.2e**.



Figure 5.3.2 Microscopic analysis of bare N-C and Fe-NPs-N-C: (a) TEM image of N-C, (b & c) TEM and the corresponding STEM image. (d) High-resolution TEM image of Fe-NPs-N-C, inset shows the lattice fringes originating from Fe-NPs and the corresponding SAED pattern. (e) Elemental mapping of Fe-NPs-N-C.
5.3.4.3 Microscopic characterization of Fe-NPs-N-C/CNT

The CNT network grown at the surface of the as-synthesized Fe-NPs-N-C was initially confirmed by capturing the low-magnification SEM and TEM images (**Figure 5.3.3**a, b and **Figure S1**) of Fe-NPs-N-C/CNT sample. Further from the high-resolution TEM image (**Figure 5.3.3**c), lattice fringes (inset of **Figure 5.3.3**c) corresponding to Fe was observed with d-spacing 0.21 nm. STEM image (**Figure 5.3.3**d) of the composite sample further demonstrates the well-dispersed network of CNT at Fe-NPs-N-C surface. EDS mapping (**Figure 5.3.3**e) showed the elemental distribution over the composite sample (Fe-NPs-N-C/CNT). Additional TEM images of composite sample at various magnification are shown in **Figure 5.3.4** confirms the successful decoration of carbon nanotubes on the surface of Fe-NPs-N-C.



Figure 5.3.3 Microscopic analysis of the Fe-NPs-N-C/CNT: (a) SEM image, (b) lowmagnification TEM image, and (c) high-resolution TEM image (inset shows the lattice fringe corresponding to C and Fe). (d) The corresponding STEM image and (e) elemental mapping of the composite.



Figure 5.3.4 Additional TEM images of the composite Fe-NPs-N-C/CNT.

5.3.4.4 Structure characterization of Fe-NPs-N-C/CNT

Figure 5.3.5a displays the powder XRD pattens of the various samples. In the case of N-C, the graphitic carbon from the carbon support exhibits a reflection of its (002) planes at an angle of $2\theta = 24.8^{\circ}$.³³ In the diffraction pattern of the Fe-NPs-N-C sample, two distinct peaks appear at $2\theta = 44.6^{\circ}$ and 65° , indicating the presence of (110) and (200) planes of Fe in the Fe-NPs. These findings are consistent with the corresponding SAED patterns mentioned earlier and identified by JCPDS No. 65-4899.^{49,50} Additionally, along with the Fe diffraction peak at $2\theta = 44.6^{\circ}$, an extra peak is observed at $2\theta = 43.4^{\circ}$ in the composite sample, suggesting the presence of the Fe₃C lattice (JCPDS No. 89-2867). The origin of Fe₃C lattice can be attributed to carbon dissolution in the Fe lattice during the initiation of CNT growth.^{51,52} This observation confirms that the growth of CNT at the surface of Fe-NPs-N-C/CNT is catalysed by the very iron nanoparticles.

Raman spectroscopy was employed to study the extent of graphitization in different samples as the electrocatalytic performance of carbon-based materials relies on the degree of graphitization the catalyst. The Raman spectra of all the samples (**Figure 5.3.5**b) show two dominant peaks at ~1328 cm⁻¹ for the D band and ~1586 cm⁻¹ for the G band. The intensity of G- and D-band is indicative of degree of graphitization and extent of defects in the carbon lattice respectively. The I_G/I_D ratios of different samples were calculated as 0.98, 1.09, and

1.12 for Fe-NPs-N-C, Fe-NPs-N-C/CNT and Fe-CNT respectively, suggesting higher extent of graphitization in the composite compared to Fe-NPs-N-C. Increased graphitization observed upon incorporating CNT at Fe-NPs-N-C surface also suggests that its electrocatalytic activity is expected to improve than Fe-NPs-N-C. Furthermore, it was shown that defects formed during the growth of CNT acts as active sites for ORR as the defects can facilitate the hydrogenation of O₂ to OOH* intermediate.⁵³ Therefore, there should be an optimized level of extent of graphitization (responsible for conductivity) and presence of defects (acts as active sites). Indeed, the trend follows here for the three samples exhibiting an optimized intermediate value of I_G/I_D in case of the composite sample reflecting in the expected trend observed for electrocatalytic performance as discussed later.



Figure 5.3.5 (*a*) *PXRD patterns of N-C, Fe-NPs-N-C and Fe-NPs-N-C/CNT.* (*b & c*) *Raman spectra and N*₂ *adsorption-desorption isotherms respectively of Fe-CNT, Fe-NPs-N-C, and Fe-NPs-N-C/CNT.*

The surface areas of the samples were estimated from BET surface area measurement. The plot of N₂ adsorption–desorption isotherms of all the samples is shown in **Figure 5.3.5**c. The corresponding multipoint BET plots are given in **Figure 5.3.6**, which yielded surface areas of 26 m²/g, 67 m²/g and 112 m²/g for Fe-CNT, Fe-NPs-N-C and the composite material (Fe-NPs-N-C/CNT) respectively. The surface area of Fe-CNT is comparable with previous reports.⁵⁴ The enhanced surface area in the composite material indicates the network of CNTs at the surface of Fe-NPs-N-C to be well dispersed and not stacked CNTs at a particular region as also observed from the low-mag TEM images of composite ((**Figure 5.3.4**). This well dispersion is a result of *in-situ* growth of CNT, found to be beneficial compared to ex-situ composite of CNT and Fe-NPs-N-C. This is because in later case stacking of a bunch of CNTs into a confined region is expected, which is counter-productive for electrocatalysis as junction resistance of stacked CNTs reduces the overall conductivity.⁵³



Figure 5.3.6 BET multipoint plots of (a) Fe-CNT, (b) Fe-NPs-N-C/CNT, and (c) Fe-NPs-N-C.

5.3.4.5 Realization of high metal retention

To determine the iron-content in all the samples thermogravimetric analysis (TGA) was performed in air with temperature elevated from 25 °C to 850 °C. Herein, aerobic heat treatment of the sample led to formation of Fe₃O₄ residue, as confirmed from PXRD pattern of residues collected after all the TGA experiments (Figure 5.3.5a, b).⁵⁵ Therefore, considering the wt.% of Fe in Fe₃O₄ the iron contents in those samples were calculated to be ~ 10%, 4 % and 5% for Fe-CNT, Fe-NPs-N-C/CNT, Fe-NPs-N-C respectively (Figure **5.3.5c**). The metal content in the samples as compared to theoretical metal-loading is \sim 75.5%, 38.5% and 19% respectively in Fe-CNT, Fe- NPs-N-C/CNT and Fe-NPs-N-C. This significant improvement in metal retention (Figure 5.3.5d) in case of Fe-NPs-N-C/CNT compared to Fe-CNT is attributed to the fact that Fe-NPs catalysing the CNT growth in the composite is strongly embedded on N-C sheets by electrostatic interaction with nitrogen whereas for Fe-CNT synthesis, iron precursor was just dropcasted on the silica boat. Moreover, the metal retention observed in case of the composite sample is lower than that found for N-C supported iron nanoparticles (Fe-NPs-N-C). It is worth mentioning that the relative metal retention in the composite formation process is higher than the one reported for atomically dispersed iron on N-C.33 Therefore, as the electrocatalytic performance suggests as discussed later this composite can bring the activity of atomically dispersed metal active sites with higher metal retention avoiding the complex synthetic protocols required for bringing atomic dispersion of metal on nitrogen-doped carbon support.



Figure 5.3.5 (a) Thermal gravimetric analysis (TGA) plots of Fe-CNT, Fe-NPs-N-C/CNT, and Fe-NPs-N-C (b) PXRD pattern of the residue collected after TGA, (c) iron content (wt.%) in different samples estimated from TGA analysis. (d) Plot showing metal retention in the various samples.

5.3.4.6 Surface composition analysis

X-ray photoelectron spectroscopy (XPS) was performed to evaluate the elemental compositions. The high-resolution C 1s spectra of both Fe-NPs-N-C and Fe-NPs-N-C/CNT were found to be similar when deconvoluted into four different components owing to C=C, C-C, C–N and O–C=O functionalities with binding energies of 284.4, 285.9, 287.3, and 289.7 eV, respectively (**Figure 5.3.6a, d**).⁵⁶ The presence of O-C=O is attributed to surface oxidation due to presence of minute amount of O₂ even during 99.99% N₂ flow.³³ For N 1s spectra (**Figure 5.3.6b, e**), the obtained peaks can be ascribed to the typical states of pyridinic N (398.2 eV), Fe–N_x (399.3 eV), pyrrolic N (400.2 eV), graphitic N (401.07 eV), and oxidised N (402.5 eV). Among these, pyridinic N plays a key role to enhance the rate of oxygen electroreduction. The strong electronegativity of N atoms can induce charge redistribution by

giving the surrounding carbon atoms a high positive charge density that facilitates O₂ chemisorption and weaken the O-O bond, thereby enhancing ORR performance. The N contents (atomic%) of different samples are depicted in Figure 5.3.6h as determined from the XPS survey scan (Figure 5.3.7). The N-content in the composite materials is found to be higher (1.66 times) than Fe-NPs-N-C. On the other hand, from the high-resolution N 1s spectra of Fe-NPs-N-C and Fe-NPs-N-C/CNT, it was found that relative abundance of pyridinic nitrogen in the composite has also increased by 1.8 times than in Fe-NPs-N-C (Figure 5.3.6h). Considering the metal composition, peak maxima at 707.3 and 720.3 eV in Fe-NPs-N-C indicate the presence of Fe (0), while those at 709.8 and 722.9 eV suggest the presence of Fe (+2), and those at 712.6 and 725.7 eV are attributed to Fe (+3). In the same spectrum, the peak at 711.3 eV corresponds to those Fe atoms that are directly attached to N in the carbon whereas the rest two peaks at 716.5 and 728.3 eV are the satellite peak (Figure 5.3.6c).⁵⁶⁻⁶⁰ The highresolution Fe 2p spectrum of the composite in Figure 5.3.6f also demonstrates the highest abundance of Fe (0) along with some amount of oxidised Fe species, originated due to metalsupport interaction, as also found in XANES spectra (Figure 5.3.8). Compared to Fe-NPs-N-C a negative shift of ~0.2 eV is observed in all the Fe peaks of the Fe-NPs-N-C/CNT, suggesting reduced interaction of Fe with N, attributed to loosening of Fe-N interaction during carbon dissolution in Fe lattice. The atomic% of Fe in the different samples are displayed in Figure 5.3.6i, consistent with TGA analysis discussed earlier.

5.3.4.6 Electrochemical activity

The electrochemical performance of the Fe-NPs-N-C/CNT was examined by rotating disk electrode (RDE) measurements in an O₂ saturated 0.1 M KOH solution and compared with Fe-NPs-N-C, Fe-CNT and the commercial Pt/C. The linear sweep voltammetry (LSV) curves (**Figure 5.3.9**a) display that Fe-NPs-N-C/CNT shows the highest ORR performance with more positive onset potential of 1.01 V and half wave potential ($E_{1/2}$) of 0.89 V which is comparable to commercial Pt/C ($E_{onset} = 1.04$ V and $E_{1/2} = 0.86$ V). As shown in **Figure 5.3.9**b, these parameters are much improved than those of Fe-NPs-N-C ($E_{onset} = 0.97$ V and $E_{1/2} = 0.81$ V) and Fe-CNT ($E_{onset} = 0.98$ V and $E_{1/2} = 0.83$ V). The enhanced performance of Fe-NPs-N-C/CNT catalyst shows that the synergy from Fe loading and CNTs incorporation plays a crucial role in enhancing ORR activity by dint of improved pyridinic N content, as revealed from XPS analysis and also from improved conductivity of the material due to the presence of CNTs interconnecting the Fe-NPs-N-C, leading to a performance matching the most efficient iron-based catalysts in alkaline medium (**Table 5.3.1**) but with significantly reduced material

production effort. Despite having higher nitrogen and iron contents, Fe-CNT shows lower activity compared to the Fe-NPs-N-C/CNT, which was found to be due to high charge-transfer resistance in the sample that significantly reduced in case of the composite. The intimate contact between the CNTs and the N-C sheets through the common to both Fe NPs results in the improved resistance as seen from electrochemical impedance spectroscopy (EIS) analysis.⁶¹ In the Nyquist plot (**Figure 5.3.9**c), Fe-NPs-N-C/CNT catalyst exhibits the lowest charge transfer resistance among all other samples, indicating facile charge transfer attributed to enhanced electrical conductivity of catalyst during the ORR reaction.



Figure 5.3.6 High resolution C-1s XPS spectra of (a) Fe-NPs-N-C and (d) Fe-NPs-N-C/CNT. High-resolution N 1s XPS spectra of (b) Fe-NPs-N-C and (e) Fe-NPs-N-C/CNT. Highresolution Fe 2p XPS spectra of (c) Fe- NPs-N-C and (f) Fe-NPs-N-C/CNT. (g) Nitrogen content in Fe-NPs-N-C, Fe-NPs-N-C/CNT and Fe-CNT. (h) Relative contents of different nitrogen functionalities present in Fe-NPs-N-C and Fe-NPs-N-C/CNT). (i) Iron contents in Fe-NPs-N-C, Fe-NPs-N-C/CNT, and Fe-CNT estimated from XPS.



Figure 5.3.7. XPS survey scans of (a) Fe-NPs-N-C, (b) Fe-NPs-N-C/CNT, and (c) Fe-CNT.



Figure 5.3.8 Fe K-edge of XANES spectra for Fe-NPs-N-C/CNT and Fe foil.



Figure 5.3.9 (a) The ORR polarization curves of Fe-NPs-N-C/CNT, Fe-CNT, Fe-NPs-N-C and Pt/C recorded at 1600 rpm in O_2 saturated 0.1 M KOH (scan rate: 10 mV/sec). (b) Comparison of onset potentials and $E_{1/2}$ of the different samples. (c) Nyquist plots of various samples recorded in 0.1 M KOH.

To study the kinetics of ORR, the LSV curves were recorded at various rotation rates ranging from 400 rpm to 2400 rpm. The Koutecky-Levich (KL) equation was used to evaluate the electron transfer number (n) per oxygen molecule in the ORR process. As seen in **Figure 5.3.10**, calculated value of n is 3.89 suggests a four-electron transfer process in Fe-NPs-N-C/CNT. The n values were also calculated for Fe-NPs-N-C, Fe-CNT and the commercial Pt/C as 3.6, 3.91 and 3.86 under similar conditions (**Figure 5.3.11-5.3.13**). Furthermore, the percentage of H_2O_2 yield were determined by performing RRDE measurements in the potential range of 0.2 to 0.8 V. The corresponding H_2O_2 yields are 5% on Fe-NPs-N-C/CNT, 16% on Fe-NPs-N-C and 4% on Fe-CNT (**Figure 5.3.14a**). Extremely low H_2O_2 yield in Fe-NPs-N-C/CNT confirmed that catalytic reduction of oxygen does not follow the 2-electron process. We point out that the n values determined from RRDE measurements (**Figure 5.3.14b**) are consistent with those based on KL analysis.



Figure 5.3.10 (*a*) *ORR* polarization curves of Fe-NPs-N-C/CNT recorded at different rotation rates in O₂ saturated 0.1 *M* KOH with a scan-rate of 10 mV/s, b) the corresponding K-L plots at different potentials w.r.t. RHE.



Figure 5.3.11 (a) ORR polarization curves of Fe NPs-N-C recorded at different rotation rates in O₂ saturated 0.1 M KOH with a scan-rate of 10 mV/s, b) the corresponding K-L plots at different potentials w.r.t. RHE.



Figure 5.3.12 (a) ORR polarization curves of FeCNT recorded at different rotation rates in O² saturated 0.1 *M* KOH with a scan-rate of 10 mV/s, b) the corresponding K-L plots at different potentials w.r.t. RHE.



Figure 5.3.13 (a) ORR polarization curves of Pt/C recorded at different rotation rates in O₂ saturated 0.1 *M* KOH with a scan-rate of 10 mV/s, b) the corresponding K-L plots at different potentials w.r.t. RHE.



Figure 5.3.14 (a) H_2O_2 yield in the range of 0.2-0.8 V (vs. RHE) and (b) Plot of electron transfer number vs. applied potential w.r.t RHE derived from RRDE measurements.

The long-term stability of the Fe-NPs-N-C/CNT was assessed by performing accelerated durability test (ADT) through continuous CV cycles from 0.6-1.1 V *vs*. RHE in O₂ saturated alkaline electrolyte. The LSV curves before and after continuous 10000 cycles (**Figure 5.3.15**a) showed nearly the same onset potential and negligible change in $E_{1/2}$. In addition to this, Fe-NPs-N-C/CNT also exhibited excellent methanol tolerance. As shown in **Figure 5.3.15b**, when 1 M methanol was injected into the electrolyte after 100 s, there is only

a slight change in ORR current of Fe-NPs-N-C/CNT. On the contrary, a sharp drop in the current visible, as expected, for commercial Pt/C.



Figure 5.3.15 (*a*) *ORR* polarization curves of Fe-NPs-N-C/CNT before and after the durability *test.* (*b*) *Chronoamperometry plot of Fe-NPs-N-C/CNT and Pt/C after injecting methanol after* 100 s.

Most interestingly, this work brings a serendipitous insight towards achieving high efficiency and keeping low precursor-loss during the synthesis of an electrocatalysts. Previous study shows that among N-C supported metal nanoparticles and atomically dispersed metal active sites on N-C an inverse relationship was found between electrochemical activity and metal-retention during the synthesis of such electrocatalysts.³³ The in-situ grown CNTs on N-C supported Fe NPs show an intermediate metal-retention compared to that found in Fe-NPs-N-C and atomically dispersed iron on N-C (Fe-N-C). Counter-intuitively, this composite shows the highest activity (even than the one found for single-atom iron embedded on N-C) among the all these catalysts (**Figure 5.3.16**) despite having an intermediate metal-retention. Hence, this study provides a landscape of tools towards further rational design of low-cost electrocatalysts with an aim of achieving extremely efficient electrocatalytic activity with minimum precursor-loss.



Figure 5.3.16 Plot showing the inverse relationship between metal retention during catalyst preparation and its electrocatalytic activity with an exception for the composite sample (Fe-NPs-N-C/CNT) (* represents the data reported for atomically dispersed Fe on N-C)³³

 Table 5.3.1 Comparison of ORR performance of Fe-NPs-N-C/CNT with recently reported

 literature data.

S.No.	Electrocatalysts	ORR E1/2 (V vs. RHE)	Electrolyte	Reference
1.	Fe-NPs-N- C/CNT	0.89	0.1 M KOH	This work
2.	MN7-10/3 CNT	0.82	0.1 M KOH	62
3.	Fe-CNTs/NC	0.84	0.1 M KOH	63
4.	N-Fe-CNT/CNP	0.87	0.1 M NaOH	64
5.	Co@NC-ZM	0.83	0.1 M KOH	65
6.	Fe-CNx/CNT	0.82	0.1 M KOH	66
7.	G-Fe/Fe3C- NC/CNTs	0.87	0.1 M KOH	67
8.	Fe@N- CNTs@rGO	0.83	0.1 M KOH	68
9.	Fe/N-CNT-0.1	0.84	0.1 M KOH	69
10.	Co/N-CNT-750	0.87	0.1 M KOH	70

5.3.5 CONCLUSIONS

In summary, we demonstrate that a composite of Fe nanoparticles loaded N-doped carbon nanosheet (Fe-NPs-N-C) and *in-situ* grown carbon nanotubes (CNTs) was achieved with lower metal-loss during the synthesis as compared to that of iron-incorporated carbon nanotubes (Fe-CNT). The composite material (Fe-NPs-N-C/CNT) exhibits efficient electrocatalytic activity for ORR in alkaline media with a very high $E_{1/2}$ of 0.89 V *vs*. RHE in the absence of any of the noble metals, attributed to synergy between Fe-N_x, pyridinic nitrogen and an improved conductivity arising from the extended conducting CNT channels. Importantly, we have shown that the *in-situ* grown CNTs on N-C supported Fe-NPs can overcome the conundrum of seemingly inverse relationship between the high activity expectations from non-noble metals and the loss of the same due to excessive metal-loss during their synthesis, as observed independently in N-doped carbon supported metal NPs and atomically dispersed Fe-N-C. Therefore, this approach retains the ease in synthesis of metal NPs and yet, exhibit high activity of single-atom catalysts. The findings provide insight towards the rational design of carbon supported transition-metal electrocatalysts with high conductivity, possessing immense potential for sustainable energy conversion.

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CHAPTER 5.4

Conclusions and future prospects

Conclusions

Carbon nanotubes (CNTs) exhibit tremendous potential in electrocatalysis due to their high surface area, excellent electrical conductivity, and chemical stability. Various synthetic methods, including arc discharge, chemical vapor deposition, and laser ablation, enable tailored CNT production with controlled properties. However, further research is imperative to understand the factors influencing catalytic variations among CNTs synthesized through different methods. The integration of CNTs with transition metal-based nanocatalysts (MNCs) in composites shows great promise for achieving efficient, noble-metal-free electrocatalysis, addressing cost and sustainability challenges associated with conventional catalysts. This synergistic approach, discussed in the last chapter of this thesis, allows for enhanced catalytic activity, selectivity, and stability, making CNT-MNC composites a transformative solution in sustainable energy conversion technologies.

Chapter 5.1 depicts the evolution of CNT synthesis, their bottlenecks, potential of CNTs in diverse application and finally outlines the gap in the research field of CNT electrolysis. The evolution of carbon nanotube (CNT) synthesis has progressed from early methods like arc discharge and laser ablation to the more controlled and scalable chemical vapor deposition (CVD) technique. However, challenges persist in understanding the governing factors behind the tuned catalytic properties of CNTs synthesized in different pathways. Despite this, CNTs' unique properties make them versatile materials with applications in nanocomposites, energy storage, and electrocatalysis. In the latter field, CNTs hold promise as excellent catalyst supports, but a critical research gap remains in achieving efficient pathways for exhibiting noble-metal-free electrocatalysis. Factors such as CNT morphology, surface functionalization, and catalyst integration require further investigation to unlock their full potential in advancing sustainable energy technologies.

In Chapter 5.2, our comprehensive study focused on the effect of reaction parameters in floating catalyst for CNT production. We observed a decline in electrocatalytic activity after a certain catalyst dose and in production yield after a limit of carbon precursor's amount, indicating a limitation in scalability Although the floating catalyst technique offers a more straightforward approach compared to the complex setups of traditional chemical vapor deposition, it has a scalability limitation, particularly concerning the amount of solid carbon precursor. Additionally, we uncovered that the oxidation state of encapsulated iron nanoparticles varies with the reaction atmosphere in which the CNTs were synthesized. Notably, CNTs produced in a reducing hydrogen atmosphere exhibited the highest abundance of metallic iron (Fe(o)), surpassing those made in inert atmospheres. Furthermore, within nitrogen and argon atmospheres, the higher thermal conductivity of nitrogen led to a relatively greater presence of metallic iron in the CNTs obtained under a nitrogen atmosphere compared to those synthesized under an argon atmosphere. This resulted in a higher proportion of Fe-N_x species, known for their contribution to superior electrocatalytic performance, as evidenced in our electrochemical studies. This was also attributed to enhanced metal-support interaction, as confirmed by electrochemical impedance spectroscopy. Ultimately, this study provides a comprehensive investigation into the optimized reaction parameters and scalability in CNT production using the floating catalyst method. Additionally, it sheds light on the underlying reasons for the variations in catalytic properties through detailed spectroscopic analysis, offering valuable insights for future research in this field.

Chapter 5.3 showcases the successful creation of a blend comprising N-doped carbon nanosheets loaded with iron nanoparticles (Fe-NPs-N-C) along with carbon nanotubes (CNTs) grown in situ. This synthesis method resulted in lower metal loss compared to incorporating iron into carbon nanotubes (Fe-CNTs). The resulting composite material (Fe-NPs-N-C/CNT) demonstrates highly efficient electrocatalytic activity for the oxygen reduction reaction (ORR) in alkaline conditions, achieving a notably high $E_{1/2}$ without the need for noble metals. This enhanced performance arises from the synergistic interplay between Fe–N_x, pyridinic nitrogen, and improved conductivity facilitated by extended CNT pathways. Crucially, our study reveals that the in situ grown CNTs on N-C supported Fe-NPs resolve the perplexing contradiction between anticipating high activity from non-noble metals and encountering losses due to excessive metal during synthesis. This phenomenon was previously observed in the first study of this thesis independently in N-doped carbon supported metal nanoparticles and atomically dispersed Fe–N-C. Therefore, this approach preserves the simplicity of metal nanoparticle synthesis while yielding the high activity typical of single-atom catalysts. These findings offer valuable insights for the deliberate design of carbon-supported transition-metal electrocatalysts with exceptional conductivity, holding great promise for sustainable energy conversion.

Future prospects

Carbon nanotubes (CNTs) have emerged as a transformative material in the field of electrocatalysis, offering a promising alternative to noble-metal catalysts. Their unique structural and electronic properties make them excellent candidates for a wide range of electrochemical reactions. There are still future research prospects in harnessing CNTs for noble-metal-free electrocatalysis and the potential of composite formations between CNTs and other low-cost, earth-abundant elements-based electrocatalysts.

Future research in CNT-based electrocatalysis will likely focus on the rational design and functionalization of CNTs to optimize their catalytic activity. Tailoring CNT properties, such as surface functional groups and defects, will play a crucial role in enhancing their performance in various electrochemical reactions.¹ Besides efforts will be directed towards a deeper understanding of the underlying reaction mechanisms on CNT surfaces. This involves studying the active sites and charge transfer processes, which will guide the development of more efficient CNT-based catalysts.²

Addressing scalability challenges in CNT production for electrocatalysis may be a critical area of future research. Methods for large-scale, cost-effective synthesis for high-quality CNT will be developed to facilitate their widespread application in energy conversion technologies. Furthermore, future research may focus on exploring novel composite materials involving CNTs and low-cost, earth-abundant elements-based electrocatalysts, such as transition metal dichalcogenides, metal-free nitrogen-doped carbon, and metal carbides/nitrides.^{3,4} These composites can provide a synergistic boost to catalytic activity. Research will be directed towards improving the durability and stability of these composite materials under harsh electrochemical conditions. This will ensure their long-term viability for practical applications.

The future of electrocatalysis lies in the strategic utilization of CNTs and the development of innovative composite materials with low-cost, earth-abundant elements-based catalysts. Through rational design, mechanistic understanding, and scalable production methods, CNTs hold great potential to drive the transition towards sustainable and efficient energy conversion technologies, marking a significant stride towards a greener future.

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