Rational Design Of Multifunctional Nanocatalysts For Environmental Remediation And Energy Conversion Technologies

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RATIONAL DESIGN OF MULTIFUNCTIONAL NANOCATALYSTS FOR
ENVIRONMENTAL REMEDIATION AND ENERGY CONVERSION
TECHNOLOGIES

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Dedication

This dissertation is dedicated to my parents for their unconditional love and support to become who I am today, my lovely wife (Anika Nawer) for her relentless support throughout my whole Ph. D. journey, my dearest son (Md Arhaam Ahsan) for being the meaning of our life and my younger brother (Md Shafikul Ahsan) for his continuous inspiration.
RATIONAL DESIGN OF MULTIFUNCTIONAL NANOCATALYSTS FOR ENVIRONMENTAL REMEDIATION AND ENERGY CONVERSION TECHNOLOGIES

by

MD ARIFUL AHSAN, M.Sc.

DISSERTATION

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Abstract

The discovery of efficient and sustainable carbon-based nanotechnologies to solve both the scarcity of drinking water and global energy crisis has become a paramount task in the last decades. Owing to the fast population growth and industrialization of the modern society, access to potable water and clean energy technologies is becoming very hard around the globe. Water pollutants have become a serious threat to the environment and ecology because of their toxic nature. Parallelly, the current hydrocarbon-based fuel industries are generating high levels of contamination across the planet, making imperative the development of cleaner energy technologies. In this regard, the utilization of carbon-based nanomaterials could facilitate the development of effective renewable nanotechnology that can provide potential solutions towards the wastewater treatment and clean energy technologies. This dissertation presents the synthetic routes to design novel carbon-based nanoheterostructures as well as their characterization and functional evaluation for water treatment processes and energy conversion reactions.

In chapter 2, the synthesis and characterization of an ecofriendly, cheap and efficient biosorbent, sulfonated spent coffee waste (SCW-SO$_3$H) for water remediation is reported. SCW-SO$_3$H was synthesized through introducing sulfonic acid polar functionalities over the polymeric biomass (cellulose and lignin) of the spent coffee waste (SCW) by a simple, facile and versatile method. ICP-OES, SEM-EDX, FT-IR, XPS, TGA, Raman and UV-Vis spectroscopy were used to analyze the developed SCW-SO$_3$H biosorbent and its adsorption capacity towards the removal of different environmental pollutants. The chemically engineered biosorbent showed excellent pollutant removal capacity of 812 mg/g, 462 mg/g and 302 mg/g toward methylene blue, tetracycline and Cr (VI), respectively. The present study can provide a platform in developing new generation of eco-friendly, cost-effective and efficient biosorbent for environmental remediation.
In chapter 3, the synthesis and development of nickel and copper-based nanocatalysts for NaBH₄-mediated reduction of environmental pollutants is reported. To achieve this, metallic Ni and Cu nanoparticles-embedded carbon sheets, namely as C@Ni and C@Cu, are synthesized through annealing of Ni-BDC and Cu-BDC metal-organic frameworks (MOFs) under an argon atmosphere at 600 °C. Their catalytic performance was tested for the catalytic reduction of environmental pollutants such as 4-nitrophenol, methyl orange and methylene blue. The obtained results from the catalytic studies are comparable with previously reported many other noble metal-based and transition metal-based nanocatalysts. Moreover, the catalytic performance of the developed catalysts dropped slightly (<3-6%) upon five times of recycling and reusing, showing the highly stable nature of the developed magnetic C@Ni and C@Cu nanocatalysts.

In chapter 4, a facile, green, cheap, scalable and environmentally benign synthetic methodology to fabricate a hierarchically porous carbon-encapsulated transition metal-based M@TP nanocatalysts (M= Cu, Ni, Fe and Co) using commercial tissue paper as a template is reported. The morphology, crystalline structure, chemical composition and textural properties of the as-synthesized M@TP nanocatalysts were thoroughly characterized. X-ray diffraction analysis confirmed the pure metallic phase of the synthesized nanocatalysts, whereas the transmission electron microscopic analysis revealed that the metal nanocatalysts are encapsulated inside the porous carbon matrix. The catalytic activity of the M@TP nanocatalysts was thoroughly investigated towards the degradation of Congo red dye from water via peroxymonosulfate activation. Remarkably, the catalytic studies revealed that the Co@TP-6 nanocatalyst was so far the most active catalysts for the degradation of CR allowing the degradation of 97.68% of CR in 30 min with a higher reaction rate constant of 0.109 min⁻¹. Quenching tests suggested that the
sulfate radicals are the dominant reactive species in the catalytic degradation process. Moreover, the Co@TP-6 nanocatalyst is very stable with a minimal activity loss after four cycling runs.

In chapter 5, the synthesis of bimetallic nickel-copper (NiCu) alloy nanoparticles confined in a sp\(^2\) carbon framework that exhibits tri-functional catalytic properties towards hydrogen evolution (HER), oxygen reduction (ORR) and oxygen evolution (OER) reactions is reported. XPS analysis revealed that the binding energy for Ni 2p\(_{3/2}\) band of the Ni\(_{0.25}\)Cu\(_{0.75}\)/C nanoparticles was shifted ~three times compared to other bimetallic systems and this was correlated to the high electrocatalytic activity observed. Interestingly, the bimetallic Ni\(_{0.25}\)Cu\(_{0.75}\)/C catalyst surpassed the OER performance of RuO\(_2\) benchmark catalyst exhibiting a small onset potential of 1.44 V vs RHE and an overpotential of 400 mV at 10 mA·cm\(^{-2}\) as well as the electrochemical long-term stability of commercial RuO\(_2\) and Pt catalysts and kept at least 90% of the initial current applied after 20000s for the OER/ORR/HER reactions. This study reveals significant insight about the structure-function relationship for non-noble bimetallic nanostructures with multifunctional electrocatalytic properties.

In chapter 6, the synthesis of a new class of hybrid 0D-2D heterostructures comprised of boron carbon nitride nanosheets (BCN NSs) and fullerene molecules (C\(_{60}\)/F) that exhibit metal-free electrocatalytic properties for the hydrogen evolution/oxidation reactions (HER/HOR) and the oxygen evolution/reduction reactions (OER/ORR) is reported. The nanohybrid supramolecular material with 10 wt% of F in BCN NSs (10% F/BCN) exhibited the largest Raman and C1s binding energy shifts in XPS, which were associated with greater cooperativity interactions and enhancing the ET processes at the F/BCN interface. The 10% F/BCN showed the highest tetrafunctional catalytic performance, outperforming the OER catalytic performance of commercial RuO\(_2\) catalysts with a η\(_{10}\) of 390 mV and very competitive onset potential values of -0.042 V and 0.92
V vs RHE for HER and ORR, respectively, and a current density value of 1.47 mA·cm⁻² at 0.1 V vs RHE with an ultralow ΔG⁺ value of -0.03 eV towards the HOR process. Additionally, the 10% F/BCN catalyst was also used as both cathode and anode in a water splitting device, delivering a cell potential of 1.61 V to reach a current density of 10 mA·cm⁻².

In chapter 7, a simple MOF-derived synthetic strategy to fabricate low-dimensional (LD) nanohybrids formed by 0D-ZrO₂ NPs and heteroatom-doped 2D-carbon nanostructures is reported. The 2D platforms controlled the electronic structures of interfacial Zr atoms, thus producing an optimized electron polarization for BCN/ZrO₂ nanohybrid. XPS and theoretical studies revealed the key role of the synergistic couple effect of B and N on the interfacial electronic polarization. The BCN/ZrO₂ showed excellent bifunctional electrocatalytic activity, delivering η₁₀ of 301 mV and E₁/₂ of 0.85 V vs RHE for OER and ORR, respectively, which are comparable to the state-of-the-art LD nanohybrids. This work establishes a new route to fabricate highly efficient multifunctional electrocatalysts by tuning the electronic polarization properties of 0D-2D electrochemical interfaces.
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Chapter 1: Multifunctional nanocatalysts for water treatment and energy conversion technologies

1.1 INTRODUCTION

The advances of nanoscience and nanotechnology constitute crucial steps towards the faster development of catalysis science. As a paramount part of nanocatalysis, the construction of metal nanoparticles with attractive physical-chemistry properties have experimented a prosperous growing in last decades. It is worth to note that metal nanoparticles exhibit high surface-to-volume ratio, rich active surface atoms and unique electronic structures, which plays a decisive role on the catalysis at the interfacial regions. Owing to have excellent properties, the nanomaterials have drawn significant attention in the field of catalysis, adsorption, photocatalysis, electrocatalysis, energy storage, photothermal therapy and drug delivery etc. Nonetheless, metal nanoparticles don’t show a thermodynamically stable behavior owed to their high surface energy. Therefore, encapsulating metal nanoparticles in carbon-based nanoshells or nanopores is expected to physically isolate the metal nanoparticles thus preventing the aggregation and improving the catalytic rates. The encapsulation of the metal nanoparticles can include various classes of carbon-based nanomaterials such as graphene, carbon nanotubes, metal−organic frameworks and organic cages, which provide not only a physical protection barrier that assure ultrahigh long-term stability under electrochemical conditions, also a very favorable electron gathering at the metal/carbon electrochemical interfaces enabling the decrease of the uphill energetic states of the intermediate catalytic species and favoring the overall catalytic activity.

1.2 POTENTIAL OF NANOCATALYSTS FOR WATER TREATMENT TECHNOLOGIES

Water is a key resource for the existence of life on the planet and therefore, the access to the clean water is crucial for the humankind and the ecosystem. Nevertheless, the quality of the
accessible water has been influenced negatively due to the continuously increasing population, increasing urbanization, rapid industrialization and careless utilization of the natural resources etc. during the last decades.\textsuperscript{11,12} A broad range of water pollutants such as textile dyes, heavy metals, antibiotics, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, perfluorooctane sulfonate and perfluorooctanoic acid etc. are usually found in the wastewater discharge that have adverse effects on human and ecology.\textsuperscript{13-16} In recent times, nanomaterials have drawn great attention in the remediation as well as degradation of these perilous organic/inorganic contaminants owing to have some exceptional physicochemical characteristics such as their large specific surface area, high physical/chemical/thermal stability, strong electron transfer ability, significant chemical reactivity and high catalytic activity.\textsuperscript{17,18} Nanostructured materials, for instance, carbon based nanoadsorbents, metallic nanoparticles, metal oxide nanoparticles, nanomembranes, photocatalysts among others, offer promising alternatives for novel wastewater treatment technologies, that can be adapted well to the customer-specific needs.\textsuperscript{19} Majority of the nano-engineered materials are well-suited with the existing water treatment technologies and thereby, can be simply integrated in the existing set-up. In this regard, they are recently employed to address different environmental problems such as water treatment, environmental monitoring and sensing etc. and most importantly, they are found to be an excellent candidate, since the reactive nanoheterostructures have potential features which make them more effective to remove as well as convert toxic contaminants into toxic-free matters.\textsuperscript{20} Although, the nanostructured materials such as Pt, Au, Pd, Ag, Cu, Ni, TiO\textsubscript{2}, Fe\textsubscript{3}O\textsubscript{4}, Co\textsubscript{3}O\textsubscript{4} etc., are very effective, constitute lower energy and require lesser time but these systems are very expensive as well as they can make secondary pollution due to their leaching after use in water treatment process.\textsuperscript{5,21-24} Furthermore, biomass-based adsorbents also have been extensively used for wastewater treatment.\textsuperscript{25,26} But, their
inferior performance makes a big room for researchers to find a way for improving their removal performance towards organic and inorganic pollutants. Therefore, these materials are not used yet in the wastewater systems on larger scale basis. In this context, there is an urgent need to engineer these nanomaterials that must be very efficient, higher activity, green, easy to handle and eco-friendly. A significant amount of research has been going on to overcome the above-mentioned problems. It was found that the immobilization of these nanoparticles on the solid support materials such as alumina, mesoporous silica, porous carbon etc. could be a great alternative in this context. However, the porous carbon matrix is found to be the best in terms of the solid support material because of their higher surface area, lower density as well as excellent conductivity. Numerous techniques such as hard-templating, explosion and chemical vapor deposition etc. have been already reported to prepare porous carbon encapsulated metal nanoparticles. However, most of the techniques involve many steps, higher energy consumption, sophisticated instruments etc. Therefore, it remains still challenging to find a simple and low-cost synthesis method for synthesizing porous carbon embedded nanoparticles. This dissertation presents numerous low-cost, scalable, novel and exciting techniques for the preparation of advanced functional nanomaterials with higher number of catalytically active surfaces and their potential applications in the adsorptive, catalytic reduction and oxidative degradation water treatment processes. Finally, these methods have been investigated intensively to remove or degrade organic and inorganic contaminants from water.

1.3 POTENTIAL OF NANOCATALYSTS FOR ENERGY CONVERSION TECHNOLOGIES

The development of clean energy technologies is of top priority in modern society due to the depletion of traditional fossil fuels and the negative impact on nature of the burning dirty energy. As a clean energy carrier, hydrogen is a promising renewable alternative because of
its high gravimetric energy density, zero carbon emissions and earth-elemental abundance.\textsuperscript{33} One of the most attractive options to produce hydrogen is to use an overall water splitting device to electrochemically split the water according to the following equation: \(2\text{H}_2\text{O} = \text{O}_2 + 2\text{H}_2\).\textsuperscript{34} The hydrogen obtained by this reaction can be stored and then oxidized to release energy and regenerate water, being able to act as a unique renewable fuel. The discovery of new nano/electro-catalysts to boost the electrocatalytic rates for the generation of hydrogen and/or oxygen as well as for oxygen reduction reactions is of paramount importance to develop the upcoming generation of electrochemical water splitting and zinc-air battery devices.\textsuperscript{35, 36} Noble metals have been used as the state-of-the-art catalysts for these electrocatalytic reactions, but their scarcity in nature and sluggish kinetics at alkaline environments are not suitable for practical catalytic applications. The development of earth-abundant catalysts with economic prices and advanced catalytic performances has been the principal objective of many researchers in the last decades.\textsuperscript{37} In order to make the HER electrochemical process more energetically favorable and reduce the overall costs, a myriad of transition metal or metal-free based low-dimensional platforms have been proposed.\textsuperscript{38, 39} With dimensional confinement, these low-dimensional nanostructures exhibit more exposed surface-facet atoms and in turn, higher atom utilization, thus providing ideal platforms for engineering physical and chemical properties at the atomic level. Remarkably, the interfacial engineering of the nanoarchitectures can synergistically optimize active sites and kinetic processes as well as regulate both the electrical conductivity and the adsorption free energy of the intermediate catalytic species. Additionally, it promotes enhanced catalytic activities of inorganic and/or organic low-dimensional nanomaterials and paves the way for the development of superior electrochemical energy conversion systems and water splitting devices.\textsuperscript{40} Particularly, the assembly of low-dimensional nanomaterial units to form vdW heterostructures benefits the
formation of highly active interfacial active sites for advanced electrocatalysis owed to the enrichment of new modes of electronic redistribution at the electrochemical interfaces, which potency the thermodynamics of hydrogen and/or oxygen adsorption at the nanometer level.\textsuperscript{41}

1.3.1 Hydrogen evolution reaction

Hydrogen evolution reaction (HER) is a multi-step electrochemical phenomena that produce molecular hydrogen at the interfacial area of cathode electrodes of the energy-related devices. The most widely accepted HER reaction mechanism in acid and alkaline environments is summarized in the following catalytic steps: (a) [Volmer step: $\text{H}^+ + \text{M} + e^- \rightleftharpoons \text{MH}_{\text{ads}}$ (in the acid media) / $\text{H}_2\text{O} + \text{M} + e^- \rightleftharpoons \text{MH}_{\text{ads}} + \text{OH}^-$ (in the alkaline media)]; (b) [Heyrovsky step: $\text{MH}_{\text{ads}} + \text{H}^+ + e^- \rightleftharpoons \text{M} + \text{H}_2$ (in the acid media) / $\text{MH}_{\text{ads}} + \text{H}_2\text{O} + e^- \rightleftharpoons \text{M} + \text{H}_2 + \text{OH}^-$ (in the alkaline media)] and (c) [Tafel step: $2\text{MH}_{\text{ads}} \rightleftharpoons 2\text{M} + \text{H}_2$], where $\text{MH}_{\text{ads}}$ represents the state that a hydrogen atom chemically adsorbs on an active site of catalysts (M).\textsuperscript{40, 41} As shown by the above equations, these are the most energetically favorable catalytic steps for the electrochemical generation of hydrogen in both acidic and alkaline media. The first catalytic step, named Volmer step, represent an electrochemical hydrogen adsorption in which a proton-coupled electron transfer process is taking place at the electrode surfaces. It is followed either by an electrochemical desorption process based on the electron-mediated reaction of an adsorbed hydrogen atom with another proton to produce molecular hydrogen (Heyrovsky step) or by the combination of two adsorbed hydrogen atoms to generate molecular hydrogen (Tafel step). The rate-determining step can be determined by the Tafel slope value from the HER polarization curve. Usually, the Tafel slope values under thermodynamic standard conditions are 120, 40, and 30 mV.dec$^{-1}$ for the Volmer, Heyrovsky, and Tafel reactions, respectively. Additionally, the calculated Tafel slope value also provides a deep understanding into the possible reaction pathway, which directly
depends on the electronic structure of the catalytic material.\textsuperscript{42} Up to now, the most successful HER catalysts are noble materials such as Pt, Pd and Ru. They drive hydrogen evolution via the Volmer–Tafel mechanism, being the Tafel step the rate-controlling step (30 mV.dec\textsuperscript{−1}). Despite their advantages as HER catalysts, the reaction is more sluggish under alkaline media due to the reversible adsorption of H atom formed from the dissociation of water molecules at the catalytic surfaces. It is worth to point out that a good HER catalyst should have an intermediate M-H bond energy sufficiently strong to bind adsorbed H atom but also weak enough to make sure of the breakage of M-H during H\textsubscript{2} release (Sabatier principle). Among the HER catalysts, Pt-based catalysts are very close to the optimum values towards the ideal thermodynamic for hydrogen adsorption. The heterostructure materials have paved the way towards the development of novel electrocatalysts. The strong coupling of different active components provides a promising approach to facilitate both the synergistic effects and the improvement of the electron-transfer rate at the electrochemical interfaces, thus boosting the HER electrocatalysis. Among the most exciting examples can be found the 0D-2D vdW nanohybrids that combines the remarkable accepting electronic properties of 0D nanomaterials such as fullerenes and the suitable electronic properties of 2D materials.\textsuperscript{41,43} 

1.3.2 Oxygen evolution reaction

Oxygen evolution reaction \textit{(OER)} constitutes a multistep electrochemical process of the oxidation of water molecule to molecular oxygen, which exhibits four proton-coupled electron transfers and the O-O bond formation and requires a significantly large overpotential to achieve the catalytic reaction. Precious metal catalysts such as Ir- and Ru-based nanomaterials exhibit outstanding OER catalytic activities with both small Tafel slope and low overpotential values, thus lowering the cell voltage of electrolyzer devices.\textsuperscript{44} Nonetheless, their high cost, low abundance
and poor stability reduce their scale-up application, giving rise to a fascinating race towards the fabrication of cost-effective and stable OER electrocatalysts. Earth-abundant heterostructure catalysts have qualified as attractive alternatives for OER. The synergistic interfacial interactions of transition metal oxides (TMOs)-carbon heterostructures have appeared as an incredibly strategy to improve the overall electrocatalytic rates via boosting the number of accessible catalytic sites as well as the electron transfer across the interfacial surfaces.

OER is composed of several catalytic steps and the mechanism is associated with the structural properties of the electrode surface. The most recognized reaction pathways for OER includes four consecutive proton and electron transfer steps, which are shown in the following equations: [Acidic media: * + H₂O → ‘OH + H⁺ + e⁻; ‘OH → ‘O + H⁺ + e⁻; followed by either 2‘O → 2* + O₂ + 2e⁻ or ‘O + H₂O → ‘OOH + H⁺ + e⁻; ‘OOH → * + O₂ + H⁺ + e⁻] and [Alkaline media: * + OH⁻ → ‘OH + e⁻; ‘OH + OH⁻ → H₂O + ‘O + e⁻; followed by either, 2‘O → 2* + O₂ + 2e⁻ or ‘O + OH⁻ → ‘OOH + e⁻; ‘OOH + OH⁻ → * + O₂ + e⁻]. As it is displayed by the above equations, the OER process is exhibit more catalytic steps than HER, producing various OER intermediates, including HO*, O*, and HOO* in both acidic and alkaline electrolytes. To get in-depth insights on the catalytic performances of OER electrocatalysts, crucial electrocatalytic parameters such as overpotential (η) at a certain current density, Tafel slope, exchange current density (j₀), turnover frequency (TOF), and long-term electrochemical stability, has been established. The overpotential and exchange current density can be acquired from the polarization curves and Tafel slopes, respectively. The overpotential represent the difference between the experimental potential to trigger the water splitting and the theoretical potential. Therefore, the larger the overpotential needed to reach the appointed current density by a catalyst, the lower the catalytic efficiency will be. Tafel slope and j₀, derived from Tafel equation (η)
\[ a + b \log j, \text{ where } b \text{ is the Tafel slope, } j_0 \text{ is associated to the rate of electron transfer under equilibrium condition) in the linear region of a Tafel plot, are known as two key kinetic parameters. TOF, defined as the number of the oxygen molecules generated per active site per unit time, is considered as the most important parameter to evaluate the efficiency of an electrocatalyst. TOF is useful for comparing performance of the similar active materials, which can be calculated by the following equation: } \text{TOF} = \frac{jA}{4nF}, \text{ where A is the area of the working electrode, and n is the number of moles of the active materials. Long-term electrochemical stability is also a crucial descriptor for evaluating an electrocatalyst in terms of practical application. A common methodology to investigate the stability is based on the measure of the current or voltage variation with time under constant potential/current. Briefly, among the desirable properties of OER catalysts can be found with smaller Tafel slopes, higher } j_0, \text{ lower overpotential and larger TOF values as well as ultrahigh long-term electrochemical stabilities.}

1.3.3 Oxygen reduction reaction

The mechanism of oxygen reduction reactions (ORR) has been extensively investigated experimentally and computationally. In ORR, oxygen (O\(_2\)) is reduced to water (H\(_2\)O) involving four protons and four electrons \([O_2 + 4(H^+ + e^-) \rightarrow 2H_2O]\). The O\(_2\) can be directly reduced to H\(_2\)O either through a direct four-electron pathway or through an indirect two-electron reduction pathway in which O\(_2\) first reduces to hydrogen peroxide and then transforms into H\(_2\)O, thus following the catalytic routes described in the OER chapter. On the catalytic surface of Pt benchmark catalysts, ORR usually adopts the four-electron pathway. It is also well-known that the four-electron ORR can occur through either a dissociative or an associative pathway. The dissociation pathway preferentially occurs when the surface binds O\(_2\) strongly or when the oxygen surface coverage is poor, while the association pathway is favored when the surface O\(_2\) adsorption
is weak or when the surface oxygen coverage is high. The ORR catalytic activity is well-understood under the Sabatier principle, which states that the interaction between the oxygen species and the catalyst surface needs to be adjusted to achieve the best ORR activity. If the surface binds oxygen too strongly, the ORR kinetics will be limited by the electron/proton transfer to the *O and *OH intermediate catalytic species, while weak binding reduces the electron/proton transfer in the mechanistic scheme. The interfacial engineering of low dimensional nanohybrids has been used as a powerful tool to regulate the adsorption energy values of the oxygen-intermediate species generated during the catalytic reaction.

1.4 Objectives and Contributions

The objective of this dissertation is to develop novel synthetic methodologies for carbon-based nanomaterials with potential applications in different wastewater treatment and energy conversion technologies. Various carbon-based nanomaterials such as functionalized graphitic carbon from biomass source, metal organic framework derived carbon embedded copper and nickel nanoparticles, porous graphitic carbon encapsulated transition metal nanoparticles (Cu/Ni/Fe/Co), porous carbon encapsulated copper nickel bimetallic nanoparticles, low dimensional boron carbon nitride and fullerene (2D-0D) nanocomposites and transition metal oxide (ZrO₂) on boron, nitrogen co-doped carbon sheet were successfully prepared using facile and scalable novel synthetic techniques. The above-mentioned first three carbon-based nanomaterials were employed for different water treatment processes such as adsorption, catalysis and advanced oxidation processes, respectively to remove and degrade the organic and inorganic contaminants from water. The rest of the above-mentioned nanomaterials were used as electrocatalysts for different energy conversion technologies such as hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR), oxygen evolution reaction (OER) and oxygen
reduction reaction (ORR). A short summary of the research works that has been included in this thesis is given as follows.

A novel method for making sulfonic acid functionalized carbon material (SCW-SO$_3$H) from coffee waste is presented in chapter 2. The as-synthesized SCW-SO$_3$H displayed excellent adsorption properties for removing organic and inorganic pollutants from water. In order to optimize and maximize adsorption capacity of the developed biosorbent, different variables such as initial concentration, biosorbent dosage, pH, time and temperature were also evaluated in this study. It was also found that adsorption of all the adsorbates follow pseudo-second order rate kinetic and thermodynamic values, $\Delta H > 0$ and $\Delta G < 0$, showed endothermic nature as well as spontaneity of the adsorption process.

A novel synthetic strategy for preparing nickel and copper metal organic frameworks, followed by their successive utilization as a sacrificial template for making carbon encapsulated nickel and copper nanoparticles is presented in chapter 3. The prepared nanomaterials showed excellent catalytic activity towards the sodium borohydride mediated catalytic reduction of a wide range of organic pollutants such as methylene blue, methyl orange and 4-nitrophenol.

A green, sustainable, low cost and scalable methodology for making hierarchically porous carbon-encapsulated transition metal-based M@TP nanocatalysts (M= Cu, Ni, Fe and Co) is presented in chapter 4. These as-synthesized nanocatalysts were utilized as Fenton like catalysts towards the oxidative degradation of organic pollutants such as Congo red dye via peroxymonosulfate activation. The synergistic interactions between the metal nanoparticles and porous carbon matrix prevented the agglomeration of the nanoparticles, thereby, boosting their degradation efficiencies. Additionally, the influence of different critical parameters such as
nanocatalyst dosage, different initial CR concentrations, PMS concentration, reaction temperature and different dyes was also evaluated.

The rational design of multi-functional catalysts that use non-noble metals to facilitate the interconversion between H₂, O₂ and H₂O is an intense area of investigation. Bimetallic nanosystems with highly tunable electronic, structural and catalytic properties that depend on their composition, structure, and size have attracted considerable attention. A novel synthetic method for making porous carbon encapsulated bimetallic copper nickel nanoparticles is reported in chapter 5. These CuNi bimetallic nanoparticles were employed as electrocatalysts for different energy conversion reactions such as hydrogen evolution (HER), oxygen reduction (ORR) and oxygen evolution (OER) reactions and displayed outstanding electrocatalytic performance towards these reactions. The electrocatalytic functions of the NiCu nanoalloys were experimentally and theoretically correlated with the composition-dependent local structural distortion of the bimetallic lattice at the nanoparticle surfaces. Our study demonstrated a downshift of the d-band of the catalysts that adjusts the binding energies of the intermediate catalytic species.

The development of low-dimensional (LD) supramolecular materials with multifunctional electrocatalytic properties has sparked the attention of the catalysis community. A novel synthetic methodology was developed to prepare 2D-0D nanohybrids, comprising of boron carbon nitride nanosheet (BCN NSs) and fullerene molecule and presented in chapter 6. These low dimensional nanohybrids displayed remarkable electrocatalytic properties towards different energy conversion reactions such as HER, OER, ORR and HOR. The electrocatalytic properties were studied with varying F:BCN ratios to optimize the intermolecular electron transfer (ET) from the BCN NSs to the electron-accepting fullerene molecules. This synergistic interfacial phenomenon resulted in highly active catalytic sites that markedly boosted electrocatalytic activity of the material.
The design of alternative earth-abundant vdW nanoheterostructures for bifunctional oxygen evolution/reduction (OER/ORR) electrocatalysis is of paramount importance to fabricate energy-related devices. A facile and scalable MOF-derived synthetic strategy was used to synthesize metal oxide (ZrO$_2$) based low dimensional 0D-2D heterostructures and is presented in chapter 7. The as-synthesized 0D-2D heterostructures were used as electrocatalysts for OER and ORR reactions and displayed impressive electrocatalytic properties. Furthermore, they also showed competitive performances for water-splitting and zinc-air battery devices.

References


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Chapter 2: Green Synthesis of a Highly Efficient Biosorbent for Organic, Pharmaceutical, and Heavy Metal Pollutants Removal: Engineering Surface Chemistry of Polymeric Biomass of Spent Coffee Waste

2.1 INTRODUCTION

Agrofood industry annually produces enormous amounts of inedible residues, originating mainly from edible cereals and vegetables. Conversion of these wastes to useful resource not just reduces ecological risk imposed by dumping them into the environment, but also eliminates the need for waste management, and the costs associated with the waste management. Due to owning unique characteristic, for instance, renewability, eco-friendlyness, abundance, low cost, and tunable chemical composition, these residues can be used as a sustainable biosorbents for environmental remediation. Unsurprisingly, biosorbents do not have many disadvantages associated with conventional adsorbents, including costly synthesis, expensive equipment requirements, high energy consumption, and environmental issues generation.

Coffee is one of the mostly used agrofood, for example, after tea, coffee is the second most popular drink in the world, and universal production of coffee residue is around 6 million tons per year deriving from manufacturing industries, domestic, and restaurants. The major components of the spent coffee waste (SCW) are cellulose and lignin, containing polar and nonpolar functionalities like hydroxyl, carboxylic, aldehydes, ketones, ether, which make SCW valuable source of fertilizer, biodiesel fuel component, animal feedstuff, and pollutants adsorbent. Indeed, tunable functionalities over polymeric biomass of SCW can be used for adsorption of different environmental pollutants. Nowadays, rapid industrial advancement resulted in generation and dumping various pollutants, e.g. heavy metals, organic pollutants, and pharmaceuticals to the environment causing increased global awareness, for instance,
pharmaceutical antibiotics like tetracyclines (TC) have been extensively used for therapy purposes in human beings and livestock.\textsuperscript{13,14} Ubiquitous distribution of highly soluble TC is posing serious environmental and health-related issues, at which the presence of TC in water can provoke drug resistance and challenge current antibiotic therapies.\textsuperscript{15,16} Synthetic dyes which are also among the most hazardous organic pollutants in industrial effluents, along with heavy metals posing a serious environmental issue due to their high biotoxicity and carcinogenic effects.\textsuperscript{17-22} Due to simplicity, low cost, and ease of operation, adsorption has been considered a versatile technique in elimination of various pollutants regardless of their physicochemical characteristic.\textsuperscript{4-9} Recently, there has been a great interest in development of SCW-based biosorbent for environmental pollutants removal. Surface modification, e.g. chemical treatment, and composite making were shown to be a versatile technique in significantly enhancing SCW adsorption capacity.\textsuperscript{7-9} However, the techniques used so far have not shown any promising results, compared to other available pollutant biosorbents, and a need for a highly efficient biosorbent can be felt.

Herein, we report fabrication of highly efficient biosorbent, sulfonated spent coffee waste (SCW-SO\textsubscript{3}H), through modification of surface chemistry and introduction of highly polar and active sulfonic acid functionalities onto the SCW (Scheme 2.1). The adsorption capacity of the developed SCW-SO\textsubscript{3}H was tested in removal of different range of environmental pollutants, including methylene blue (MB), tetracycline (TC), and chromium (Cr(VI)). In comparison to the previous reports on pollutant removal using spent coffee waste as adsorbent, our biosorbent shows significant enhancement in adsorption capacity which makes the developed biosorbent a promising alternative for water remediation.
2.2 MATERIALS AND METHODS

2.2.1 Materials

Spent coffee waste was collected from the Starbucks. Hydrochloric acid (36.5-38%) and concentrated sulfuric acid (95-98%) were purchased from BDH chemicals. Tetracycline (>88% HPLC) and Sodium hydroxide (>97%) were purchased from Sigma Aldrich. Methylene blue was purchased from Millipore Sigma and Sodium dichromate (99.5%) was purchased from Allied chemicals. Milli-Q (18.2 MΩ) water was used in all experiments.

2.2.2 Fabrication of the adsorbent

Initially, the collected spent coffee waste was washed with Milli-Q water and then boiled for 1 h to remove any coloring materials (caffeine, tannin and other dyes). The solid was then filtered and washed with water repeatedly until no colored water was observed. The solid (spent coffee waste) was dried in a vacuum oven at 70 °C for 12 h. Then 3g of dried spent coffee waste was taken in a round bottom flask and 45 ml of sulfuric acid was added slowly into it. Then the flask was placed in an oil bath to maintain a constant temperature of about 70 °C. The reaction
mixture was stirred continuously and heated for 3 h at 70 °C. Then the mixture was poured out into a beaker (1000 mL) and cooled down to room temperature. 700 ml of ice-cold water was then added into the beaker slowly to dilute the acid. Then the mixture was vacuum filtered and washed with copious amount of water to remove any excess acid. The sample was then placed in a vacuum oven and heated for 12 h at 80 °C. The dried sample was ground into fine powder for further use.

2.2.3 Batch adsorption studies

At first, 800 ppm MB, 600 ppm TC and 400 ppm Cr(VI) stock solutions were prepared by dissolving them in deionized water and solutions of the each pollutants at desired concentrations were prepared by successive dilutions of their stock solutions. For the batch adsorption study, 10 mg of SCW-SO\textsubscript{3}H adsorbent was added to 20 mL of adsorbate solution (MB, TC and Cr(VI)) in a glass vial with constant stirring for 24 h except for the time study where 20 mg adsorbent was added to 40 mL of adsorbate solution. The adsorbate solution was bath sonicated for 30 min after adding the adsorbent into it. 1 M HCl or 1 M NaOH solution was used to adjust the pH of the adsorbate solution. An oil bath was used for the temperature study and the adsorption process was carried out at three different temperatures viz. 25 °C, 45 °C and 65 °C. After 24 h of constant stirring, the MB, TC and Cr(VI) samples were collected in centrifuge tubes by filtering through a 0.45 µm syringe filter. Then the collected MB and TC samples were analyzed by UV-Vis spectroscopy to calculate the remaining concentration of MB and TC after adsorption. The collected Cr(VI) samples were analyzed by ICP-OES to calculate the remaining Cr(VI) concentration in the solution after adsorption. The adsorption maxima considered for MB and SMX were 616 nm and 357 nm, respectively. The adsorption capacity (mg/g) and percentage adsorption (%) were calculated by the using the following equations 1 and 2, respectively:

\[
Q_e = \frac{(C_0 - C_e) \times V}{m}
\]  

(1)
Adsorption(%) = \frac{C_0 - C_e}{C_0} \times 100(\%)

(2)

Where, $C_0$ is the initial concentration and $C_e$ is the equilibrium concentration of the adsorbate (MB, TC and Cr(VI)) solutions, $V$ is the volume of adsorbate solution (mL), $m$ is the weight of the adsorbent (mg) and $Q_e$ is the adsorption capacity of the adsorbent.

2.2.4 Water Purification using Continuous-Flow Column

SCW-SO$_3$H and sand were packed in a glass chromatographic column with dimensions 20× 26× 45.7 cm. With this respect, 1 g of SCW-SO$_3$H along with 110 g of sand were mixed homogeneously and filled the column as dry. To support the column sand was used at the top and cotton was used at the bottom. 500 mL DI water was used to wash the column prior to filtering MB solution. An aqueous solution of 20 ppm MB was filtered through the column at which the filtrate was analyzed using UV-Vis spectroscopy to measure adsorption capacity of the filter.

2.2.5 Experimental data modeling

The Langmuir, Freundlich, Temkin and Dubinin Radushkevich (D-R) isotherm models were applied to examine the reaction behavior between the target pollutants and adsorbent.$^{23,24}$

Langmuir isotherm model: The Langmuir isotherm is expressed by the following equation 3.

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}K_L} + \frac{C_e}{Q_{max}}$$

(3)

Where $Q_e$ is adsorption capacity (mg/g) of the SCW-SO$_3$H, $Q_{max}$ is the maximum adsorption capacity (mg/g), $C_e$ is the equilibrium concentration and $K_L$ is the Langmuir constant (L/mg).

Freundlich isotherm model: The Freundlich isotherm is expressed by the following equation 4.

$$\ln(Q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e)$$

(4)

Where $Q_e$ is the adsorption capacity (mg/g), $C_e$ is the equilibrium concentration, $K_F$ is the Freundlich constant and $1/n$ is the intensity of adsorption.

Temkin isotherm model: The linear equation of the Temkin isotherm model is shown as follows
\[ Q_e = B \ln a_T + B \ln C_e \]  
\[ B = \frac{RT}{b_T} \]

Where \( T \) is the temperature (K), \( R \) is the universal gas constant, \( a_T \) is the equilibrium gas constant, \( b_T \) and \( B \) is the Temkin constant related to the sorption heat.

D-R isotherm model: The linear presentation of the D-R isotherm model is expressed by the following equation.

\[ \ln Q_e = \ln Q_m - \beta \varepsilon^2 \]  
\[ \varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \]

Where \( Q_m \) is the maximum adsorption capacity (mg/g), \( Q_e \) is the adsorption capacity (mg/g), \( \varepsilon \) is the Polanyi potential and \( \beta \) is the activity coefficient.

Pseudo-first order, pseudo-second order, intra-particle diffusion and liquid film diffusion kinetic models were used to fit the kinetic data of the adsorption experiments.\( ^{23,24} \)

Pseudo-first order model: The pseudo-first order kinetic model is expressed by the following equation 9.

\[ \log(q_e - q_t) = \log(q_e) - \frac{k_1}{2303} t \]  
\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{k_1 q_e} \]

Pseudo-second order model: The pseudo-second kinetic model is expressed by the following equation 10.

Where \( t \) is adsorption time, \( q_e \) is the adsorption capacity at equilibrium time, \( q_t \) is the adsorption capacity at time \( t \), \( k_1 \) is the pseudo-first order rate constant (min\(^{-1}\)) and \( k_2 \) is the pseudo-second order rate constant (gm\(g^ {-1}\)min\(^{-1}\)).
Intra-particle diffusion model: This kinetic model was used further to analyze the diffusion mechanism.

\[ Q_t = K_i t^{0.5} + C \]  

(11)

Where \( k_i \) is the intra-particle diffusion rate constant (mg\( g^{-1} \) min\(^{0.5} \)) and \( c \) is a constant (mg/g), related to the boundary layer thickness.

Liquid film diffusion model: This model was applied to determine the actual rate-controlling step whether it is from pore diffusion or film diffusion.

\[ \ln(1 - F) = -K_{fd} t \]  

(12)

Where \( k_{fd} \) is the adsorption rate constant and \( F \) is defined as the fractional achievement of the equilibrium at time \( t \), which can be calculated by the following equation.

\[ F = \frac{Q_t}{Q_e} \]  

(13)

2.3 RESULTS AND DISCUSSION

2.3.1 SEM and EDS analysis

Morphological and elemental analysis of the SCW-SO\(_3\)H biosorbent was investigated by SEM-EDS and the findings are shown in Figure 2.1. SEM analysis shows that the developed SCW-SO\(_3\)H biosorbent is formed of irregular microparticles as shown in Figure 2.1a. As it can be seen from Figure 2.1b, EDS shows presence of all the elemental composition of the SCW as well as introduced sulfonic acid functionalities with elemental ratio of 75.13, 22.76, and 2.11 with respect to carbon, oxygen and sulfur, respectively. Figure 2.1(c-e) shows the elemental color mapping of the as-synthesized biosorbent revealing the presence of C, O and S, respectively.
2.3.2 Zeta potential and Raman analysis

Zeta potential analysis was carried out to find out surface charge of the developed SCW-SO$_3$H biosorbent. According to the findings as shown in Figure 2.2a, the SCW-SO$_3$H shows a highly negative surface charge as expected of introduced sulfonic acid groups. This large negative charge over the surface of SCW-SO$_3$H can induce a strong charge-charge electrostatic interactions with pollutants and as a result high pollutant adsorption can be achieved. Raman spectra of SCW-SO$_3$H shows a prominent G band peak at around 1583 cm$^{-1}$ revealing the SP$^2$ type carbon or graphitic nature of the biosorbent as shown in Figure 2.2b.$^{25,26}$
2.3.3 FT-IR and TGA analysis

To investigate the functional groups of the developed SCW-SO$_3$H biosorbent and character of interactions between the biosorbent and adsorbates, FT-IR analysis was conducted as shown in Figure 2.3a. Presence of SO$_3^-$ stretching peak at around 1153 cm$^{-1}$, O=S=O stretching signal at around 1356 cm$^{-1}$ and C=O peak at around 1700 cm$^{-1}$ proves successful incorporation of sulfone functionality over the surface of SCW. Furthermore, coexistence of signals related to the biosorbent and pollutants show physical character of interactions between biosorbent and adsorbates with no chemical reactions. TGA curves of SCW-SO$_3$H biosorbent before and after adsorption of Cr(VI) are shown in Figure 2.3b. The curve of bare SCW-SO$_3$H shows two weight losses in the applied temperature range. The first one is around 100-200 °C which is related to evaporation of free water as well as water adsorbed over molecular space of the biosorbent. The second weight loss is deriving from decomposition of polymeric biomass and the process ends at around 650 °C. However, upon Cr(VI) adsorption over SCW-SO$_3$H surface, there is negligible mass lose at below 100 °C resulting from moisture evaporation and considerable mass loss starts from around 110 °C and continues to around 500 °C. In comparison to bare SCW-SO$_3$H, the increased threshold of mass lose in the Cr(VI)-loaded SCW-SO$_3$H can be attributed to Cr ions occupying water positions and formation of chromium oxide may be the reason for the Cr(VI)-
loaded SCW-SO$_3$H material not to be fully decomposed even till 800 °C. These results also show considerable adsorption of Cr(VI) by biosorbent.$^{28}$

![Figure 2.3: (a) FT-IR spectra of SCW-SO$_3$H before and after exposure to the pollutants and (b) TGA curves of SCW-SO$_3$H and Cr(VI)-adsorbed SCW-SO$_3$H.](image)

2.3.4 XPS analysis

XPS was performed to investigate elemental composition as well as chemical and electronic state of the Cr(VI) loaded SCW-SO$_3$H biosorbent, which the corresponding results are plotted in Figure 2.4. According to the findings, Cr 2p$_{1/2}$-orbital, Cr 2p$_{3/2}$-orbital, O 1s-orbital, C 1s-orbital, S 2p- orbital, Cr 2s-orbital, and O 2s-orbital were detected in the samples in the regions 586.0 eV, 577.7 eV, 531.4 eV, 284.8 eV, 167.4 eV, 80.9 eV, 75.1 eV, 43.6 eV and 24.9 eV, respectively, as shown in Figure 2.4a. According to Figure 2.4b, the signals observed at BE of 586.0 eV and 577.7 eV are related to chromium trioxide (Cr$_2$O$_3$) and chromium (III) hydroxide (Cr(OH)$_3$), respectively.$^{29,30}$ The three signals related to electronic structure of O 1s-orbital observed at 531.4, 532.1, and 530.5 eV, as shown in Figure 2.4c, correspond the species chromium (III) hydroxide oxide (Cr(OH)O), chromium (III) sulfate (Cr$_2$(SO$_4$)$_3$) and chromium trioxide (Cr$_2$O$_3$), respectively.$^{31-33}$ According to Figure 2.4d, the observed signals related to C 1s-orbital at 283.3 eV, 284.8 eV and 286.2 eV which can be ascribed to trichromium dicarbide (Cr$_3$C$_2$), carbon-
carbon (C-C) bonding, and carbon-oxygen (C-O) bonding, respectively. The signal related to S 2p-orbital was observed at 167.4 eV as shown.
in Figure 2.4e. Figure 2.4f shows irregular peaks observed at 75.1 eV and 80.9 eV, which can be ascribed to Cr 3s-orbital, are related to dichromium trisulfide (Cr$_2$S$_3$) and chromium trioxide (Cr$_2$O$_3$), respectively. The signals observed at 43.6 eV (Figure 2.4g) and 24.9 eV (Figure 2.4h) correspond to Cr 3p-orbital of chromium trioxide (Cr$_2$O$_3$) and O 2s-orbital of hydroxide (OH) and C-O.

2.3.5 Adsorption study: effect of biosorbent dosage, exposure time, pH and temperature

The influence of several variables such as dosage of SCW-SO$_3$H, extent of time at which the pollutants are exposed to the biosorbent, pH of the solution and temperature over adsorption capacity of the developed SCW-SO$_3$H biosorbent was tested and analyzed. As shown in Figure 2.5a, adsorption of all the three pollutants of MB, TC and Cr(VI) was increased upon increasing dosage of biosorbent which can be attributed to more available functionalities and chemical sites over the surface of SCW to interact with the pollutants.$^6,13$ Similar results were found by increasing time exposure of pollutants to the SCW-SO$_3$H biosorbent as shown in Figure 2.5b. It is apparent from this figure that the maximum adsorption of these pollutants onto SCW-SO$_3$H biosorbent occurred within 30 minutes of the time exposure. However, different results were found regarding influence of pH of the solution over adsorption capacity of SCW-SO$_3$H biosorbent. It is known that pH of the solution plays an important role in adsorption capacity of the adsorbent in several ways: influencing surface charge of adsorbent, degree of ionization of the pollutants, dissociation extent of functionalities over active sites of the adsorbent and structure of the pollutant. While with respect to MB and Cr(VI) a straight relationship between pH of the solution and the adsorption extent is found,$^7,18,37$ TC shows completely different behavior.$^{13-16}$ The influence of solution pH over adsorption of Cr(VI) onto SCW-SO$_3$H was studied in pH range of 2-8. As shown in Figure
2.5c and in accordance with previous reports, maximum Cr(VI) adsorption can be achieved in acidic environments. Indeed, depending on the pH of the solution, different hexavalent chromium species of CrO$_4^{2-}$, HCrO$_4^-$, H$_2$CrO$_4$, HCr$_2$O$_7^-$, or Cr$_2$O$_7^{2-}$ can exist.

![Figure 2.5](image)

Figure 2.5: (a) effect of biosorbent dosage: 20 ml of 100 ppm adsorbate solution containing 5, 10, 15 and 20 mg biosorbent; (b) effect of pH: 20 ml of 100 ppm solution containing 10 mg biosorbent in pH range of 2-10 and (c) effect of time: 40 ml of 50 ppm solution containing 20 mg of biosorbent in 0-360 min time exposure.

At lower pH CrO$_4^{2-}$ is the main species and due to relatively positive surface charge of biomass of SCW at that pH, strong electrostatic interactions between the biosorbent and adsorbates results in very high adsorption. CrO$_4^{2-}$ converts to HCrO$_4^-$ and then Cr$_2$O$_7^{2-}$ as pH of the solution rises to around pH of 6 and above. Although Cr$_2$O$_7^{2-}$ specie have the same charge as CrO$_4^{2-}$, but due to repulsion between the negatively charged functionalities over SCW-SO$_3$H at high pH and
negatively charges hexavalent chromium, adsorption capacity of SCW-SO$_3$H at very high pH is even lower than mid-pH where HCrO$_4$ is the main existing specie.$^{7,37}$ MB adsorption over SCW-SO$_3$H biosorbent increases as the pH of the solution raises.$^{18}$

![Chemical Structures](image)

Figure 2.6: (a-b) Chemical structure of TCs and MB [14,18].

This phenomenon can be explained by referring to the chemical structure of MB and its cationic state as shown in Figure 2.6a. In fact, at low pH there is small interaction between SCW-SO$_3$H surface and cationic dye which can be due to non-electrostatic interactions like π-π stacking between aromatic rings of polymers (cellulose and lignin) existing in SCW-SO$_3$H and MB dye.$^{18}$ In addition, presence of H$^+$ at low pH can results in repulsion with MB cationic state and lower the adsorption capacity. However, by increasing pH of the solution, more sulfonic acid groups of SCW-SO$_3$H get dissociated and as a result more negative charge would be available for cationic MB dye to interact. This strong electrostatic interaction leads to high adsorption found at high pH values.$^{18,21}$ Due to having complex structure and functionalities, TCs are expected to show different results than that of Cr(VI) and MB dye. The chemical structures of TC are given in Figure
Depending on the pH of the solution, TC can exist in three forms of TCH⁺, TCH⁻ and TCH⁻. As shown in Figure 2.6c, at pHs below pKa of TC there is some interactions between TC and SCW-SO₃H which might be due to π-π stacking between the aromatic rings as well as π-bonds of the adsorbent and adsorbate. However, in pH more than pKa of TC, and due to formation of negative charged surface of TC and SCW biosorbent, there is an electrostatic repulsion which is the reason behind decreased adsorption in high pH values.

![Graphs showing effect of temperature over adsorption capacity of SCW-SO₃H](image)

Figure 2.7: Effect of temperature over adsorption capacity of SCW-SO₃H toward (a) MB; (b) TC and (c) Cr(VI) pollutants.

Temperature of the solution has shown to have significant effect on adsorption capacity of SCW-SO₃H biosorbent. According to the findings shown in Figure 2.7, increasing temperature resulted in sharp increases in adsorption of TC and Cr(VI). This can be explained by increased
kinetic energy of adsorbates as well as SCW-SO$_3$H functionalities which are more available to interact with the pollutants at elevated temperatures$^{6,7}$ In addition, at elevated temperature and due to expansion of the biosorbent, more interaction sites would be available for the biosorbent and pollutants and as a result more adsorption is expected. However, no temperature influence was found with respect to MB adsorption up to 400 ppm. However, temperature is shown to have positive impact on the adsorption of MB dye over SCW-SO$_3$H at applied concentration higher than 500 ppm.

2.3.6 Isotherm Study

To analyze nature of interactive mechanism between the biosorbent and adsorbate, and to design, model and evaluate an adsorption system, adsorption isotherm is considered a strong tool. The isotherm models such as Langmuir, Freundlich, Temkin and Dubinin-Redushkevich (D-R) are among the well-known isotherm models were applied in this study$^{23,24}$ Hence, in the current study, we carried out isotherm study on the developed SCW-SO$_3$H biosorbent using different isotherms to fit our experimental data. In the Langmuir isotherm model, it is assumed that adsorption occurs onto a homogenous surface of adsorbent which means that all of binding sites over an adsorbent are similarly interactive$^{23,24}$ On the other hand, in the Freundlich isotherm model, it is assumed that the strength of all binding sites over an adsorbent are heterogeneous. Where Temkin isotherm model includes a factor to investigate interaction between adsorbent and adsorbate, Dubinin-Redushkevich isotherm model is used to explore nature of an adsorption process as chemical or physical.$^{23,24}$ Our findings regarding isotherm study of interaction between SCW-SO$_3$H biosorbent and pollutants using Langmuir, Freundlich, Temkin and Dubinin-Redushkevich isotherm models are shown in Figure 2.8(a-d). As it can be seen, MB and TC patterns match up Langmuir isotherm with $R^2$ value of 0.999 and 0.988, respectively,
demonstrating that the developed SCW-SO$_3$H biosorbent acts as having uniform binding sites toward adsorbing MB and TC pollutants.

![Figure 2.8: (a) Langmuir Isotherm; (b) Freundlich Isotherm; (c) Temkin Isotherm and (d) Dubinin-Redushkevich isotherm of adsorption of MB, TC and Cr(VI) over SCW-SO$_3$H biosorbent.](image)

On the other hand, Cr(VI) pattern matches up Freundlich isotherm with $R^2$ value of 0.996, showing that the SCW-SO$_3$H biosorbent acts as having heterogeneous binding sites toward adsorbing Cr(VI) pollutant.

### 2.3.7 Kinetic and thermodynamic Study

Based on different kinetic models such as pseudo-first order, pseudo-second order, intra-particle diffusion and liquid film diffusion, extent of pollutant adsorption per gram of adsorbent ($Q_e$) after adsorption over SCW-SO$_3$H biosorbent is measured as plotted in Figure 2.9(a-d).
According to the findings, adsorption of all the adsorbates over SCW-SO$_3$H biosorbent follows Pseudo-second order kinetic at which experimental data fits very well the calculated data.$^{23,24}$ While fitting experimental data to theoretical data using pseudo-first order and pseudo-second order might not provide absolute sorption mechanism, intra-particle diffusion and liquid film diffusion kinetic models were also performed.$^{23,24}$ However, both the intra-particle diffusion and liquid film diffusion kinetic models failed in fitting between experimental and theoretical data, as evident from significantly lower $R^2$ value compared to pseudo-first order and pseudo-second order models. Hence, it shows that it is unlikely that intra-

![Graphs](image-url)

Figure 2.9: (a) pseudo-first order; (b) pseudo-second order; (c) intra-particle diffusion and (d) liquid film diffusion kinetic model graph of adsorption of MB, TC and Cr(VI) over SCW-SO$_3$H biosorbent.
particle diffusion is the rate determining step in the sorption of pollutants over SCW-SO3H biosorbent.\textsuperscript{23,24}

The thermodynamic study gives valuable information about an adsorption process whether it is occurring spontaneously or not as well as we can get the values of $\Delta H^0$, $\Delta G^0$ and $\Delta S^0$ by calculating the fundamental thermodynamic parameters.\textsuperscript{38,39} With this respect and to better realize the influence of temperature on the MB, TC and Cr(VI) adsorption over the SCW-SO3H biosorbent, the thermodynamic parameters of $\Delta G^0$, $\Delta H^0$, and $\Delta S^0$ were calculated by using the following equations:\textsuperscript{38,39}

\begin{align}
K_c &= \frac{Q_e}{C_e} \quad (14) \\
\Delta G^0 &= -RT \ln K_c \quad (15) \\
\ln K_c &= -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (16)
\end{align}

Where, $T$ (K) is absolute temperature, $R$ (8.314 Jmol$^{-1}$K$^{-1}$) is universal gas constant, $K_c$ is the adsorption equilibrium constant (Lg$^{-1}$), $C_e$ is the equilibrium concentration of the pollutants in the solution. $\Delta G^0$, $\Delta S^0$ and $\Delta H^0$ are standard Gibb’s free energy, entropy and enthalpy changes, respectively. From Table 2.1, we can be seen that the $K_c$ values are increasing with increasing temperature from 298 K to 338K, which suggests the endothermic nature of the process ($\Delta H^0 >0$). The negative value of $\Delta G^0$ also indicates the spontaneity of the adsorption process with no need for foreign energy source for interactions. The $\Delta G^0$ values are more negative at higher temperatures showing that at higher temperature the biosorption process is more favorable. Furthermore, a biosorption process can be identified whether it is physical or chemical based on the $\Delta G^0$ values as the $\Delta G^0$ values ranging from 0 to -20 kJ/mol is physical in nature and -80 to -400 kJ/mol is chemical in nature. Based on the obtained $\Delta G^0$ values for MB, TC and Cr(VI) adsorption onto SCW-SO3H, it is apparent that the adsorption process is physical in nature in all cases.
Table 2.1: Thermodynamic values of $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ at three temperatures of 298, 318, and 338 K with respect to adsorption of MB, TC and Cr(VI) over SCW-SO$_3$H biosorbent.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Pollutants</th>
<th>T, K</th>
<th>$K_2$</th>
<th>$\Delta G^\circ$, KJmol$^{-1}$</th>
<th>$\Delta H^\circ$, KJmol$^{-1}$</th>
<th>$\Delta S^\circ$, Jmol$^{-1}$K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCW-SO$_3$H</td>
<td>MB</td>
<td>298</td>
<td>4.19</td>
<td>-3.55</td>
<td>8.19</td>
<td>39.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>318</td>
<td>4.88</td>
<td>-4.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>338</td>
<td>6.21</td>
<td>-5.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TC</td>
<td>298</td>
<td>1.25</td>
<td>-0.56</td>
<td>11.91</td>
<td>41.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>318</td>
<td>1.69</td>
<td>-1.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>338</td>
<td>2.21</td>
<td>-2.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr(VI)</td>
<td>298</td>
<td>1.22</td>
<td>-0.49</td>
<td>9.34</td>
<td>32.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>318</td>
<td>1.45</td>
<td>-0.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>338</td>
<td>1.91</td>
<td>-1.82</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Positive value of $\Delta S^\circ$ confirms an increased disorder and accident in the solid (biosorbent) and solution interface, as well as high affinity towards the adsorption process.$^{38,39}$

2.3.8 A filter based on the developed SCW-SO$_3$H biosorbent for pollutant removal

The packed SCW-SO$_3$H-based filter was used to remove 20 ppm MB aqueous solution in a continuous mode and the filtrate was analyzed using UV-Vis spectroscopy to measure the extent of MB adsorption using the developed biosorbent. According to the results shown in Figure 2.10, which shows plot of filtered water versus % MB removal, ~100% of the MB was adsorbed over the biosorbent and removed by the filter. Moreover, Figure 2.10 shows that the filter is capable of removing all the MB till 13 L of MB solution and after that small drop in adsorption capacity of the filter is observed which can be due to saturation of the biosorbent by MB.
2.4 CONCLUSION

It is shown that our developed biosorbent, sulfonated spent coffee waste (SCW-SO$_3$H) synthesized via introduction of sulfonic acid polar functionalities over the polymeric biomass (cellulose and lignin) of the SCW, was an efficient biosorbent in removal of different environmental pollutants of MB, TC and Cr(VI) with higher adsorption capacities of 812, 462 and 302 mg/g, respectively. Kinetic study showed that all the adsorbates were adsorbed over SCW-SO$_3$H following pseudo second-order rate, and thermodynamic study showed $\Delta H >0$ and $\Delta G <0$ values demonstrating endothermic nature and spontaneity of the adsorption of pollutants over SCW-SO$_3$H biosorbent. It was also shown that while adsorption of MB and TC follow Langmuir isotherm, Cr(VI) adsorption matches up with Freundlich isotherm. Due to superior adsorption capacity observed by SCW-SO$_3$H compared to recently reported SCW-based biosorbents, authors hope that this report acts as platform in designing and fabrication of highly efficient biosorbents toward pollutant removal and water remediation.
References


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Chapter 3: Ultrafast Catalytic Reduction of Environmental Pollutants in Water via MOF-derived Cu and Magnetic Ni Nanoparticles Encapsulated in Porous Carbon

3.1 INTRODUCTION

As organometallic compounds, metal-organic frameworks (MOFs) are made of metal centers (inorganic nodes) chemically bonded to organic ligands (linkers) resulting in three-dimensional porous materials. Copper-1,4-benzenedicarboxylate (Cu-BDC) and nickel-1,4-benzenedicarboxylate (Ni-BDC) are examples of MOFs composed of metallic centers of Cu and Ni, respectively, linked through BDC organic ligands. Due to many advantages of Cu-BDC and Ni-BDC MOFs including high porosity, tunability of pore sizes and shapes, and valuable functionalities, these MOFs are widely used for numerous applications, e.g. gas adsorption, storage and separation, catalysis, batteries, sensing and so on. In addition to their direct use and owning to presence of metals and carbon as well as an inherent porosity, MOFs (as precursors) can be converted to MOF-derived products through a carbonization process. Deriving from a catalytic nature of many transitional metals in their metallic form, metal particles-embedded porous carbon composite materials can be made through carbonization of MOFs in an inert atmosphere. e.g. N₂ or Ar. These materials have metallic nanoparticles embedded in a highly porous carbon substrate. Stemming from numerous advantages including the high surface area of the metal particles due to the presence of highly segregated nanoscale particles over the carbon substrate, and inertness of carbon substrate toward chemical reactions, these composite materials can have numerous applications in metal-catalyzed systems.17

Metal nanoparticles (NPs), especially copper and nickel NPs have drawn a great attention over the last few decades due to their low cost as well as their potential applications in sensing, hydrogen generation, catalytic hydrogenation, supercapacitors and catalysis. But, due to their
high surface energy, these NPs tend to agglomerate easily resulting in a significant reduction of their performance during the catalysis process. An effective way to overcome these problems is to immobilize the NPs on the solid support such as carbon, alumina and mesoporous silica materials [23-35]. Among them, mesoporous carbon materials are known to be a good candidate as a solid support due to their high surface area, excellent conductivity and low density, etc. Many efforts have been made to design efficient methods including chemical vapor deposition, explosion and hard-templating approach to make carbon supported metal NPs. Most of the methods require a multi-step synthetic process, high energy consumption and a sophisticated apparatus. So, it remains challenging to prepare carbon encapsulated metal nanoparticles via a cost effective and simple method. In this regard, MOF templating synthesis of carbon encapsulated metal nanoparticles could be an effective alternative method. In recent times, carbon encapsulated copper and nickel nanoparticles have been synthesized easily via direct carbonization of the MOFs under an inert (N\textsubscript{2} or Ar) atmosphere. However, many nickel and copper-based MOFs have been utilized as precursors to make their respective metal-carbon composites, but the synthesis procedure for most of the MOFs require a long time, high temperature, toxic organic solvents and expensive ligands. Among the many Cu and Ni-MOFs, Cu-BDC and Ni-BDC MOFs can be easily prepared by utilizing a readily available and inexpensive ligand. The purpose of this work is based on using a cheap ligand, terephthalic acid to make Cu-BDC and Ni-BDC MOFs as precursors for making C@Ni and C@Cu nanocatalysts by their direct carbonization. Unlike relatively expensive ligands, for instance, trimesic acid or 1,3,5-benzenetricarboxylic acid which is a tridentate ligand and reported in few articles for synthesis of metal@carbon nanocomposites, the ligand used in this study, terephthalic acid is much cheaper and also is a bidentate ligand which may leads to a large difference in properties of the resulting MOFs including porosity,
geometry, etc. Therefore, which to best of our knowledge is for the first time, magnetic C@Ni and C@Cu nanocatalysts are synthesized through carbonization of Ni-BDC and Cu-BDC MOFs at 600 °C under Ar atmosphere. Furthermore, unlike the reported metal@carbon nanocomposites which were used for sensing, hydrogen generation, catalytic hydrogenation and supercapacitors, our synthesized Cu@C and Ni@C nanocatalysts were used for catalytic reduction of organic pollutants whereas they showed superior performance toward the reduction of 4-nitrophenol (4-NP), methylene blue (MB), and methyl orange (MO).

Nitrophenols are organic pollutants which are common in industrial effluents of various industries, e.g. pesticide and pharmaceutical industries, and are categorized as a “Priority Pollutants” by the United States Environmental Protection Agency (EPA) whereas their concentration limit is <10 ng L⁻¹. On the other hand, 4-aminophenol (4-AP) as a product of reduction of 4-nitrophenol (4-NP), is considered an essential precursor for organic synthesis and in pharmaceutical industry. The azo dyes such as methyl orange (MO) and methylene blue (MB) exist in sewage of many industries such as textile industries and are proven to result in health-related issues especially in high dosages as a result of their toxicity and carcinogenic effects. While the water pollutants can be removed from water and wastewater by various means including photocatalysis, adsorption, coagulation and so on, however, catalytic reduction of the pollutants to valuable compounds not just deals with the issue of environmental pollution, but also is an economical process converting harmful compounds into beneficial ones.

In the current study, we have prepared the C@Cu and magnetic C@Ni nanocatalysts via direct carbonization of Cu-BDC and Ni-BDC MOFs, respectively. The precursor materials are synthesized by using a simple and green solvothermal method. The developed nanocatalysts are characterized by XRD, SEM, TEM, EDS, TGA, FTIR, Raman and VSM instruments. The catalytic
performance of the developed magnetic C@Ni and C@Cu nanocatalysts towards the reduction of 4-NP, MO and MB is carried out in presence of NaBH₄ as a reducing agent. Finally, reusability of the developed magnetic C@Ni and C@Cu nanocatalysts is tested through several times recycling and reuse of the catalysts.

![Scheme 3.1: Synthesis of Ni-BDC MOF and Ni@C nanocatalyst.](image)

### 3.2 MATERIALS AND METHODS

#### 3.2.1 Materials

All chemicals were reagent grade and used without further purification. Following chemicals were used to prepare the magnetic C@Ni and C@Cu nanocatalyst. Terephthalic acid or benzene-1,4-dicarboxylic acid (BDC), dimethylformamide (DMF), Ni(NO₃)₂·6H₂O and Cu(NO₃)₂·2.5H₂O were purchased from Sigma-Aldrich. Sodium borohydride (NaBH₄), methylene blue, methyl orange and 4-nitrophenol were purchased from Sigma-Aldrich. Deionized (DI) water was obtained from Milli-Q® instrument, Millipore Corporation.
3.2.2 Synthesis of Ni-BDC MOF

The Ni-BDC and Cu-BDC MOFs were synthesized by a facile solvothermal method. In a typical experiment of making Ni-BDC MOF, at first, 720 mg of Ni(NO₃)₂.6H₂O was dissolved in 10 mL of deionized water and was then mixed with BDC solution of 132 mg BDC in 10 mL DMF. The resulting solution was then stirred for 15 minutes. Afterward, the solution was placed into a glass reactor and was closed tightly. The glass reactor was inserted into an oven and heated for 24 h at 100 °C. The glass reactor was cooled down to room temperature, and the light green solid of Ni-BDC MOF was collected through vacuum filtration followed by washing with water and DMF for three times. The solid was put in a vacuum oven for 12 h at 110 °C for drying and then was kept in a glass vial for further use.

3.2.3 Synthesis of Cu-BDC MOF

Cu-BDC MOFs were synthesized by using a similar experimental procedure except Cu(NO₃)₂.2.5 H₂O was used instead of Ni(NO₃)₂.6H₂O. The obtained blue solid of Cu-BDC MOF was kept in a glass vial.

3.2.4 Synthesis of magnetic C@Ni nanocatalyst

Magnetic C@Ni nanocatalyst was synthesized by direct carbonization of Ni-BDC MOFs at 600 °C in a furnace under an argon gas flow for 1 h with a heating rate of 5 °C/min. The black product which was distinct from green Ni-BDC MOFs was taken out from the furnace and cooled down to room temperature and was kept in a glass vial.

3.2.5 Synthesis of C@Cu nanocatalyst

C@Cu nanocatalyst was prepared by a similar procedure to C@Ni nanocatalyst except Cu-BDC MOFs were used in place of Ni-BDC MOFs and likewise, the black product which was
distinct from blue Cu-BDC MOFs was taken out from the furnace and cooled down to room temperature and was kept in a glass vial.

3.2.6 Typical procedure for catalytic reduction of 4-NP, MO and MB

The catalytic reduction of MB, 4-NP and MO was performed in a quartz cuvette having a path length of 1.0 cm. In all catalytic reduction experiments, 4 mL of 20 ppm pollutant (MB, 4-NP and MO) solution, 1 mg nanocatalyst (C@Ni and C@Cu) and 5 mg NaBH₄ as a reducing agent were used. Initially, the nanocatalyst was added to the pollutant solution and was subjected to sonication in a water bath for 2 min. Then NaBH₄ was added to the solution mixture to induce the catalytic reduction of the pollutants, and the catalytic reduction reaction was continued until the solution became colorless. The catalytic reduction of the pollutants was monitored by UV-visible spectroscopy at different time intervals over the range of 200 to 800 nm. The kinetics data for reduction of 4-NP, MO and MB were obtained by monitoring the absorbance at maximum lambda of 400, 465 and 660 nm for 4-NP, MO and MB, respectively. The percent reduction of 4-NP, MO and MB were calculated by the following equation 1.32

\[
\% \text{ Conversion} = \left( \frac{C_o - C_t}{C_o} \right) \times 100\%
\]  

(1)

Where Co and Ct are the concentrations of the pollutants at time 0 and t of the catalytic reduction.

3.3 RESULTS AND DISCUSSION

3.3.1 Analysis of crystalline structure by XRD

The Ni-BDC and Cu-BDC MOF precursors were prepared by a green solvothermal method. Then the synthesized MOF powders were carbonized directly at 600 ºC under an argon gas flow to obtain magnetic C@Ni and C@Cu nanocatalysts. To analyze the crystalline structure of the synthesized Cu-BDC and Ni-BDC MOFs as precursors and the corresponding C@Ni and
C@Cu nanocatalysts, XRD analysis was carried out, at which the crystalline pattern of the materials, as shown in Figure 3.1(a-b).

Figure 3.1: XRD pattern of (a) Ni-BDC and Cu-BDC MOFs; (b) C@Ni and C@Cu nanocatalysts.

According to the findings shown in Figure 3.1a, Cu-BDC and Ni-BDC MOFs show a very crystalline property, confirming the successful synthesis of these MOFs. As it can be seen from XRD patterns of C@Ni and C@Cu nanocomposites, as shown in Figure 3.1b, Ni-BDC and Cu-BDC MOFs are completely decomposed to the corresponding nanocomposites, at which the crystalline peaks of Cu-BDC and Ni-BDC MOFs disappear upon carbonization and new sharp peaks related to metallic Ni and Cu appear. The sharp signals at around $2\theta = 43.6$, $50.8$ and $74.4$ for C@Cu correspond to metallic Cu (JCPDS 04-0836). With respect to C@Ni, three sharp signals at around $2\theta = 44.48^\circ$, $51.28^\circ$, and $76.35^\circ$ correspond to cubic-phase Ni metal (JCPDS no. 04-0850) and a small signal at around $2\theta = 26$ related to (002) lattice of graphite carbon. These findings confirm the successful conversion of Cu-BDC and Ni-BDC MOFs to the corresponding C@Cu and C@Ni nanocatalysts upon carbonization of the MOFs.
3.3.2 Morphological analysis by SEM and TEM

To study the morphological characteristic of the synthesized Ni-BDC and Cu-BDC MOFs and the corresponding metal nanocatalysts, SEM and TEM analyses were carried out. The SEM images of the magnetic C@Ni and C@Cu nanocatalysts along with their corresponding MOFs are presented in Figure 3.2(a-d). According to the SEM image shown in Figure 3.2a, Ni-BDC MOF is composed of micron-sized particles. Upon conversion of Ni-BDC MOF to the corresponding magnetic C@Ni nanocomposites via carbonization process, the morphology of Ni-BDC MOF undergoes a change, where the nano-sized nickel particles are decorated over the carbon sheets as shown in Figure 3.2b. Furthermore, the SEM image of Cu-BDC MOF also shows micro size MOF particles with a needle-like shape as shown in Figure 3.2c. Similar results are found in case of C@Cu nanocatalyst at which carbonization of Cu-BDC MOF results in the formation of nano-sized copper particles over the carbon sheets as seen in Figure 3.2d.

Figure 3.2: SEM micrographs of (a) Ni-BDC MOF; (b) C@Ni nanocatalyst; (c) Cu-BDC MOF; and (d) C@Cu nanocatalyst.
TEM microscopic analysis was further performed to investigate the morphology of the prepared nanocatalysts and their corresponding parent materials, and the findings are shown are in Figure 3.3(a-d). As seen from the TEM images of Ni-BDC and Cu-BDC MOF in Figure 3.3a and Figure 3.3c that the MOF particles are micron in size with a rod like shape morphology. But the morphology of the MOF particles undergoes a change due to the formation of Ni and Cu nanoparticles upon carbonization treatment as seen in Figure 3.3b and Figure 3.3d.

As seen in Figure 3.3b and Figure 3.3d, it is clear that the Ni and Cu nanoparticles are uniformly dispersed in the porous carbon and most interestingly, all the nanoparticles are wrapped by the thin porous carbon matrix. This wrapping prevents them from further oxidation and this statement can be verified by the XRD results as there were no peaks related to nickel oxide or copper oxide observed in XRD pattern for C@Ni and C@Cu samples. SEM and TEM findings further verify the successful conversion of Ni-BDC and Cu-BDC MOFs into magnetic C@Ni and C@Cu nanocatalysts upon carbonization. Moreover, it is noteworthy that the size of metallic Cu and Ni
formed over the carbon platform is in range of several nanometers. Hence, due to the presence of catalytic sites with a large surface area and well dispersion of the metallic particles over the carbon platform, a superior catalytic activity by the developed magnetic C@Ni and C@Cu nanocatalysts is expected.

3.3.3 Chemical composition analysis by EDS

To determine the chemical composition of the synthesized magnetic C@Ni and C@Cu nanocatalysts, the samples were subjected to EDS analysis, which the corresponding results are shown in Figure 3.4(a-d).

Elemental analysis reveals that the C@Ni nanocatalyst is composed of only C (25.991%) and Ni (74.009%) as seen in Figure 3.4a. The absence of O in the nanocatalyst sample is due to the fact
that the metallic Ni doesn’t undergo any oxidation because of their wrapping in the porous carbon matrix. Similar results were found in case of C@Cu nanocatalyst. Based on the EDS analysis, the C@Cu nanocatalyst contains only C (23.433%) and Cu (76.567%) as seen in Figure 3.4c. This nanocatalyst also doesn’t undergo any oxidation as they are well wrapped by the porous carbon matrix. Moreover, EDS elemental color mapping of each sample was also carried out to see the elements that are present in the samples. Based on the findings, the magnetic C@Ni nanocomposite own only C and Ni elements as seen in Figure 3.4b, whereas the C@Cu nanocomposite owns only C and Cu elements as seen in Figure 3.4d which has a good agreement with the EDS elemental analysis. These findings further prove the successful conversion of Ni-BDC and Cu-BDC MOFs into the corresponding magnetic C@Ni and C@Cu nanocomposites.

3.3.4 Raman analysis

Raman analysis of the C@Ni and C@Cu nanocatalysts are shown in Figure 3.5. According to the findings, carbonization of Ni-BDC MOF results in the formation of carbon as graphite with D and G bands around 1346 cm\(^{-1}\) and 1583 cm\(^{-1}\), respectively.\(^4\) Furthermore, the Raman analysis of the C@Cu nanocatalyst sample also showed two broad peaks at around 1342 cm\(^{-1}\) and 1576 cm\(^{-1}\) for the D and G band of the graphitic carbon. The D band is attributed to disorder-induced mode, whereas the G band is attributed to \(E_{2g}\) mode from the graphitic or sp\(^2\) type carbon.\(^4\) In Raman spectra, the relative ratio of the D to G band (\(I_D/I_G\)) values were 0.88 and 0.78 for magnetic C@Ni and C@Cu nanocatalysts, respectively demonstrating the crystallization degree of the sp\(^2\) or graphitic carbon. These calculated \(I_D/I_G\) ratio values for magnetic C@Ni and C@Cu nanocatalysts were comparable to those measured values for rGO and GO (\(\sim 1\)), showing that the high-quality 3D graphitic type carbon was formed. These findings show successful carbonization of the MOFs and formation of Cu@C and Ni@C nanocatalysts.
3.3.5 TGA analysis

TGA analysis was carried out at 25 to 1000 °C temperature range to investigate the thermal stability as well as the percentage loading of the Ni and Cu nanoparticles in the C@Ni and C@Cu samples along with the MOF samples. According to the TGA analysis shown in Figure 3.6(a-b), in the case of Cu-BDC and Ni-BDC MOFs, there is a small weight loss at around 100 °C which can be attributed to dehydration. Furthermore, most of the Cu-BDC and Ni-BDC MOFs decompose at around 350 °C and 450 °C, respectively, due to the degradation of organic moiety and the undecomposed part can be ascribed to the metals and their corresponding oxides.45-47 However, in the case of the corresponding magnetic C@Ni and C@Cu nanocatalysts, only a little change was observed over the studied temperature range. From the thermogram, the calculated percentage loading of Ni and Cu in the porous carbon were 83.43% and 84.08%, respectively as shown in Figure 3.6(a-b). Evidently, the metal (Ni/Cu) contents increased during carbonization, while the carbon content was usually dropped as elevating the temperature. These results show the successful carbonization of the Cu-BDC MOF and Ni-BDC MOF samples.
Figure 3.6: TGA curves of Ni-BDC and Cu-BDC MOFs and the corresponding C@Ni and C@Cu nanocatalysts.

3.3.6 FT-IR analysis

FT-IR analysis was performed to identify the functional groups of the Ni-BDC and Cu-BDC MOFs along with the nanocatalysts that are derived from them and the results are given in Figure 3.7(a-b).

Figure 3.7: FT-IR analysis of (a) Ni-BDC MOF and magnetic C@Ni nanocatalyst; (b) Cu-BDC MOF and C@Cu nanocatalyst.

There is a broad signal at 3440 cm\(^{-1}\) in both MOF samples that is due to the O–H stretching vibrations for the adsorbed water.\(^{48}\) In both MOF samples, there are two characteristic broad peaks
for symmetric and asymmetric vibrations of (–COO-) groups at 1398 cm\(^{-1}\) and 1597 cm\(^{-1}\), respectively indicating the presence of dicarboxylate linker in the MOF samples.\(^{49}\) But all the characteristic peaks are absent in the C@Ni and C@Cu nanocatalyst samples indicating that the both MOFs are completely decomposed upon carbonization to form the corresponding nanocatalysts.

### 3.3.7 Magnetic Measurement of the C@Ni nanocatalyst

The magnetic properties of the synthesized C@Ni nanocatalyst have been characterized using vibrating sample magnetometer (VSM) at 300 K.

![Magnetization dependence of magnetic field at 300 K for magnetic C@Ni nanoparticles.](image)

**Figure 3.8:** Magnetization dependence of magnetic field at 300 K for magnetic C@Ni nanoparticles.

Figure 3.8 shows closed hysteresis loops of the magnetization dependence on magnetic field plot revealing superparamagnetic behavior of C@Ni nanoparticles. The sample yields saturation magnetization (MS) of 24 emu/g and coercivity (HC) of 23 Oe. Based on the magnetic results, the mass ratio of the magnetic materials in the carbon-impeded matrices can be determined by comparing the MS value of the related bulk Fe yielding 44 wt% of the magnetic Ni in the C@Ni system.\(^{50}\) Moreover, the magnetic domain size can be obtained from the hysteresis loop by
calculating the initial slope of the hysteresis loop. The analysis yields magnetic domain size of 12 nm for the Fe magnetic core.

### 3.3.8 Catalytic reduction of 4-NP, MO, and MB over magnetic C@Ni nanocatalyst

To analyze the catalytic performance of the developed magnetic C@Ni nanocatalysts, three organic pollutants viz. 4-NP, MO and MB were reduced over the nanocatalyst in presence of NaBH₄ as a reducing agent. The catalytic reduction reactions of MB, MO and 4-NP are presented in Figure 3.9.

![Methylene blue (MB)](image)

**Figure 3.9:** Catalytic reduction of MB, MO and 4-NP over C@Ni and C@Cu nanocatalysts in presence of NaBH₄.

Figure 3.10(a-c) presents the time-dependent UV-vis absorption experiments of 4-NP, MO and MB reduction reactions, respectively. At first, we tested the magnetic C@Ni nanocatalyst towards the catalytic reduction of 4-NP. The reduction reaction of 4-NP to 4-AP with reducing agent NaBH₄ in aqueous medium has been developed as a model reaction in recent times that many
groups utilized to test catalytic performance. This reduction reaction can be monitored precisely through UV-vis spectroscopy. It is apparent that the 4-NP solution with NaBH₄ shows a strong adsorption band at around 400 nm and the shifting of this peak to 300 nm indicating the successful reduction of 4-NP to 4-AP. The 4-NP solution color was light yellow initially but it turned to deep yellow upon addition of NaBH₄. Afterward, the color of the solution was changed to colorless within 1 min after adding the magnetic C@Ni nanocatalyst due to the formation of 4-AP. The progress of this reaction was measured timely by the UV-vis spectroscopy and the results are given in Figure 3.10a. As seen from the figure, the reduction reaction of 4-NP proceeded immediately after the addition of NaBH₄ and nanocatalyst and we collected the UV-vis spectra in every fifteen seconds. The intensity of the 4-NP peak at 400 nm declined sharply, while the 4-AP peak at 300 nm increased. No other peaks were observed in the UV-vis spectra, demonstrating no side reaction had occurred during the catalytic reduction of 4-NP. When the adsorption peak for 4-NP was no longer present and the corresponding solution color changed from dark yellow to a colorless solution, indicating the catalytic reduction reaction of 4-NP finished. In the case of MO and MB, it is obvious that their reduction occurred instantly upon the addition of magnetic C@Ni nanocatalyst and NaBH₄ as seen in Figure 3.10(b-c). The decolorization of MO and MB was also finished in about 1 min. These findings indicate that the developed nanocatalyst is liable for the probable cleavage of the chromophoric group or N=N double bond that is present in MO and MB resulting in the decolorization of the solutions. The adsorption maxima were considered at 465 nm and 660 nm for MO and MB, respectively for the catalysis experiments and the change in absorbance according to these values was monitored over time. The formation of the aromatic compounds due to the reduction of MO and MB can be noticed as the new peaks are observed in the UV-vis spectra over reaction time.
Further, the kinetics of the catalytic reduction reactions were analyzed to get more information about the catalytic performance of the newly prepared magnetic C@Ni nanocatalyst and the results are given in Figure 3.10d and Table 3.1. In the studied catalytic reduction reactions, the NaBH₄ concentration was higher than the pollutants and hence, it can be taken as a constant over the reaction time. Therefore, the pseudo-first order kinetic model can be used to calculate the apparent rate constant and the kinetic equation can be expressed by the following equation 2.⁵²

\[ \ln(C_t/C_0) = -kt \]  

(2)

Where \( C_0 \) and \( C_t \) is the concentration of pollutant solution at time 0 and t, \( k \) is the apparent rate constant and \( t \) is the time. The calculated rate constants for the catalytic reduction of 4-NP, MO,
and MB were found to be 0.075 s\(^{-1}\), 0.123 s\(^{-1}\), and 0.114 s\(^{-1}\), respectively which is higher than many other catalysts reported in literature.\(^{42,53,54}\)

Table 3.1: Kinetics of catalytic reduction of 4-NP, MO and MB by magnetic C@Ni and C@Cu nanocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pollutants</th>
<th>Amount of Catalyst</th>
<th>Reaction Time</th>
<th>Rate Constant</th>
<th>Yield (%)</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>C@Ni</td>
<td>4-NP</td>
<td>1 mg</td>
<td>60 Sec</td>
<td>0.075 s(^{-1})</td>
<td>98.25</td>
<td>0.898</td>
</tr>
<tr>
<td></td>
<td>MO</td>
<td>1 mg</td>
<td>60 Sec</td>
<td>0.123 s(^{-1})</td>
<td>99.90</td>
<td>0.977</td>
</tr>
<tr>
<td></td>
<td>MB</td>
<td>1 mg</td>
<td>60 Sec</td>
<td>0.114 s(^{-1})</td>
<td>99.84</td>
<td>0.943</td>
</tr>
<tr>
<td>C@Cu</td>
<td>4-NP</td>
<td>1 mg</td>
<td>60 Sec</td>
<td>0.059 s(^{-1})</td>
<td>95.35</td>
<td>0.859</td>
</tr>
<tr>
<td></td>
<td>MO</td>
<td>1 mg</td>
<td>60 Sec</td>
<td>0.062 s(^{-1})</td>
<td>96.84</td>
<td>0.894</td>
</tr>
<tr>
<td></td>
<td>MB</td>
<td>1 mg</td>
<td>60 Sec</td>
<td>0.089 s(^{-1})</td>
<td>99.33</td>
<td>0.943</td>
</tr>
</tbody>
</table>

3.3.9 Catalytic reduction of 4-NP, MO, and MB over C@Cu nanocatalyst

In order to examine the catalytic performance of the prepared C@Cu nanocatalyst, again the 4-NP, MO and MB pollutant solutions were used as the input for the catalytic reduction reaction. As seen in Figure 3.11a, the adsorption band at 400 nm decreased significantly within 1 min after the addition of nanocatalyst and NaBH\(_4\), and at the same time, a new adsorption peak was appeared at 300 nm which is due to the conversion of 4-NP to 4-AP. Furthermore, the C@Cu nanocatalyst was then tested for the catalytic reduction of MO in presence of NaBH\(_4\) and the results are given in Figure 3.11b. From the figure, it is clear that the adsorption maxima at 465 nm was also decreased drastically within 1 min once the nanocatalyst and reducing were added to the MO solution while introducing a new peak in UV-vis spectra which is due to the formation of hydrazine derivatives as a reduced product of MO. Further, another dye solution, MB was also tested and the results are presented in Figure 3.11c.
As seen in the figure, the adsorption peak for MB at around 660 nm was also diminished quickly in 1 min upon the addition of C@Cu and NaBH₄ while showing some new peaks in UV spectra for the leuco MB formation from the reduction reaction. After observing the obtained results, it can be noted that the conversion of 4-NP to 4-AP, MO to hydrazine derivatives and MB to leuco MB were completed. The apparent rate constants were also calculated for the catalytic reduction of 4-NP, MO and MB by using equation 2 from the kinetic study as seen in Figure 3.11d. The rate constants for reduction of 4-NP, MO, and MB were found to be 0.059 s⁻¹, 0.062 s⁻¹, and 0.089 s⁻¹, respectively and the corresponding results are presented in Table 3.1. Based on our findings, these rate constant values are higher than many other previously reported catalysts. These findings show highly efficient catalytic nature of the developed magnetic C@Ni and C@Cu nanocatalysts.
The catalytic reduction reactions of 4-NP, MO and MB were also performed in this current study in presence of only NaBH₄ without using any nanocatalyst and the corresponding results are presented in Figure 3.12.

Figure 3.12: Catalytic reduction of (a) 4-NP, (b) MO and (c) MB in presence of only NaBH₄.

As seen in Figure 3.12, it is clear that the NaBH₄ has only negligible effect on the catalytic reduction of all studied pollutants. While comparing our prepared C@Ni and C@Cu nanocatalysts with the previously reported nanocatalysts for the 4-NP, MO and MB catalytic reduction reactions, all the other nanocatalysts are either precious noble metal based and highly expensive or they required a longer time to complete the reduction reactions. Furthermore, the conditions for our reduction reaction system are very convenient, simple, ultrafast with a good percentage yield and the synthesis procedure for making C@Ni and C@Cu nanocatalysts are environmentally friendly.

3.3.10 Mechanism of catalytic reduction

A possible mechanism for catalytic reduction of 4-NP by NaBH₄ and magnetic C@Ni nanocatalysts is shown in Figure 3.13. BH₄⁻ has a low standard redox potential of -1.2E⁰/V which as a strong reducing agent is capable to reduce a broad range of substrates including organic pollutants. However, it shows a limited reducing activity toward anionic contaminants such as 4-NP, deriving from a charge-charge repulsion between the reducing agent (BH₄⁻) and the
negatively charged pollutant molecules. In fact, in the presence of water, NaBH₄ generates sodium hydroxide, as shown below, which makes the solution basic and deprotonate the pollutant molecules generating negatively charged species which result in an electronic repulsion between BH₄⁻ species, lowering reduction performance.

\[
\text{NaBH}_4 + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_3\text{BO}_3 + 4\text{H}_2
\]

However, the anionic pollutants reduction by NaBH₄ proceeds very well in the presence of metallic catalysts. The probable mechanism for the catalytic reduction of 4-NP by NaBH₄ in presence of the magnetic C@Ni nanocatalyst is suggested as follows (1) at first, the BH₄⁻ is chemisorbed on the surface of the C@Ni nanocatalyst or the binding of 4-nitrophenolate anion to the nanocatalyst surface is happened by anchoring the two oxygen atoms of the nitro group, (2) and then the electrical reaction between the 4-nitrophenolate anion and BH₄⁻ is occurred on the C@Ni nanocatalyst surface. The surface of the Ni nanocatalyst is assumed to play a vital role to connect the two adsorbates electrically across the catalyst surface in a way so that the electrons can be transported to the reduction site from the oxidation site.⁵⁶ Ma et al. have proposed that the Langmuir–Hinshelwood mechanism can explain the catalytic reduction reaction of 4-NP well including the dissociative sorption of solutes onto the nanocatalyst surface followed by the reaction between the adsorbed species.⁵⁷ Furthermore, a recent report discovered that the metals with an electronic configuration of dⁿ (~5-9) were found to show excellent catalytic performance for the reduction of 4-NP, which has a good agreement with Ni (d⁸).⁵⁸
Figure 3.13: A possible mechanism for catalytic reduction of 4-NP over magnetic C@Ni nanocatalysts.

3.3.11 Reusability of magnetic C@Ni and C@Cu nanocatalysts

Reusability of the developed magnetic C@Ni and C@Cu nanocatalysts was tested by recycling the used catalysts for five consecutive cycles at which the results are shown in Figure 3.14(a-b). According to the findings, the catalytic activity of the developed C@Ni and C@Cu nanocatalysts only slightly decreased by ~ 3% and ~ 6%, respectively through reusing the nanocatalysts. The slight decrease of the reduction performance of the nanocatalysts in consecutive cycles may be due to their weight loss during the recovering and washing processes, and also the active sites of the nanocatalysts might be blocked by the reaction products during the consecutive cycles. We assume that the magnetic property of the prepared C@Ni nanocatalyst which enables them to be magnetically separable could play a major role for their higher performance in the reusability test as compared to the C@Cu nanocatalyst.
These findings also confirmed the very stable nature of the developed nanocatalysts which denotes them as promising catalysts for catalytic reduction reactions.

**3.4 CONCLUSION**

Magnetic C@Ni and C@Cu nanocatalysts are synthesized successfully by annealing Ni-BDC and Cu-BDC MOFs at 600 °C under argon atmosphere. XRD analysis showed the conversion of peaks related to Cu-BDC and Ni-BDC MOFs to the corresponding C@Cu and C@Ni nanocatalysts and morphological analysis by SEM and TEM illustrated the formation of nanoscale metallic Cu and Ni particles over porous carbon sheets upon annealing. TGA showed successful carbonization of the MOFs and enhanced resistance to thermal decomposition of the magnetic C@Ni and C@Cu nanocatalysts compared to the parental MOFs. The resulting catalysts were used in NaBH₄-mediated reduction of 4-nitrophenol (4-NP), methylene blue (MB), and methyl orange (MO) as model organic compounds. Using the developed C@Ni and C@Cu nanocatalysts, 4-NP, MO and MB were reduced to the corresponding organic molecules in about 60 seconds, showing the highly efficient nature of C@Ni and C@Cu catalysts. Reusability of the developed C@Ni and C@Cu catalysts was tested by recycling and reusing the catalysts for five cycles, at which no
considerable reduction in the performance of the catalysts was observed after the fifth cycle showing highly stable nature of the developed catalysts.

References


Chapter 4: Tissue paper-derived hierarchically porous carbon encapsulated transition metal nanocatalysts for the oxidative degradation of organic pollutants via peroxymonosulfate activation

4.1 INTRODUCTION

The scarcity of drinking water has turned into a serious issue around the world due to the current water pollution problems which seem to be the most challenging matter in recent times. Water contamination has numerous harmful effects on the environment and ecology. Particularly, industrial organic dyes that are present in wastewater are making a challenge for water decontamination due to their recalcitrance and toxicity. Over the years, many conventional water treatment methods have been extensively used for alleviating water pollution. In recent times, advanced oxidation processes, also known as AOPs have drawn immense attention due to their environmental friendliness and effectiveness for the degradation or mineralization of organic contaminants in the aquatic environment. Generally, these processes involve superoxides and oxidants such as hydroperoxide, oxygen, ozone and numerous radicals that are able to destroy the target organic pollutants to harmless species. Hydroxyl radicals are mostly observed in the AOPs including ozonation, Fenton reaction and UV oxidation due to their superior oxidation capability towards the organic contaminants with almost no selectivity. Thus far, the drawbacks associated with most of the hydroxyl radical based Fenton reactions such as metal leaching, narrow pH (~3) condition and excess sludge production, are the bottleneck limits. Comparably, sulfate radicals offer an outstanding alternative to the hydroxyl radicals due to their higher oxidation potential of about 2.5–3.1 V than the hydroxyl radicals that have a potential value of 2.7 V. Similar to Fenton like oxidation processes, the sulfate radicals can also be generated by activating peroxymonosulfate (PMS) through different activation methods including heating, UV-light
irradiation, carbon catalysis, transition metal and metal oxide-based catalysis for the degradation of organic pollutants\textsuperscript{9,14-16}.

Among different activation technologies, transition metals have attracted much attention due to their lower energy consumption and higher activation efficiency. Many transition metals such as Co, Fe, Ce, Mn, Ru, and Ni, etc. have been reported as efficient catalysts for the activation of PMS and as far, cobalt metal has shown the best activity towards the activation of PMS\textsuperscript{11}. Unfortunately, the Co/PMS system is unfavorable in terms of the practical applications due to the toxicity of cobalt\textsuperscript{17,18}. Furthermore, it is also easy for these metal particles to aggregate between themselves because of the intersheet van der Waals forces and higher surface energy, which greatly restricts their applications in catalysis. Moreover, the metal NPs are inevitably sintered at higher temperatures, leading to a severe decrease in their catalytic performance and selectivity\textsuperscript{18}. Thus, the preparation of supported metal nanocatalysts with outstanding high-temperature stability is a significant challenge. An effective approach to get rid of the secondary pollution due to the metal leaching as well as to improve the catalytic performance and stability of the metal nanoparticles is to utilize the heterogeneous catalytic system by using solid support to encapsulate them.

Porous carbons are widely used as solid carriers among others such as alumina, pumice, NaCl crystal, polymer nanoparticle, mesoporous silica, etc. for capturing or loading nanoparticles, restraining them from agglomeration and also improving the interactions between the carriers and guest species due to their large surface area, multiple pore size distribution, good surface functionality, notable chemical stability and high conductivity\textsuperscript{19-22}. Therefore, the porous carbon can be employed as a promising solid support material to disperse and stabilize metal nanoparticles to enhance their activity for catalytic reactions. Finally, the unique architecture of porous carbon and the outstanding catalytic activity of the transition metal NPs together offer a potential and
green heterogeneous catalytic system having porous carbon as promising solid matrix to judiciously decorate metal NPs over its porous surface. To date, many synthesis approaches including chemical vapor deposition, arc-discharge and explosion method have been employed to prepare carbon-coated metal NPs. Most of them are time-consuming, use sophisticated instruments and require high energy consumption. Furthermore, many carbon-based solid supports such as carbon nanotubes, graphene oxide and graphene are also not suitable in this regard due to their high production cost, multi-step synthesis procedure and usage of harsh chemicals during their synthesis process. Therefore, it is very much needed to design a simple and green synthesis method to make porous carbon encapsulated metal NPs.

To overcome the aforementioned problems, we have used commercial tissue paper as a carbon source to synthesize porous carbon encapsulated transition metal-based green and sustainable heterogeneous nanocatalysts (M@TP). The catalytic performance of the as-synthesized M@TP nanocatalysts is evaluated for the oxidative degradation of congo red (CR) dye via peroxymonosulfate activation as it is always identified as an organic pollutant in wastewater. A series of catalytic experiments are performed to investigate the effect of the newly developed catalytic system for CR degradation and mineralization. Specially, the metal loading type on the porous carbon and operating parameters including initial dye concentration, nanocatalyst dosage, PMS concentration, reaction temperature and different types of dyes are studied. Furthermore, several radical scavengers are used to identify the main reactive species and a possible reaction mechanism is proposed for the CR degradation according to this quenching test. Finally, the catalytic degradation reactions are run in four cycles to examine the reusability and stability of the Co@TP nanocatalysts for CR degradation through PMS activation. To the best of our knowledge, this is the first example of hierarchically porous carbon-encapsulated metal-
based nanocatalysts using commercial tissue paper template with remarkable catalytic CR dye degradation yields.

Scheme 4.1: Synthesis of M@TP nanocatalysts and their applications for water treatment.

4.2 MATERIALS AND METHODS

4.2.1 Materials

All of the chemicals were used as received without any further purification. Commercial tissue paper was purchased from a local store. Peroxymonosulfate (Ozone), ammonium peroxydisulfate (PDS), hydrogen peroxide (H₂O₂), sodium chloride (NaCl), congo red (CR), methyl orange (MO), methylene blue (MB), iron nitrate (Fe(NO₃)₂.6H₂O), cobalt nitrate (Co(NO₃)₂.6H₂O), nickel nitrate (Ni(NO₃)₂.6H₂O), copper nitrate (Cu(NO₃)₂.2.5H₂O), methanol, ethanol, tert-butanol and 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) were obtained from Anachemia, Aldrich, Fisher Scientific, Sigma Aldrich, and Sigma. Deionized (DI) water was used from the Milli-Q® instrument (Millipore Corporation).
4.2.2 Synthesis of tissue paper derived carbon encapsulated metal nanocatalysts, M@TP (M= Cu, Ni, Fe and Co)

At the very beginning, 1.5 g of tissue paper was measured and cut into small pieces. Then 3 g of cobalt nitrate salt was measured and dissolved in 10 mL of DI water in a 250 mL beaker. Afterward, the small pieces of tissue paper were soaked well in the cobalt salt solution until all of the tissue pieces were colored. Then the beaker was heated at 100 °C on a hot plate to evaporate the water. Finally, all of the dried tissue pieces were taken into a ceramic boat and then placed into a tubular furnace. The samples were carbonized at three different temperatures viz. 600, 700 and 800 °C for 2 h under an argon atmosphere in that furnace. The heating rate was 5 °C/min for all of the carbonization treatments. After normal cooling to room temperature, the sample was taken out from the furnace. The samples are referred to as Co@TP-6, Co@TP-7 and Co@TP-8 depending on the carbonization temperatures such as 600, 700 and 800 °C, respectively. For comparison, we further synthesized tissue paper derived carbon encapsulated Fe (Fe@TP-600, Fe@TP-700 and Fe@TP-800), Ni (Ni@TP-600, Ni@TP-700 and Ni@TP-800) and Cu (Cu@TP-600, Cu@TP-700 and Cu@TP-800) nanocatalysts by replacing Co²⁺ with Fe²⁺, Ni²⁺ or Cu²⁺ following the same synthesis procedure as mentioned earlier. The synthesis process is shown in Scheme 4.1. As a control, cobalt nitrate salt was only carbonized at 600 °C for 2 h and also, mixture of cobalt nitrate salt and tissue paper were annealed in air at 600 °C for 2 h, whereas, both of them produced cobalt oxide NPs.

4.2.3 Catalytic degradation tests

Unless specified otherwise, all catalytic degradation experiments were conducted in a 50 mL glass vial containing 40 mL dye solution placed on a stirring plate at 300 rpm constant stirring under ambient conditions at room temperature. In a typical experiment, 10 mg of nanocatalyst was
added to the 40 mL of 20 ppm CR dye solution. Before the reaction, the glass vials of having nanocatalysts and dye solutions were bath sonicated for 15 min to reach the adsorption-desorption equilibrium. Then, 0.5 mL of 5 mM PMS solution was added to the dye solution to initiate the catalytic degradation reaction. Once the reaction started, 1 mL of dye solution was withdrawn in every 5 min from the glass vial using a 0.45 μm syringe filter and then mixed with 1 mL of methanol to quench the active radicals. Afterward, the remaining concentration of the dyes was determined using a Uv-vis spectrophotometer (Model: Agilent Cary 50 Conc) at λ = 497 nm, 465 nm and 616 nm for CR, MO and MB, respectively. Furthermore, 5 mL of CR dye solution was taken after the degradation reaction for the ICP-OES analysis to identify the leaching amount of metal. Temperature study was performed in an oil bath having a 40 mL of 50 ppm CR dye solution and 10 mg nanocatalyst in a glass vial at different temperatures viz. 45 °C and 55 °C. After each run, the nanocatalyst was recovered using an external magnet and washed with DI water for several times before drying in a vacuum oven at 60 °C for reuse. The experiments of the reused nanocatalyst were performed under the same experimental conditions. For the quenching tests, a known amount of methanol and tert-butanol was added to the CR dye solution before adding PMS. The degradation efficiency of CR dye using the M@TP/PMS system was evaluated by using equation 1.20

\[
\text{Degradation efficiency} = \frac{C_i - C_t}{C_i} \times 100\% \quad (1)
\]

The catalytic degradation of CR dye was assessed by using the following pseudo-first order kinetic equation 2.20

\[
\ln \left( \frac{C_t}{C_i} \right) = -Kt \quad (2)
\]

Where \(C_i\) and \(C_t\) are the concentrations of CR dye at time 0 and \(t\), respectively, \(t\) is the reaction time and \(K\) is the pseudo-first order reaction rate constant.
4.3 RESULTS AND DISCUSSION

4.3.1 XRD pattern of M@TP nanocatalysts

In this work, M@TP nanocatalysts were synthesized by a novel and green hydrothermal method using tissue paper as a sacrificial template. The crystallinity and phase purity of the prepared nanocatalysts were evaluated by XRD technique and the results are shown in Figure 4.1(a-d). Figure 4.1a shows the XRD patterns of the Co@TP-(6/7/8) nanocatalysts at different carbonization temperatures and the results show that each sample are composed of three broad peaks at around 44.2°, 51.53° and 75.86° demonstrates the diffraction from the 111, 200 and 220 crystallographic planes. The obtained peak locations as well as the corresponding diffraction intensities from different lattice planes indicate the formation of face center cubic structure (fcc) of crystalline Co phase.29 Furthermore, any specific diffraction peaks related to the cobalt oxide were not observed in the XRD pattern confirming the presence of pure metallic phase of the cobalt in the nanocatalyst sample. The XRD patterns of the Ni@TP-(6/7/8) nanocatalysts are presented in Figure 4.1b and it can be clearly observed that all of the Ni@TP nanocatalysts exhibit three broad peaks at 44.48°, 51.28°, and 76.35° revealing the formation of fcc structure of the crystalline nickel phase without impurities such as nickel oxide based on the JCPDS card no. 04-0850.20 On the other hand, the XRD pattern of the Fe@TP-6 nanocatalyst showed diffraction bands at around 30°, 35°, 43°, 57° and 63° indicating the formation of iron oxide instead of metallic iron as seen in Figure 4.1c.30 Furthermore, the XRD pattern of the Fe@TP-7 nanocatalyst displayed three major diffraction peaks at around 44.8° and 65.1° due to the presence of pure iron metallic phase with some additional peaks for iron oxide.31 However, the XRD analysis of the Fe@TP-8 nanocatalyst showed only three peaks associated with the metallic iron indicating the successful synthesis of pure metallic iron nanoparticles at 800 °C.
These results suggest that the carbonization temperature at 600 and 700 °C is not enough to complete the phase transformation. Moreover, the XRD pattern of the Cu@TP-(6/7/8) nanocatalysts showed three characteristic peaks at around 43.6, 50.8 and 74.4° that are attributed to the pure metallic copper phase as seen in Figure 4.1d. The reflection peaks of Cu@TP nanocatalysts that are indexed to 111, 200 and 220 can be ascribed to the face centered cubic phase of metallic copper. Figure 4.1(a-d) also reveals that the carbonization process at different temperatures viz. 600, 700 and 800 °C might produce different crystallinity of the as-synthesized M@TP nanocatalysts including the peaks intensity. As seen in the XRD patterns, the nanocatalysts that are prepared at 800 °C possess the highest peak intensity as compared to the other nanocatalysts prepared at 600 and 700 °C indicating their high crystallinity. This behavior has been stated by Torad and co-workers. The presence of a single metallic phase (Co/Ni/Fe/Cu) in our
M@TP nanocatalysts in this study proves that all metal species were wrapped and well-distributed by residual porous carbon layer that helps to protected them from any oxidation.

### 4.3.2 Raman spectra of M@TP nanocatalysts

Raman spectroscopic analysis was further performed to investigate the degree of graphitization and defect level of the as-synthesized M@TP nanocatalysts. The obtained results are presented in Figure 4.2 and as seen from the Figure, two characteristic peaks are observed at around 1340 cm\(^{-1}\) and 1583 cm\(^{-1}\) for the D and G bands, respectively.\(^{31}\) Generally, the D band characterizes the disorder arrangement or the defects of the carbon atoms, whereas, the G band represents the E\(_{2g}\) vibration mode of the sp\(^2\)-hybridized carbon.

![Raman Analysis of Nanocatalysts](image)

**Figure 4.2**: Raman analysis of the Co@TP-6, Ni@TP-6, Fe@TP-8 and Cu@TP-6 nanocatalysts, respectively.

Thus, the intensity ratio of the D and G band (I\(_D\)/I\(_G\)) can be considered as an important factor to signify the atomic ordered degree (such as relative degree of graphitization) of the carbon materials. Raman spectra of all the nanocatalysts revealed that the intensity of the D band is lower than that of the G band, indicating the presence of sp\(^2\) hybridized carbon species in graphitized pore walls. The I\(_D\)/I\(_G\) values for the M@TP nanocatalysts are found to be in the range of 0.94-0.98. These obtained I\(_D\)/I\(_G\) values are comparable to those I\(_D\)/I\(_G\) values of reduced graphene oxide
and graphene oxide (~1), indicating the formation of high quality three-dimensional graphitic carbon.31, 32

4.3.3 TGA analysis of M@TP nanocatalysts

The quantity of metal loading per gram of nanocatalyst can affect the catalytic activity of the M@TP nanocatalysts. In this regard, TGA analysis was carried out to quantify the relative amount of metals in the M@TP nanocatalysts system. The TGA analysis of the nanocatalyst samples was performed at 25–800 °C under N2 condition and the results are presented in Figure 4.3.

Figure 4.3: TGA analysis of the Co@TP-6, Ni@TP-6, Fe@TP-8 and Cu@TP-6 nanocatalysts, respectively.

The TGA analysis of the M@TP nanocatalysts displayed a slight change over the whole temperature range due to the presence of higher metallic content. The obtained metal loading was 82-86% in the M@TP nanocatalysts. It was also observed from the Figure that the nanocatalyst samples could stable up to 400 °C. This thermally stable characteristics of the prepared nanocatalysts made them a potential candidate to be employed in a broad range of high temperature catalytic applications.
4.3.4 TEM and STEM analysis of M@TP nanocatalysts

The carbonization process structurally transformed the soaked tissue paper with metal salts structure to M@TP nanocatalyst’s 2D structure by reducing the metal ions through carbothermal reduction process at high temperature and then fused them to get metallic nanoparticles and porous carbon matrix which was observed by the TEM analysis as shown in Figure 4.4(a-l). The analysis revealed that all of the metal nanoparticles (Co/Ni/Fe/Cu) are well deposited in the porous carbon matrix. It was not observed any serious particle agglomeration in the M@TP nanocatalyst samples that are prepared at 600 °C and 700 °C. But significant particles sintering was observed in the M@TP nanocatalysts that are prepared at 800 °C. Furthermore, it was also observed that the particle size of the nanocatalysts increase with increasing carbonization temperature. In all cases, the particle size of the M@TP-6 nanocatalysts are smaller than the M@TP-7 and M@TP-8 nanocatalysts due to the fact that the lower temperature favors the slower particle nucleation. The increase in carbonization temperature might endorse faster metal nanoparticle nucleation as we found in the M@TP-7 nanocatalysts that exhibited somewhat larger particles and the M@TP-8 nanocatalysts showed extensive particle sintering with higher particle size than M@TP-6 and M@TP-7 nanocatalysts as predicted. In conclusion, this porous carbon matrix acted not only as a support but also a protective layer for the metal NPs that could protect the NPs from further oxidation. Furthermore, the STEM-EDS color mapping experiment was carried out to identify qualitatively the composition of the Co@TP-6 nanocatalyst and the results are presented in Figure 4.5(a-c). As seen, the color mapping of the Co@TP-6 confirmed the presence of carbon and cobalt in the nanocatalyst as expected. A close investigation of the STEM image of the Co@TP-6 nanocatalyst revealed that the cobalt NPs exhibited clear lattice fringes in scanning transmission electron microscopy (STEM) images with spacing of 0.204 nm as seen in Figure 4.5(d-e),
Figure 4.4: (a-l) TEM images of the Co@TP-(6/7/8), Ni@TP-(6/7/8), Fe@TP (6/7/8) and Cu@TP (6/7/8) nanocatalysts, respectively.

consistent with a face centered cubic cobalt structure demonstrating the highly crystalline nature of the prepared NPs.33
4.3.5 XPS analysis of M@TP nanocatalysts

X-ray photoelectron spectroscopy was carried out to unravel the chemical surface states of the carbon-encapsulated transition metal nanoparticles (Figure 4.6). The survey spectra showed that all the nanocatalysts exhibit C, O and the corresponding metal signals, indicating the successful inclusion of the transition metals into the porous carbon network, as seen in Figure 4.6(a-d). Ni@TP-6 nanocatalysts displayed two well-defined nickel species, which were deconvoluted in two bands at 853 and 870.2 eV for the Ni$^{2+}$ contribution and, 856.4 and 875 eV for the pure metallic phase (Figure 4.6e). The Co- and Cu-based nanoparticles were further analyzed. There were two remarkable Co 2p$_{3/2}$ and Cu 2p$_{3/2}$ peaks, located at 778 and 934 eV,
respectively, which revealed the presence of both metallic and oxide states in the nanoparticle surfaces (Figure 4.6f and Figure 4.6g).

![Figure 4.6: (a-d) XPS survey spectra of Ni@TP-6, Co@TP-6, Cu@TP-6 and Fe@TP-6, respectively; and Fitting (e) Ni 2p, (f) Co 2p, (g) Cu 2p and (h) Fe 2p envelopes of the nanocatalysts.](image)

Importantly, the Fe 2p XPS band revealed that the Fe@TP-6 nanoparticles are mainly in the form of iron oxide, predominantly Fe$^{2+}$ and Fe$^{3+}$ species (Figure 4.6h), which could decrease the electron mobility across the nanoparticle surfaces, and in turn, their overall catalytic performance. In summary, after the fitting of the M 2p envelopes, we concluded that the zero-valent Ni, Co and Cu species have the larger atomic concentrations in the Ni@TP-6, Co@TP-6 and Cu@TP-6 nanocatalysts, while the Fe@TP-6 nanoparticles are mainly in the form of iron oxide species [3, 23, 31, 38].

4.3.6 Oxidative degradation of CR by M@TP nanocatalysts

Oxidative degradation of CR is chosen as a model reaction to systematically evaluate the catalytic activity of the as-synthesized M@TP nanocatalysts. Transition metals mediated activation of PMS is one of the most economic and easy method than other activation methods.
Furthermore, the PMS oxidant can generate both sulfate and hydroxyl radicals because of its unsymmetrical peroxide, thereby integrating the properties of both H$_2$O$_2$ and persulfate (PS), as seen in equations (3-4).\textsuperscript{13, 34}

$$\text{HSO}_5^- + M^{n+} \rightarrow M^{(n+1)+} + \text{SO}_4^{2-} + \text{OH}^- \quad (3)$$

$$\text{HSO}_5^- + M^{n+} \rightarrow M^{(n+1)+} + \text{SO}_4^{2-} + \bullet \text{OH} \quad (4)$$

Therefore, four different transition metals (Co, Ni, Fe and Cu) were employed in this study to evaluate their reactivity towards the activation of PMS for CR dye degradation and the results are presented in Figure 4.7. As seen in Figure 4.7a, it is clear that the transition metals or PMS by itself had a very slight effect on the CR degradation. But a significant effect was observed when they were added together for the catalytic degradation reaction and the obtained results illustrated that the higher CR dye degradation was achieved by the Co-TP/PMS system followed by the Fe-TP/PMS > Cu-TP/PMS > Ni-TP/PMS system. It was observed from the Figure that the CR degradation efficiencies were about to 78.23%, 65.72% and 56.76% for the Fe-TP/PMS, Cu-TP/PMS and Ni-TP/PMS systems, whereas, the Co-TP/PMS system could able to degrade the CR of about 97.68% in 30 min. The standard reduction potential (SRP) values of these transition metals can be used to explain this fact. The SRP values of Ni$^{2+}$/Ni, Cu$^{2+}$/Cu$^+$ and Fe$^{3+}$/Fe$^{2+}$ are lower [(-0.25 V), (+0.153 V) and (+0.77 V), respectively] as compared to the corresponding Co$^{3+}$/Co$^{2+}$ (+1.92 V) demonstrating that they cannot be efficiently reduced by PMS.\textsuperscript{35} On the other hand, the cobalt metal is capable of getting an effective self-recycling of the Co$^{2+}$ for the CR degradation reactions till the PMS oxidant has been consumed completely due to its higher SRP value. The corresponding reaction rate constants are presented in Figure 4.7c and Figure 4.8, as seen the Co-TP/PMS system showed higher rate constant value of 0.109 min$^{-1}$ as expected. These obtained results suggested that the Co-TP/PMS system is an effective method for the degradation
of organic pollutants from wastewater. Two other oxidants such as peroxydisulfate (PDS) and hydrogen peroxide (H₂O₂) were also employed for the catalytic oxidative degradation of CR dye as they are also widely used oxidants in AOPs to evaluate the catalytic oxidation activity of the Co@TP-6 nanocatalyst. The results are presented in Figure 4.7b. As seen, it was observed that both of the Co@TP@-6/PDS and Co@TP@-6/H₂O₂ systems could able to degrade the CR dye but the degradation efficiency is very less compared to the Co@TP@-6/PMS system. In order to further evaluate the difference among the PMS, PDS and H₂O₂ oxidants in regards to the catalytic oxidation performance, the pseudo-first order kinetic model as described in equation 2 was employed and the obtained rate constant (0.1096 min⁻¹) for Co@TP@-6/PMS system is almost five-fold higher than the Co@TP@-6/PDS system (0.0231 min⁻¹) and eight-fold higher than the Co@TP@-6/H₂O₂ system (0.0142 min⁻¹). These findings suggest that the Co@TP-6 nanocatalyst is more efficient in activating PMS compared to PDS and H₂O₂. A comparative study was also performed for the catalytic degradation of CR dye using different cobalt based nanocatalysts namely Co@TP-6, Co@TP-7 and Co-TP-8 to investigate the effect of carbonization temperature at which the nanocatalysts were prepared and the results are presented in Figure 4.7c. The results demonstrated that the carbonization temperature has an effect on the catalytic performance of the prepared Co@TP nanocatalysts. As seen, the cobalt nanocatalyst sample that is prepared at 600 °C has the highest catalytic activity for CR degradation than the other cobalt nanocatalysts that are prepared at 700 °C and 800 °C. The degradation efficiency decreased from 97.68 to 86.26% and the corresponding rate constant was decreased from 0.109 to 0.065 min⁻¹ when the carbonization temperature was increased from 600 °C to 800 °C.
The catalytic performance of the nanocatalysts is strongly dependent on their textural properties such as porosity and specific surface area. The nanocatalyst with higher specific surface area has larger pores and thereby, can provide more active sites for catalytic degradation reaction. The $N_2$
adsorption/desorption experiments were performed to further study the surface properties of the Co@TP nanocatalysts and the results are presented in Figure 4.7d. As seen, the N₂ adsorption-desorption isotherms of the Co@TP nanocatalysts showed a typical type IV isotherm with a hysteresis loop. Furthermore, the BET surface areas of the Co@TP-6, Co@TP-7 and Co@TP-8 nanocatalysts were 12.01, 4.08 and 0.78 m²g⁻¹, which demonstrated that the carbonization temperature has a significant effect on the specific surface area. According to the obtained results, the surface area of the Co@TP nanocatalysts decreased while increased the carbonization temperature and here, the Co@TP-6 nanocatalyst sample could provide more catalytic active sites for having higher surface area which is consistent with the observed results in the catalytic degradation of CR. Likewise, the Co@TP-6 nanocatalyst had also a larger pore volume of 0.0182 cm³g⁻¹ than the Co@TP-8 nanocatalyst (0.0007 cm³g⁻¹). Based on the findings, the Co@TP-6 nanocatalyst can be a good and potential candidate for PMS activation due to their higher pore volume and surface area. Similar trends were observed for both Cu@TP and Ni@TP nanocatalysts except for Fe@TP nanocatalysts as seen in Figure 4.8.

Figure 4.8: PMS mediated catalytic degradation of CR dye using Ni@TP-(6/7/8), Fe@TP (6/7/8) and Cu@TP-(6/7/8) nanocatalysts, respectively. [Unless specified otherwise, Reaction condition: 40 mL of 20 ppm CR solution, 10 mg nanocatalyst, 5 mM oxidant solution and room temperature and each experiment were repeated for three times].
In case of Fe@TP nanocatalysts, the carbonization temperature had a positive effect and Fe@TP-8 nanocatalyst showed highest degradation efficiency among the three iron-based nanocatalysts. These findings suggest that the metallic form of iron is much more active for CR degradation than other iron species such as iron oxide that is present in both Fe@TP-6 and Fe@TP-7 nanocatalysts. Therefore, the PMS/Co@TP-6 activation system was chosen for further catalytic degradation studies due to their higher catalytic performance among all the prepared nanocatalysts.

4.3.7 Effect of catalyst dosage, PMS concentration, initial dye concentration and temperature

In the catalytic degradation of CR using Co@TP-6/PMS system, different experimental parameters can influence the degradation rate. Therefore, the effect of numerous factors including nanocatalyst dosage, PMS concentration, different initial dye concentrations, reaction temperature, different dyes and inorganic ions, on the catalytic performance of Co@TP-6 nanocatalyst was studied. The Co@TP-6 nanocatalyst dosage can influence the degradation performance significantly as the nanocatalyst provides Co (II) that is the primary species responsible for activating PMS to generate the sulfate radical. The dosages study has been carried out for the CR degradation and the results are presented in Figure 4.7e and Figure 4.9a. As seen, the degradation rate of CR increased with increasing the amount of dosage and the removal of CR increased from 31.55% to 97.68% when the catalyst dosage was increased from 1 mg to 10 mg. This is due to the fact that the increasing amount of Co@TP-6 nanocatalyst favors the formation of sulfate radicals that leads to increasing CR degradation.\(^{36}\) However, when the amount of Co@TP-6 nanocatalyst was increased from 10 mg to 12 mg, the degradation of CR was decreased from 97.68 to 95.32%. The further increase in the amount of Co@TP-6 nanocatalyst might overproduce oxidizing radicals that promoted the interactions among the active radicals as seen in equation (5-7) leading to a
decrease in the CR degradation performance. Therefore, 10 mg of nanocatalyst dose was used in the catalytic experiments in consideration of both cost and catalytic efficiency.

\[
\text{SO}_4^{\cdot-} + \text{SO}_4^{\cdot-} \rightarrow \text{S}_2\text{O}_8^{2-} \quad (5)
\]

\[
\text{•OH} + \text{•OH} \rightarrow \text{H}_2\text{O}_2 \quad (6)
\]

\[
\text{SO}_4^{\cdot-} + \text{•OH} \rightarrow \text{HSO}_5^{\cdot-} \quad (7)
\]

The PMS concentration also plays a major role on the CR degradation performance for being the source of sulfate radicals. Therefore, the effect of PMS concentrations on the CR degradation efficiency was performed and the corresponding results are shown Figure 4.7f and Figure 4.9b. As seen, the degradation efficiency of CR was increased from 41.1% to 97.68%, while increasing the dose of 5 mM PMS from 0.1 mL to 0.5 mL. However, it was also observed from the Figure that the further increase in PMS concentration had only a slight increase in the degradation performance. This could be due to the presence of excess HSO$_5^{\cdot-}$ that can scavenge the active radicals, thereby decreasing the available quantities of hydroxyl and sulfate radicals by generating less reactive SO$_5^{\cdot-}$ radicals as seen in equation (8).\(^{38-40}\)

\[
\text{HSO}_5^{\cdot-} + \text{SO}_4^{\cdot-}/\text{•OH} \rightarrow \text{SO}_5^{\cdot-} + \text{SO}_4^{2-} + \text{H}^+ / \text{OH}^- \quad (8)
\]

Radical-radical reactions might also happen prior to the radical-organic reactions.\(^{40}\)

\[
\text{SO}_4^{\cdot-} + \text{SO}_4^{\cdot-} \rightarrow \text{S}_2\text{O}_8^{2-} \quad (9)
\]

The effect of initial dye concentrations on the CR degradation performance was performed and the results are presented in Figure 4.7g. As seen, CR dye was almost completely removed in about 10 min, when the initial concentration of CR was 10 ppm. But, when the initial concentration of CR was increased from 10 ppm to 20 ppm, it took about 30 min to degrade 97.68% of 20 ppm CR dye.
Figure 4.9: The pseudo-first order rate constants for the (a) nanocatalyst dosage; (b) PMS dosage; (c) initial CR concentration; and (d) temperature dependent catalytic degradation reactions of CR using Co@TP-6/PMS system. [Unless specified otherwise, Reaction condition: 40 mL of 20 ppm CR solution, 10 mg nanocatalyst, 5 mM PMS and room temperature and each experiment were repeated for three times].

Furthermore, the degradation efficiency of CR was decreased to 63.44% when the initial concentration was increased from 20 ppm to 50 ppm. Also, the rate constant value of the corresponding degradation reaction decreased from 0.163 min$^{-1}$ to 0.027 min$^{-1}$ when the initial CR concentration was increased from 10 ppm to 50 ppm as seen in Figure 4.9c. At the same PMS concentration and Co-TP-6 dose, the amount of generated sulfate radical was unchanged. As the initial CR concentration increased, the formation of active radicals was not enough for CR degradation, resulting in a decrease of the CR removal efficiency.$^{38}$

The reaction temperature has a significant effect on the CR degradation performance. The effect of temperature on the degradation efficiency was carried out and the results are shown in
Figure 4.7h. As seen, when the reaction temperature was increased from 25 °C to 55 °C, the degradation efficiency of CR was increased from 63.44% to 84.90% and the reaction rate constant was also increased from 0.027 min⁻¹ to 0.051 min⁻¹ as seen in Figure 4.9d. This is because of the fact that the high temperature favors the decomposition of PMS for generating reactive radicals. The collision frequency is also increased between the molecules at the nanocatalyst surface, thus accelerating the reaction rates.  

The impacts of reaction temperature could be evaluated by assessing the activation energy for the CR degradation reaction using the following Arrhenius equation:

$$\ln k_1 = \ln A - \frac{E_a}{RT}$$

Where $E_a$ is the activation energy, $k_1$ is the first order reaction rate constant, $T$ is temperature (K), $R$ is the universal gas constant, and $A$ is the frequency factor. The activation energy was found to be 15.26 kJ/mol for the degradation reaction of CR.

4.3.8 Effect of different pollutants and inorganic salts on the overall catalytic performance

The catalytic performance of the Co@TP-6/PMS system was also evaluated towards the catalytic degradation of other organic pollutants and the results are presented in Figure 4.7i. As seen, the Co@TP-6/PMS system was able to degrade methylene blue and methyl orange efficiently with a percentage degradation of 96.59 and 95.88, respectively. These results evidently confirm that the generation of active radicals in the Co@TP-6/PMS system was not affected by the contaminants and thereby, concluding that the system is very efficient for the removal of organic pollutants present in the industrial effluents. The composition of industrial wastewater containing organic dyes is complex and comprises of a wide variety of inorganic ions. To some degree, the presence of the inorganic ions is likely to influence the production of sulfate radicals.
Figure 4.10: (a) Effect of chloride ion on the degradation of CR using Co@TP-6/PMS system; (b) degradation of CR dye in multiple use of Co@TP-6 nanocatalyst; (c) effect of radical scavengers (MeOH and TBA) on the removal of CR using Co@TP-6/PMS system [insets: the pseudo-first order rate constants for the corresponding catalytic degradation reactions] and (d) EPR signal of the Co@TP-6/PMS/CR/DMPO system after 30 min of the reaction. [Unless specified otherwise, Reaction condition: 40 mL of 20 ppm CR solution, 10 mg nanocatalyst, 5 mM oxidant solution and room temperature; and each experiment were repeated for three times].

Sodium chloride is widely utilized in the dyeing industry to transfer the dyes quickly from their aqueous phase to fiber phase. Therefore, sodium chloride salt was chosen in this study as a model inorganic salt to examine their effect on the CR dye degradation and the results are presented in Figure 4.10a. As seen, the CR dye degradation efficiency was decreased from 97.68% to 69.83%, when 5mM NaCl was used with the Co@TP-6/PMS system, demonstrating that the NaCl has a negative effect on the CR dye degradation. The decrease in dye removal efficiency might be due
to the reaction of sulfate or hydroxyl active radicals with Cl\(^-\) to produce less reactive Cl\(_2\)\(^-\) radicals, thereby inhibiting the removal of CR dye as seen in equation (11-14).\(^{43, 44}\)

\[
\begin{align*}
\text{SO}_4^{\bullet^-} + \text{Cl}^- & \rightarrow \text{SO}_4^{2^-} + \text{Cl}^\bullet \\
\bullet\text{OH} + \text{Cl}^- & \rightarrow \text{ClOH}^{\bullet^-} \\
\text{ClOH}^{\bullet^-} + \text{H}^+ & \rightarrow \text{Cl}^\bullet + \text{H}_2\text{O} \\
\text{Cl}^\bullet + \text{Cl}^- & \rightarrow \text{Cl}_2^{\bullet^-}
\end{align*}
\]

(11) \quad (12) \quad (13) \quad (14)

4.3.9 Reusability of Co@TP-6 nanocatalyst

The stability and reusability of the as-synthesized Co@TP-6 was evaluated for four successive cycles and the results are presented in Figure 4.10b. After each run, the Co@TP-6 nanocatalyst was separated using an external magnet and washed several times with DI water to get rid of any impurities. As seen, the removal efficiency of the CR dye decreases gradually while increasing the repeating runs. The loss in catalytic degradation performance might be due to the deterioration of the catalytic active sites on the Co@TP-6 surface which are primarily responsible for PMS activation and also, the contamination of the nanocatalyst surface as a result of the adsorption of the intermediates and organic compounds. But, the removal efficiency for CR dye still remains as high as 94.9% after four consecutive recycling experiments. This demonstrates the highly stable catalytic performance of the prepared Co@TP-6 nanocatalyst for the dye degradation.

4.3.10 Identification of reactive species

The PMS activation mechanism for the CR dye degradation was clarified by utilizing radical scavengers. To find the typical contribution of sulfate and hydroxyl radicals to CR degradation in a Co-TP-6/PMS system, methanol (MeOH) and tert-butanol (TBA) were used as radical scavengers. Methanol is an efficient quenching agent for both of the radicals, whereas the
TBA is mainly active towards hydroxyl radical. This is due to the fact that the rate constant for scavenging $'OH$ by TBA is $3.8 \sim 7.6 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$, which is 418-1900 times higher than that of SO$_4$$^-$$^-$ ($4 \sim 9.1 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$) resulting less reactivity towards the sulfate radicals.$^{45}$ In contrast, methanol can scavenge both of the hydroxyl ($9.7 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$) and sulfate ($3.2 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$) radicals by generating $'\text{CH}_2\text{OH}$ radicals according to the following equations (15-16).$^{45, 46}$

\begin{align*}
'\text{OH} + \text{CH}_3\text{OH} & \rightarrow '\text{CH}_2\text{OH} + \text{H}_2\text{O} \quad (15) \\
\text{SO}_4'^- + \text{CH}_3\text{OH} & \rightarrow '\text{CH}_2\text{OH} + \text{HSO}_4^- \quad (16)
\end{align*}

The CR degradation performance in presence of both scavengers is presented in Figure 4.10c and it is clear that the scavengers affected the degradation performance of CR dye in the Co@TP-6/PMS system. Co@TP-6/PMS system degraded 97.68% of CR dye in 30 min in absence of any scavengers. But, the removal efficiency of CR decreased from 97.68% to 83.96% after adding TBA in the Co@TP/PMS system. The degradation efficiency of CR decreased significantly in comparison with TBA from 97.68% to 48.67% while adding methanol in the Co@TP-6/PMS system. The findings suggest that the SO$_4'^-$ and $'\text{OH}$ are both responsible for the degradation of the CR dye and hence, the sulfate radical plays the main role for activating PMS.

4.3.11 Proposed degradation mechanism

The above-mentioned findings demonstrated that the addition of the PMS oxidant to the as-synthesized Co@TP-6 nanocatalyst could degrade the CR dye efficiently. But the addition of only nanocatalyst or PMS had insignificant effects on the degradation of CR. Therefore, it was assumed that the Co@TP-6 nanocatalyst could accelerate the PMS activation process resulting the generation of abundant hydroxyl and sulfate radicals for the oxidative degradation of CR. In reaction, the Co$^{2+}$ ions can be released through the aerobic oxidation of zerovalent cobalt (Co$^0$) as well as from the reaction of zerovalent cobalt and PMS.
Also, the Co$^{3+}$ ions can be deposited on the surfaces of Co$^0$ to release Co$^{2+}$ ion.$^{34,47}$ Subsequently, the Co$^{2+}$ ions in the Co@TP-6 nanocatalyst activated the HSO$_5^-$ to produce sulfate radical and in the meantime, the Co$^{2+}$ ions are converted to Co$^{3+}$. Then the formed Co$^{3+}$ ions can further activate the HSO$_5^-$ to yield Co$^{2+}$ ion and SO$_5^{2-}$.$^{48}$ The produced sulfate radical could degrade the chromophoric groups of the CR dye due to their powerful oxidizing potential leading to the decolorization of CR dye. Afterward, the decolorized CR dye might be degraded to carbon dioxide and water by sulfate radical and the probable reactions are presented in equations (17-25).$^{38,49-51}$

The proposed mechanism for the PMS mediated catalytic degradation of CR by Co@TP-6 nanocatalyst is presented in Figure 4.11. In the meantime, the hydroxyl radical can also be produced from the reaction between water and sulfate radical, and the EPR analysis confirmed the production of hydroxyl radicals, as shown in Figure 4.10d. These results demonstrate that the degradation of CR is a radical pathway, where both of the sulfate and hydroxyl radicals contribute to CR removal and most importantly, the sulfate radical plays a key role.

\[ \text{Co}^0 \rightarrow \text{Co}^{2+} + 2e^- \quad \text{E} = 0.28 \text{ V} \quad (17) \]
\[
2\text{Co}^0 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Co}^{2+} + 4\text{OH}^- \quad (18)
\]
\[
\text{Co}^0 + 2\text{HSO}_5^- \rightarrow \text{Co}^{2+} + 2\text{SO}_4^{2-} + 2\text{OH}^- \quad (19)
\]
\[
\text{Co}^0 + \text{HSO}_5^- + 2\text{H}^+ \rightarrow \text{Co}^{2+} + \text{HSO}_4^- + \text{H}_2\text{O} \quad (20)
\]
\[
\text{Co}^0 + 2\text{Co}^{3+} \rightarrow 3\text{Co}^{2+} \quad (21)
\]
\[
\text{HSO}_5^- + \text{Co}^{2+} \rightarrow \text{Co}^{3+} + \text{SO}_4^{2-} + \text{OH}^- \quad (22)
\]
\[
\text{HSO}_5^- + \text{Co}^{3+} \rightarrow \text{Co}^{2+} + \text{SO}_5^{2-} + \text{H}^+ \quad (23)
\]
\[
\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \cdot\text{OH} \quad (24)
\]
\[
\text{SO}_4^{2-} + \cdot\text{OH} + \text{CR} \rightarrow \text{[many steps]} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (25)
\]

### 4.4 Conclusion

We have developed for the first time a facile, toxic chemical-free and simple preparation method to synthesize transition metal based nanocatalysts encapsulated in porous carbon derived from commercial tissue paper for the oxidative degradation of CR by activating PMS. The metal NPs are highly dispersed and anchored tightly on the functional moieties of the porous carbon surface that helps the generation of the NPs by in situ reduction, thereby preventing the aggregation of the NPs on the porous carbon surface. Additionally, the interfacial interactions between the porous carbon and metal NPs generate a hierarchically porous organic-inorganic network, which further increase the catalytic activation of PMS for CR degradation. Among all the nanocatalysts studied, the Co@TP exhibits the best catalytic performance with a reaction rate constant of 0.109 min\(^{-1}\) for catalytic degradation of CR in the presence of PMS. The reusability studies showed the highly stable nature of the Co@TP-6 nanocatalyst with a higher degree of CR degradation for at least four consecutive catalytic cycles with negligible cobalt leaching. According to the quenching experiments, the sulfate radicals are evidenced to be the main reactive species for CR degradation.
Henceforth, the development of cobalt NPs inserted into hierarchically porous carbon represents a promising strategy for the catalytic degradation of many hazardous substances.

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Chapter 5: Tuning of tri-functional NiCu bimetallic nanoparticles confined in a porous carbon network with surface composition and local structural distortions for the electrocatalytic oxygen reduction, oxygen and hydrogen evolution reactions

5.1 INTRODUCTION

The development of sustainable-energy materials and green nanotechnologies to fabricate fuel-cells, metal-air batteries and water-splitting systems has become a promising way to solve the increasing energy demands as well as the environmental-related issues of the modern society.1-5 Among the possible renewable energy technologies, the hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are leading the storage and energy conversion processes owing to their potential to create energy with zero emission. To efficiently carry out those reactions, a stable and electrochemically highly active material is critical. In this direction, noble metal catalysts, for instance, Pt-based nanomaterials demonstrated outstanding bifunctional performances towards HER and ORR. Similarly, Ru and Ir-based catalysts are the best OER-electrocatalysts.6,7 Nevertheless, the very high prices, poor stability and scarcity of the conventional noble metals have markedly inhibited their large-scale integration to the commercial renewable energy technologies. Hence, the sustenance of a future based on clean energy technologies, will benefit from the development of inexpensive nanomaterials with enhanced multifunctional electrocatalytic properties.

Dedicated efforts in this direction resulted in the creation of a myriad of alternative materials with bifunctional or trifunctional electrocatalytic performances, including nanocarbons,8 metal oxides,9 carbides/nitrides, and their composites.10-12 Among them, the development of carbon-coated transitional metal-based nanoalloys are recently gaining increasing attention due to their fast electron transfer (ET) rates, the plethora of functionalities afforded by the carbon shell
as well as the possibility to employ the volcano plots to tune their properties. Especially, the presence of multiple metals mixed at the nano level also leads to a promising strategy to improve electrocatalytic performance towards many catalytic reactions. It is worthwhile to investigate the structure-catalytic function of bimetallic transition metal nanoparticles owing to the fact that their geometric and electronic surface structure can be tailored using a wide range of controlled phase compositions and morphologies.\textsuperscript{13} Thus, the electrocatalytic rates of bimetallic nanosystems are markedly controlled by the engineering of their nanostructure morphology, composition as well as defect density and strain, which, in turn, facilitate the control of the binding energy states of the reactants and the intermediates catalytic species at the electrochemical interfaces. Therefore, the development of non-noble bimetallic nanostructures with multifunctional catalytic properties is currently becoming a hotspot into the energy field.

Though significant progress has been achieved regarding the synthesis of bimetallic catalysts and their use as electrocatalysts with enhanced activity,\textsuperscript{14-17} very few efforts were made to optimize their structure to derive trifunctional catalytic properties.\textsuperscript{18, 19} Especially disentangling the underlying structural parameters that govern the electrocatalytic activity,\textsuperscript{20} which can help to further tune and optimize the catalytic properties is rarely attempted. In this work, a facile and eco-friendly strategy to prepare NiCu bimetallic nanoparticles (NPs) with varying Ni:Cu ratios encapsulated in a hierarchically structured carbon framework is presented. The synthesis involves the capillary force assisted spontaneous adsorption of the metal precursors into the facial tissue and the subsequent simultaneous thermal reduction and carbonization. The resulting nanoalloys displayed an efficient trifunctional catalytic activity towards HER/OER/ORR (Scheme 5.1). Though all bimetallic catalysts demonstrated superior catalytic activity compared to their monometallic counterparts, the ultimate catalytical efficacy intimately depended on the
composition (ratio between Ni and Cu) of the alloys. For example, the Ni$_{0.25}$Cu$_{0.75}$/C electrocatalyst surpassed the electrocatalytic performances of its counterparts as well as exhibited better electrocatalytic performances than commercial RuO$_2$ and Pt. To the best of our knowledge, this is the first report of the structural and electronic properties of non-noble NiCu nanoparticles together with their tri-functional electrocatalytic properties, which finely controlled by varying the alloy composition. Density functional theory (DFT) calculations were carried out to validate our experimental results, as well as elucidate the underlying catalytic mechanisms of NiCu bimetallic nanoparticles (NPs) with various compositions. Finally, the DFT-calculated binding energy values were used as an optimal descriptor of the trifunctional catalytic activity and Simulation results showed that three-fold hollow sites containing one Ni atom and two Cu atoms are the active sites for the trifunctional catalytic activity of the NiCu nanoparticles.

Scheme 5.1: NiCu nanoparticles for HER, OER and ORR reactions.
5.2 MATERIALS AND METHODS

5.2.1 Materials

All of the chemicals were used as received without any further purification. Commercial tissue paper was obtained from a local store at El Paso, Texas, USA. Copper nitrate (Cu(NO₃)₂.2.5H₂O), nickel nitrate (Ni(NO₃)₂.6H₂O), methanol, Nafion solution, sulfuric acid, sodium hydroxide and Pt/C (20%) were purchased from Aldrich, Fisher Scientific and Sigma Aldrich. Deionized (DI) water was obtained from the Milli-Q® instrument (Millipore Corporation).

5.2.2 Synthesis of the electrocatalysts

1.5 g of Cu(NO₃)₂.2.5H₂O and 1.5 g of Ni(NO₃)₂.6H₂O were added into a 100 mL beaker and dissolved in 10 mL of DI water. Afterwards, 3.0 g of tissue paper were dipped into the salt solution and the mixture was bath sonicated so that all the metal ions (Cu²⁺ and Ni²⁺) were adsorbed on the surface of the tissue paper. The tissue paper was then heated to 100 °C to remove all the water. Subsequently, the tissue papers were carbonized in a tube furnace at 700 °C. High purity argon gas was passed through the tube furnace to remove air for at least one hour prior to the carbonization process. The heating rate of the carbonization was set as 5°C min⁻¹. The process was carried out in a high-purity argon atmosphere. The sample was carbonized for 3 h in a quartz boat. The carbonized product was taken out once the temperature reached room temperature and the product was then dispersed in a 1.0 M sulfuric acid solution with the assistance of ultrasonication to remove any unstable metallic substances. The etching process was performed for 24 h. The product was collected by centrifugation and washed for several times using DI water. The obtained product was then brought to neutral pH and vacuum dried at 70 °C for 12 h. The product was denoted as Ni₀.⁵Cu₀.⁵/C. Afterward, the product was put into a glass vial for further use. Two
other bimetallic electrocatalysts were also prepared, namely Ni$_{0.25}$Cu$_{0.75}$/C and Ni$_{0.75}$Cu$_{0.25}$/C by varying the wt% of the copper and nickel salts. As controls, Cu/C and Ni/C monometallic electrocatalysts were synthesized following the same procedure with only copper or nickel salt used in the synthesis process.

### 5.2.3 Electrochemical Measurements

Measurements of HER, OER and ORR activity of the as-prepared electrocatalysts were performed with a traditional three-electrode system (CHI-640). The working, counter and reference electrodes were glassy carbon, a graphitic rod and Ag/AgCl (KCl saturated) electrodes, respectively. 1.0 mg of electrocatalyst was mixed with 1.0 mL of methanol and bath sonicated for 30 min to make the catalyst ink. Then the catalyst ink was drop casted onto the working electrode and allowed to dry in air prior to use in the electrochemical reactions. All electrochemical HER experiments were performed in 0.5 M H$_2$SO$_4$ solution in a nitrogen saturated solution at a scan rate of 2 mV/s and all electrochemical OER and ORR experiments were performed in 0.5 M NaOH solution in an oxygen saturated solution at a scan rate of 2 mV/s. The following equation was used to calibrate the experimental potentials.$^{22}$

$$E_{\text{RHE}} = E_{\text{Ag}/\text{AgCl}} + 0.197 + 0.059pH$$

(1)

The Tafel slope is a key parameter to describe the electrocatalytic performance and kinetics of a reaction and it can be expressed by the following equation.$^{22}$

$$\eta = a + \frac{2.3 \text{ RT}}{\text{nF}} \log j$$

(2)

where $j$, $a$, $F$ and $\eta$ are the current density, transfer coefficient, Faraday constant and overpotential, respectively; $n$ is the number of electrons involved in the reaction and the slope is given by $b = \frac{2.3 \text{ RT}}{anF}$.  

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The electrochemically active surface area (ECSA) of the electrocatalysts was estimated by evaluating the cyclic voltammetry (CV) measurements and the electrochemical double-layer capacitance that was tested from 0 to 0.30 V (vs. RHE) in a N$_2$-saturated 0.5 M H$_2$SO$_4$ solution for the HER process or measurements were made between 1.0 and 1.30 V (vs. RHE) in an O$_2$-saturated 0.5 M NaOH solution at different scan rates (5, 20, 50, 100, 150 and 200 mV/s) for the OER and ORR processes. The difference between the anodic and cathodic current (at 0.15 V vs RHE for HER or at 1.15 V vs RHE for OER and ORR) were plotted against the scan rate to obtain a linear relationship and the slopes correspond to the electrochemical double-layer capacitance ($C_{dl}$). The ECSA was then estimated by using the following equation.$^{23}$

$$ECSA = \frac{C_{dl}}{C_s}$$  \hspace{1cm} (3)

where $C_s$ is the specific capacitance of the electrocatalysts, reported to be 0.035 and 0.04 mF⋅cm$^{-2}$ in acidic and alkaline solution for the Ni-based electrocatalysts.$^{22, 23}$

The roughness factors (RF) were calculated using the following equation.

$$RF = \frac{(ECSA)}{(geometric \ area \ of \ the \ electrode)}$$  \hspace{1cm} (4)

A glassy carbon disc of 5 mm in diameter (Pine Instruments Company) was used as the working electrode for the rotating disc electrode (RDE) measurements. All electrochemical experiments were performed employing a potential range from 0.00 to −0.75 V vs Ag/AgCl at a scan rate of 10 mV/s. All potentials were referenced to the RHE. The kinetic parameters were estimated by applying the Koutecky-Levich (K-L) equations.$^{21}$

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B \omega^{1/2}} + \frac{1}{J_K}$$  \hspace{1cm} (5)

$$B = 0.20 \ nF C_0 D_0^{2/3} \nu^{-1/6}$$  \hspace{1cm} (6)

$$J_K = nFkC_0$$  \hspace{1cm} (7)
where \( J \) is the measured current density, \( J_K \) and \( J_L \) are the kinetic and diffusion limiting current densities, respectively, \( \omega \) is the electrode rotation rate, \( n \) is the overall number of electrons transferred for the oxygen reduction, \( F \) is the Faraday constant, \( C_0 \) is the bulk concentration of \( O_2 \) dissolved in the electrolyte (\( 1.03 \times 10^{-3} \text{ mol L}^{-1} \) for 0.5 M KOH), \( D_0 \) is the diffusion coefficient of \( O_2 \) (\( 1.63 \times 10^{-5} \text{ cm}^{2} \text{s}^{-1} \) for 0.5 M NaOH), \( v \) is the kinematic viscosity of the electrolyte (\( 0.01 \text{ cm}^{2} \text{s}^{-1} \) for 0.5 M NaOH), and \( k \) is the electron transfer rate constant during ORR. \( B^* \) is a constant (\( 2.76 \times 10^{-2} \text{ A cm}^{-2} \text{ rpm}^{-1/2} \)) for all the performed experiments.

5.3 RESULTS AND DISCUSSION

5.3.1 Structural and morphological characterization of Ni, Cu and bimetallic NiCu nanostructures

Synthesis of the NiCu@C electrocatalysts was achieved via a two-steps process involving the adsorption of the corresponding metal ions into cellulose-based paper towel followed by a high-temperature carbonization, Figure 5.1A. First, the highly porous structure of the tissue paper that is primarily composed of lignin and cellulose was leveraged to spontaneously adsorb the corresponding metal ions (Cu\(^{2+}\) and Ni\(^{2+}\)) aided by capillary force. During the carbonization step, the tissue paper serves as the carbon source and the metal ions serve as a metal precursor to form the final carbon encapsulated structure. Here, the tissue paper retains the templated porous structure during the carbonization under inert atmosphere and gets transformed to porous carbon matrix. Simultaneously, the metal ions get reduced to NiCu nanoparticles, assisted by the in-situ generated oxidative-reductive conditions during the carbothermal method. Finally, the product was treated with \( \text{H}_2\text{SO}_4 \) to remove unstable metal species formed during the reaction. Thus, through a simultaneous templated carbonization and reduction, a nanocomposite composed of uniformly
dispersed and surface-clean NiCu nanoparticles encapsulated in hierarchically porous carbon was generated.

Figure 5.1: (A) Schematic representation of the synthesis of NiCu/C electrocatalysts; (B-C) XRD analysis of the Ni/C, Cu/C and NiCu/C bimetallic electrocatalysts; (D) Raman spectra of the as-synthesized electrocatalysts; (E) TGA analysis of Ni/C, Cu/C and Ni0.25Cu0.75/C electrocatalysts and (F) N2 adsorption-desorption isotherm of the Ni0.25Cu0.75/C electrocatalyst (corresponding BJH pore size distribution).

The crystalline phase and structure of the as-synthesized electrocatalysts were first characterized by XRD (Figure 5.1(B-C)). The XRD had three characteristic peaks in both Cu/C and Ni/C electrocatalysts. These sharp characteristic peaks at nearly 43.4°, 50.6°, and 74.1°; and 44.5°, 51.2°, and 76.3° can be well indexed to the (111), (200), and (220) crystal planes of the face-centered cubic (FCC) Cu (JCPDS 04-0836) and Ni nanoparticles (JCPDS no. 04-0850), respectively.13,24 The XRD analysis of the NiCu/C bimetallic nanoparticles also showed a similar diffraction pattern with slight shift compared to the Cu and Ni nanoparticles. The features can be
indexed to the (111), (200), and (220) crystal planes of the FCC NiCu bimetallic alloys matching with the previously reported NiCu alloys.\textsuperscript{13, 24} Further, leveraging Bragg’s law and crystal geometry equation of the FCC crystals, we analyzed the structural change and lattice strain during the alloy formation (Table 5.1). The results indicated that the incorporation of nickel into the lattice of Cu to form the NiCu bimetallic system leads to the lattice contraction of the copper crystal structure and the highest lattice contraction was observed in the case of Ni\textsubscript{0.25}Cu\textsubscript{0.75}/C bimetallic system. Nonetheless, diffraction spectrum did not demonstrate any new peaks, pointing to the high purity of the as-synthesized electrocatalysts.

Compared to the characteristic high intensity peaks of the metallic Cu, Ni or bimetallic NiCu system, the diffraction peaks of the carbon are hardly visible. However, the existence of the porous carbon matrix was verified using the Raman spectroscopy. The Raman spectra was obtained from the various electrocatalysts are presented in Figure 5.1D. Two characteristic peaks at \textasciitilde1350 and \textasciitilde1583 cm\textsuperscript{-1} were observed in all the samples that correspond to the D and G bands of the porous carbon matrix, respectively.\textsuperscript{25} Usually, the D band represents the disordered sp\textsuperscript{3} carbon, whereas, the G band reflects the sp\textsuperscript{2} type graphitic carbon. Furthermore, the graphitization degree and defect density of carbon-based materials can be estimated by calculating the intensity ratio (I_D/I_G) of the D and G bands.\textsuperscript{25} The calculated I_D/I_G values were found to be 0.86, 0.91, 0.94, 0.96 and 0.99 for the Ni/C, Cu/C, Ni\textsubscript{0.75}Cu\textsubscript{0.25}/C, Ni\textsubscript{0.50}Cu\textsubscript{0.50}/C and Ni\textsubscript{0.25}Cu\textsubscript{0.75}/C electrocatalysts, respectively. In the carbonization process, the tissue paper is carbonized and subsequently, the corresponding metal ions are also reduced. Moreover, the nickel can play an important catalytic role during the carbonization process and facilitate the graphitization of the porous carbon matrix.\textsuperscript{26} Interestingly, the I_D/I_G values of the bimetallic catalysts decreased with increasing the nickel concentration, plausibly due to the promotive effect of Ni in the formation of graphitic carbon
during the carbonization reaction. Furthermore, the comparatively higher I_D/I_G value of Ni_{0.25}Cu_{0.75}/C electrocatalyst compared to other bimetallic systems points to the presence of higher number of defect sites especially the disordered/nongraphitic carbon in the Ni_{0.25}Cu_{0.75}/C. Such defect sites are known to be beneficial to enhance the HER, OER and ORR activity.\textsuperscript{27, 28} Thermogravimetric analysis (TGA) was then performed to investigate the thermal stability of the prepared electrocatalysts and the Ni_{0.25}Cu_{0.75}/C electrocatalyst displayed better thermal stability than their monometallic counterparts as seen in Figure 5.1E. The metal content was found to be 79.39, 87.98 and 91.75\% (wt\%) for Cu/C, Ni/C and Ni_{0.25}Cu_{0.75}/C electrocatalysts from the TGA analysis, respectively. Since the initial analysis indicated that Ni_{0.25}Cu_{0.75}/C electrocatalyst could have superior catalytic properties, Brunauer–Emmett–Teller (BET) gas sorption measurements was conducted to investigate its surface properties. Figure 5.1F illustrates the nitrogen adsorption-desorption isotherm as well as the pore-size distributions (inset) of the Ni_{0.25}Cu_{0.75}/C electrocatalyst. The BET surface area of Ni_{0.25}Cu_{0.75}/C was found to be 157 m^2 g^{-1}. The obtained isotherm was recognized as type II that is characteristic of mesoporous materials and the pore-size distribution revealed that the Ni_{0.25}Cu_{0.75}/C electrocatalyst exhibit a unique mesoporous structure with an average pore size of 7.74 nm. The pore volume was found to be 0.31 cm^3 g^{-1}. The mesopores in the Ni_{0.25}Cu_{0.75}/C electrocatalyst can improve the electrolyte transport and the mobility of the catalytic reactant species toward the HER/OER/ORR active sites decreasing the mass transfer resistance. The higher BET surface area and pore volume of the Ni_{0.25}Cu_{0.75}/C can also improve the mass transport during electrocatalytic reactions.\textsuperscript{29}

The microstructure and morphology of the electrocatalysts investigated by the TEM as well (Figure 5.2(A-C) and Figure 5.3(A-B)). As seen, the nanoparticles are uniformly anchored and distributed in the porous carbon matrix.
Figure 5.2: (A-C) TEM images of the Ni$_{0.5}$Cu$_{0.5}$/C, Ni$_{0.75}$Cu$_{0.25}$/C and Ni$_{0.25}$Cu$_{0.75}$/C electrocatalysts; (D-F) STEM images of the Ni$_{0.25}$Cu$_{0.75}$/C electrocatalyst at different magnifications; (G-I) high-angle annular dark field (HAADF)-STEM image, elemental mapping images and EELS spectra of the Ni$_{0.25}$Cu$_{0.75}$/C electrocatalyst, respectively.

Hence, the porous carbon matrix serves both as a substrate and a protecting layer for the nanoparticles and protect from further oxidation. The average particle size of the electrocatalysts were determined to be 21.04 ± 1.71, 13.86 ± 1.73, 14.51 ± 2.90, 11.58 ± 2.02 and 9.76 ± 2.52 for the Cu/C, Ni/C, Ni$_{0.5}$Cu$_{0.5}$/C, Ni$_{0.75}$Cu$_{0.25}$/C and Ni$_{0.25}$Cu$_{0.75}$/C electrocatalysts, respectively. It is well-established that the electrocatalytic reactions over a metal electrocatalyst are usually size-
dependent. Therefore, one can expect that the smallest nano-sized Ni_{0.25}Cu_{0.75}/C electrocatalyst among others with a narrow size distribution can offer an abundance of accessible electrocatalytic active sites, resulting in superior efficacy for electrocatalytic applications.

![Figure 5.3: (A-B) TEM images of the Ni/C and Cu/C electrocatalysts, respectively.](image)

Scanning transmission electron microscopy (STEM) was leveraged to examine the crystal structure of the NiCu bimetallic NPs, especially the Ni_{0.25}Cu_{0.75}/C nanohybrid system. At lower magnification, the STEM images showed a consistent result to the TEM image of the Ni_{0.25}Cu_{0.75}/C electrocatalyst as shown in Figure 5.2(D-E) demonstrating that the NiCu NPs are incorporated into the porous carbon structure. The bimetallic NPs are also rarely agglomerated, demonstrating a good dispersion into the porous carbon matrix. Hence it is reasonable to conclude that the framework of carbon matrix on which the nano-sized NiCu NPs uniformly embedded, can efficiently prevent the NPs from being excessively oxidized and agglomerating, and might facilitate the faster electron transport between the NiCu NPs and the carbon matrix, leading to efficient electrocatalytic performance. It should also be mentioned that the transition metals or their oxide phases within the carbon shells are expected to be conducive to significantly enhance the catalytic performance of the electrocatalysts that has been reported previously. Hence, it is also most likely that our developed NiCu/C nanohybrid system may work following the similar mechanism due to the inherent interaction between the carbon matrix and the small sized NiCu
NPs. The STEM image also demonstrated that the NPs are highly crystalline as seen in Figure 5.2F, with an interplanar spacing of ~0.21 nm that corresponds to the (111) facet of the bimetallic NiCu alloy.\textsuperscript{26} Additionally, the high-angle annular dark field (HAADF)-STEM imaging and electron energy-loss spectroscopy (EELS) was leveraged to confirm the formation of carbon-wrapped NiCu bimetallic nanoparticles at single nanoparticle levels. The HAADF-STEM image of the Ni\textsubscript{0.25}Cu\textsubscript{0.75}/C electrocatalyst displayed the carbon-wrapped NiCu bimetallic nanoparticles (Figure 5.2G). The STEM-based elemental mapping of the Ni\textsubscript{0.25}Cu\textsubscript{0.75}/C confirmed the coexistence and distribution of the C, Cu and Ni elements in the sample (Figure 5.2H). As seen in Figure 5.2I, the EELS detected three signals including C K edge (~ 284 eV), Ni L edge (~ 855 eV) and Cu L edge (~ 935 eV) confirming the presence of C, Ni, and Cu in the Ni\textsubscript{0.25}Cu\textsubscript{0.75}/C electrocatalyst. In the case of 3d transition metals, the intensities of the L\textsubscript{2,3} white lines decrease nearly linearly with the increasing atomic number, indicating the filling of the d orbitals. As seen in Figure 5.2I, the metallic nickel showed the two L\textsubscript{3} and L\textsubscript{2} lines clearly in the energy-loss spectra, whereas the metallic copper did not show the L\textsubscript{3} and L\textsubscript{2} lines owing to the fully occupied d orbitals in copper.\textsuperscript{31}

XPS measurements were used to interrogate the chemical forms of the mono and bimetallic carbon-encapsulated metallic nanoparticles as shown in Figure 5.4. Monometallic Ni/C nanoparticles show at least two nickel species, where the Ni 2p\textsubscript{3/2} signal can be decomposed in two contributions at Ni 2p\textsubscript{3/2} and Ni 2p\textsubscript{1/2} at 853.0 and 853.6 eV. The former is assigned to Ni\textsuperscript{0} and the later to Ni\textsuperscript{2+}. While the Cu/C nanoparticles also display two contributions in the Cu 2p\textsubscript{3/2} signal at 932.8 and 935.2 eV, assigned to Cu\textsuperscript{0} and Cu\textsuperscript{2+}, respectively. The assignation to Cu\textsuperscript{0} was also supported with the Cu LMM signal (not shown). Remarkably, all the bimetallic nanoalloys
underwent a positive shift of the main Ni 2p$_{3/2}$ core peak indicating a change in the electronic properties of the resulting nanoalloys.

Figure 5.4: XPS spectra of Ni$_{0.25}$Cu$_{0.75}$/C electrocatalyst: (A-E) survey spectra, C 1s, O 1s, Cu 2p and Ni 2p, respectively; and (F) comparison of Ni 2p spectra in different electrocatalyst samples.

The blue-shifts of the binding energies are intimately related to the d-band shifts in different bimetallic nanosystems and, in turn, with their electrocatalytic activities.\textsuperscript{13, 32} Notably, the binding energy for Ni 2p$_{3/2}$ band of the Ni$_{0.25}$Cu$_{0.75}$/C nanoparticles were shifted ~three times (DBE) compared to other bimetallic systems (Figure 5.4F), suggesting a substantial change in the surface electronic properties for the Ni$_{0.25}$Cu$_{0.75}$/C nanoalloys.\textsuperscript{13} This shift could further facilitate the downshift of the d-band center and, consequently, boost the overall rates of interfacial catalytic processes. Ni and Cu contents at the nanoalloy surfaces were estimated from the integrated areas
of the Ni 2p and Cu 2p regions. It is very important to point out that the Ni0.25Cu0.75/C nanoalloys showed the lesser number of Ni contents on the nanoparticle surfaces (~ 5.3 %), almost two times smaller compared with the other two bimetallic nanoparticles. Taking into account the role of Ni content in enhancing the number of nanoalloy structural defects (see Raman analysis), it is reasonable to state that the Ni0.25Cu0.75/C bimetallic nanoparticles hold the larger number of surface defect sites on their metallic frameworks. Additionally, the C 1s and O 1s spectra were also recorded to obtain in-depth information about the oxygen-containing species. The C 1s band was deconvoluted into four peaks with binding energies of oxygen-containing species. The C 1s band was deconvoluted into four peaks with binding energies of 284.8, 286.2, 287.8, and 289.3, which are attributed to C–C, C–O, O=C–H and O=C–O bonds, respectively (Figure 5.4B).29 Furthermore, the O 1s spectrum was deconvoluted into three components with binding energies of 530, 531.7, and 533.4 eV, which are associated to O2−, bridging hydroxyls and physically absorbed water, respectively (Figure 5.4C).33 Furthermore, the TGA analysis revealed that the total mass fraction of copper and nickel is about 91.75 wt% (Figure 5.1E) in Ni0.75Cu0.25/C sample, which is much larger than that obtained from the XPS analysis (21.99 wt%). This is due to the fact that the XPS measurements are more sensitive to the surface chemical composition, which could barely detect the NiCu nanoparticles deeply embedded in the carbon matrix.

5.3.2 OER activities of Ni, Cu and bimetallic NiCu nanostructures

The OER properties of the Cu/C and Ni/C nanoparticles, as well as their bimetallic mixtures, were measured in 0.5 M NaOH solutions. Figure 5.5A displays the OER polarization curves for Ni0.75Cu0.25/C, Ni0.50Cu0.50/C and Ni0.25Cu0.75/C bimetallic nanocatalysts, along with Ni/C, Cu/C and the benchmark RuO2. The overall OER activity of the binary nanoalloys surpassed by far the performance of the individual metals indicating that the combination of Ni and Cu is
generating highly active sites and boosting the catalytic rates for the generation of molecular oxygen. For example, the overpotential value to reach 10 mA·cm⁻², which represents a suitable
descriptor of the catalytic activity, significantly lower for the bimetallic nanoparticles compared to the monometallic counterparts. Moreover, among the different nanoalloys, $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ exhibited the best OER performance, delivering a current density of 10 mA·cm$^{-2}$ at a low overpotential of 400 mV and an onset potential of 1.44 V vs RHE, while $\text{Ni}_{0.75}\text{Cu}_{0.25}/\text{C}$ and $\text{Ni}_{0.50}\text{Cu}_{0.50}/\text{C}$ require 470 mV and 480 mV to achieve the same current density and exhibit onset potential values of 1.49 V and 1.52 V vs RHE, respectively (Table 5.2). It is worth noting that the $\eta_{10}$ for $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ is $\sim$10 mV lower than that of commercial RuO$_2$ and comparable to other carbon-coated transition bimetallic OER catalysts.$^{14, 34}$ From the Tafel plots of different catalysts in Figure 5.5B, we can see that the Tafel slope of $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ is 80 mV·dec$^{-1}$, which is the lowest value of all the samples studied including commercial RuO$_2$. The lower Tafel slope indicates the faster electrokinetic of the water oxidation process on the surfaces of $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ nanoparticles. Interestingly, there are substantial changes in the anodic peak potentials and intensity values of the bimetallic nanocatalysts compared to the monometallic Ni/C catalysts (Figure 5.5A: inset). The anodic peak of the Ni/C OER polarization curve is approximately 1.40V, which is typically attributed to redox reactions on surface active Ni sites.$^{35}$ The area under the anodic peaks of $\text{Ni}_{0.75}\text{Cu}_{0.25}/\text{C}$, $\text{Ni}_{0.50}\text{Cu}_{0.50}/\text{C}$ and $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$, which are centered at 1.38 V, 1.44V and 1.48V, respectively, are very different (Figure 5.6). Taking into account the area under the peaks, which is mainly associated with NiOOH formation,$^{36}$ the number of accessible Ni sites for $\text{Ni}_{0.75}\text{Cu}_{0.25}/\text{C}$, $\text{Ni}_{0.50}\text{Cu}_{0.50}/\text{C}$ and $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ were estimated to be $4.58 \cdot 10^{14}$, $5.28 \cdot 10^{14}$ and $7.90 \cdot 10^{14}$, respectively, showing that $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ exhibits the largest number of in-situ Ni active sites at the surfaces. From the XPS analyses, the wt% of Ni at the surface of the bimetallic catalysts were 9.45, 9.97 and 5.27 for $\text{Ni}_{0.75}\text{Cu}_{0.25}/\text{C}$, $\text{Ni}_{0.50}\text{Cu}_{0.50}/\text{C}$ and $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$, respectively.
These results illustrate that although Ni$_{0.25}$Cu$_{0.75}$/C has fewer Ni species at the surface, it has more in-situ effective OER active sites. These findings can be rationalized by the fact that not all of the Ni atoms at the surface of the bimetallic nanoparticles are electrochemically active. It means that only a small percent of surface Ni atoms are capable of efficiently catalyzing the water oxidation processes. It has been reported that the OER catalytic performance of nickel (oxy)hydroxide films is substantially improved upon the addition of small quantities of iron atoms. This behavior was explained on the basis of structural distortions produced through the incorporation of iron atoms into the coordination environment of Ni atoms, leading to improved overall catalytic activity. Hence, it is reasonable to think that increasing the number of Cu atoms at the bimetallic nanoparticle surfaces induces the changes in their lattice structures, which, in turn, influence both the adsorption energies of the intermediate catalytic species and the electrochemical performance of the Ni active sites. Ni$_{0.25}$Cu$_{0.75}$/C also had the largest number of structural defects, which was
confirmed by Raman experiments. Additionally, it was shown by XPS that the binding energy shifts on the Ni 2p3/2 band of Ni0.25Cu0.75/C surpassed by almost a factor of 3 than those of the other two bimetallic structures. The aforementioned binding energy shift is most likely produced by more disorder in the coordination environment of the Ni atoms, which in fact, markedly increase the strain energy at the interfaces of the nanodomains, thus facilitating the downshift of the d-band center as well as the lowering of the binding energies of the intermediate catalytic species38, 39 and, in turn, the activation of a larger number of Ni active sites at the nanoparticle surfaces.

The Ni-based catalysts follow three well-defined steps in the OER process:40, 41

\[
\begin{align*}
\text{NiOOH} + \text{OH}^- & \rightleftharpoons \text{NiO(OH)} + \text{e}^- & E^o= 1.43 \text{ V} \\
\text{NiO(OH)}_2 + 2\text{OH}^- & \rightleftharpoons \text{NiOO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- & E^o=1.55 \text{ V} \\
\text{NiOO}_2 + \text{OH}^- & \rightleftharpoons \text{NiOOH} + \text{O}_2 + \text{e}^- & 
\end{align*}
\]

Steps 8 and 9 are both reversible processes and step 10 is irreversible and usually regulates the overall OER rates. Consequently, catalytic materials speed up step 10. We believe that the enhanced catalytic activity of Ni0.25Cu0.75/C is driven by the introduction of additional surface defects into the crystalline NiCu framework. To get in-depth information on the intrinsic activity of the electrocatalysts, the electrochemical surface areas (ECSA) and roughness factor (RF) of the monometallic and bimetallic nanoparticles were calculated from the double layer capacitance $C_{dl}$ (Table 5.5). The $C_{dl}$ of Ni0.25Cu0.75/C nanocatalysts surpassed by a factor of 2 than the values of the other bimetallic nanoparticles, reaching 1.4 mF·cm$^{-2}$ (Figure 5.5C), which clearly confirmed the higher number of accessible OER active sites on these nanocatalysts. The OER polarization curves were normalized by ECSA (Figure 5.5D) and Ni0.25Cu0.75/C still exhibited the best OER activity with the smallest onset potential values (1.50 V vs RHE).
Valuable insights were obtained by plotting both overpotential and unit cell volume values of all the carbon-encapsulated metallic nanoparticles as a function of the DFT-calculated OH⁻ adsorption energy (E_{OHB}) (Figure 5.5E). The superior performance of Ni_{0.25}Cu_{0.75}/C perfectly matches the moderate value of E_{OHB}, which greatly favors the adsorption of the hydroxyl groups on each catalytic step since the adsorption of these anions is not too strong, nor too weak as stated by the Sabatier rule for ideal catalysts. The plot of the experimental OER onset potential values as a function of the E_{OHB} followed the typical volcano-shape trend, where the Ni_{0.25}Cu_{0.75}/C is situated at the minimum of the peak, indicating superior electrocatalytic activity. These findings could be explained in terms of local structural distortions of the electrochemical interfaces of Ni_{0.25}Cu_{0.75}/C which activates several Ni sites, allowing the adsorption/desorption processes of the hydroxyl anions and improving the overall OER rates. It was also observed a pronounced lattice contraction of the Ni_{0.25}Cu_{0.75}/C metallic frameworks (Table 5.1). The lattice contraction results in additional strain effects at the interfaces which potentially favors the processes discussed above and, therefore, the catalytic efficiency of Ni_{0.25}Cu_{0.75}/C nanocatalysts. To determine whether the local structural changes at the surfaces of the bimetallic nanoparticles were beneficial to the OER reaction, the free energy diagrams were calculated by DFT (Figure 5.5F). According to the simulation results, Ni_{0.25}Cu_{0.75}/C system exhibited the lowest overpotential of 0.79 eV, which indicated that the formation of the O*, OH* and OOH* intermediate catalytic species were more energetically favorable on the highly distorted Ni_{0.25}Cu_{0.75}/C surfaces. It implied that the surface defects of the nanoalloy material decreased the uphill energy states of each step of the OER process and enhanced the overall catalytic activity towards the water oxidation. Interestingly, the Ni_{0.25}Cu_{0.75}/C exhibited a considerably lower η^{OER} value (0.79 eV) than that of the Ni_{0.75}Cu_{0.25}/C (1.17 eV), Ni_{0.50}Cu_{0.50}/C (1.73 eV), Cu/C (4.48 eV) and Ni/C (1.04 eV) (Figure 5.5G). 

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Additionally, DFT calculations revealed that the more energetically favorable catalytic active sites on the NiCu nanoalloys were located in the three-fold hollow sites of NiCu (111) surfaces (Figure 5.7).

The oxygen turnover frequencies (TOF) were calculated to further examine the intrinsic OER activities (Table 5.2). The TOF value of Ni$_{0.25}$Cu$_{0.75}$/C was found to be much higher than the others, indicating their superior intrinsic activity for the OER. The current densities were normalized to TOF and then plotted against potential to verify the theoretical results (Figure 5.5H), and as shown, the higher performance of Ni$_{0.25}$Cu$_{0.75}$/C compared to the other nanocatalysts
reinforces the observed larger OER intrinsic activity for Ni$_{0.25}$Cu$_{0.75}$/C nanoalloys. It was further demonstrated by their higher mass and specific activity values (Table 5.2). Additionally, Ni$_{0.25}$Cu$_{0.75}$/C nanoalloys showed excellent electrochemical long-term stability properties in basic media, keeping 97% of the initial current applied after 20000s and beating the stability of Pt/C under the same experimental conditions (Figure 5.5I).

5.3.3 HER activities of Ni, Cu and bimetallic NiCu nanostructures

The HER properties of the bimetallic nanoparticles were evaluated using a three-electrode electrochemical system in 0.5 M H$_2$SO$_4$ (Figure 5.8A). All the potentials were referred to the reversible hydrogen electrode (RHE) and all the linear sweep voltammograms (LSVs) are shown with the corresponding iR-correction. Among all the samples, Ni$_{0.25}$Cu$_{0.75}$/C exhibited the highest electrocatalytic performance, delivering a very low onset potential of -75 mV vs RHE as well as an overpotential of 184 mV at a geometrical current density of 10 mA·cm$^{-2}$, which is lower than that for Ni$_{0.75}$Cu$_{0.25}$/C (334 mV), Ni$_{0.50}$Cu$_{0.50}$/C, (400 mV), Cu/C (471 mV) and Ni/C (437 mV). These values are comparable or even better than many other recently reported electrocatalysts. To gain further insight on the HER kinetics, Tafel plots were fitted to the equation \( \eta = a \log j + b \), where \( \eta \) is the overpotential, \( a \) is the slope and \( j \) is the current density (Figure 5.8B). The Tafel slope for Ni$_{0.25}$Cu$_{0.75}$/C (84 mV·dec$^{-1}$) is much smaller than for both pure Ni/C (106 mV·s$^{-1}$) and Cu/C (179 mV·s$^{-1}$) and the other two nanoalloys Ni$_{0.75}$Cu$_{0.25}$/C (114 mV·s$^{-1}$) and Ni$_{0.50}$Cu$_{0.50}$/C (125 mV·s$^{-1}$), indicating that the Ni:Cu (1:3) ratio into the NiCu nanodomains markedly improves the kinetics of the HER processes through a Volmer-Heyrovsky mechanism. To investigate the intrinsic activity of the as-synthesized electrocatalysts, the electrochemical surface area (ECSA) and RF of the electrocatalysts were calculated from the double layer capacitance (C$_{dl}$) values using cyclic voltammetry (CV) and the results are presented in Figure 5.8C.\textsuperscript{44}
Figure 5.8: A) Polarization curves of HER process and B) the corresponding Tafel plots for Cu/C, Ni/C, Ni\textsubscript{0.50}Cu\textsubscript{0.50}/C, Ni\textsubscript{0.25}Cu\textsubscript{0.75}/C, Ni\textsubscript{0.75}Cu\textsubscript{0.25}/C and commercial Pt/C in 0.5 M H\textsubscript{2}SO\textsubscript{4} at 2mV·s\textsuperscript{-1}. C) Plots of the difference of anodic and cathodic current densities against the scan rate for all the catalysts. D) Polarization curves normalized by ECSA for Cu/C, Ni/C, Ni\textsubscript{0.50}Cu\textsubscript{0.50}/C, Ni\textsubscript{0.25}Cu\textsubscript{0.75}/C and Ni\textsubscript{0.75}Cu\textsubscript{0.25}/C nanocatalysts. E) The onset potential and unit cell volume values for Cu/C, Ni/C, Ni\textsubscript{0.50}Cu\textsubscript{0.50}/C, Ni\textsubscript{0.25}Cu\textsubscript{0.75}/C and Ni\textsubscript{0.75}Cu\textsubscript{0.25}/C as a function of the DFT-calculated E\textsubscript{HB}. F) The corresponding ΔG\textsubscript{H\textsuperscript{+}} for each nanoalloy. The closer the line is to 0 indicates a better HER performance. G) Relationship between the C\textsubscript{dl} and ΔG\textsubscript{H\textsuperscript{+}} values for all the electrocatalysts. H) The average turn-over frequencies (TOF\textsubscript{avg}) of the nanocatalysts displayed in (A) per surface site. I) I-t curves of Ni\textsubscript{0.25}Cu\textsubscript{0.75} and its comparison with commercial Pt/C at -0.35 V vs RHE.
The Ni$_{0.25}$Cu$_{0.75}$/C electrocatalyst displayed the highest ECSA of about 115 cm$^2$, which is several times higher than that of the other electrocatalysts. The results obtained from both approaches demonstrate more electrocatalytically active sites in Ni$_{0.25}$Cu$_{0.75}$/C than in the others, confirming its better electrocatalytic performance for HER process. The polarization HER curves were normalized by ECSA (Figure 5.8D) and Ni$_{0.25}$Cu$_{0.75}$/C still exhibited better HER activities with the lowest onset potential value (-0.11 V vs RHE). It is well known that the hybridization state of different atoms in nanostructured alloys can finely tune their electrocatalytic properties. For instance, it has been demonstrated that the combination of Ni and Mo significantly improves the electrocatalytic properties for hydrogen generation.$^{45,46}$ On the other hand, it is possible to regulate the catalytic activity of bimetallic nanostructures by controlling their electronic structure as well as the strain energy and/or lattice contractions via changes of their metal-metal ratios.$^{13,47-49}$ As it was explained in the OER section, the surface defects induced by an increase of Cu atoms in the crystalline framework of Ni$_{0.75}$Cu$_{0.25}$/C plays a significant role in the electrocatalytic activity. It is reasonable to assume that other composition-dependent effects derived from local structural distortion processes of multimetallic nanocrystal interfaces such as the lattice dimension, the strain energy and/or the number of energetically favourable binding sites, could be directly controlling the electronic structures of the resulting bimetallic nanocatalysts and, in turn, their HER performances.$^{50}$ The strain effects are caused when the surface atom geometries are compressed or expanded. In a bimetallic nanosystem, it can regulate both the electronic structure and the binding energy of intermediate HER catalytic species, such as H*, on the nanoalloy surfaces, which results in the deactivation or activation of the catalytically active surface sites.$^{51}$ To probe the underlying factors that govern the HER activity in our bimetallic NiCu particles, their onset potential and the unit cell volume values were plotted as a function of the DFT-calculated hydrogen
binding energy ($E_{\text{HB}}$) (Figure 5.8E). The $E_{\text{HB}}$ is an excellent descriptor of the HER catalytic activity and it is closely linked with the position of the metal d-band center relative to the Fermi level of the nanocatalyst.\textsuperscript{13} Interestingly, the unit cell volume values of the bimetallic nanostructures decreases together with the onset potential values, following the trend $\text{Ni}_{0.50}\text{Cu}_{0.50}/\text{C} > \text{Ni}_{0.75}\text{Cu}_{0.25}/\text{C} > \text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$, which indicates that the lattice contraction of the nanoalloys is markedly improving their catalytic performance. It is well-known that when two metals with different lattice parameters are mixed to form a bimetallic system, a lattice mismatch is generated at the interface of the metal nanodomains, which leads to a lattice distortion in the crystalline framework.\textsuperscript{50, 52, 53} The defective sites can create additional strain effects at the interfaces of the nanodomains which facilitate the distortion of the lattice parameters, and in turn, their pronounced lattice contraction. The lattice contraction gives rise to the downshift of the d-band center, which, in turn, decreases the adsorption energy of the reaction intermediate species boosting the catalytic efficiency of $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ towards the generation of molecular hydrogen.\textsuperscript{54-56} The Sabatier principle predicts that interactions between reactants and intermediates and the catalyst surface must be ideally balanced to reach very high catalytic performances. In this sense, the hydrogen adsorption value estimated for the $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ catalytic surfaces is neither too small nor too large, which maximizes the HER efficiency by optimizing the interactions of the reactants and intermediate species at the electrochemical interfaces. It should be pointed out that the catalytic active sites for hydrogen adsorption were localized at the three-fold hollow sites of $\text{NiCu} (111)$ surfaces (Figure 5.7).

Our DFT calculations show that $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ has a $\Delta G_{\text{H}^+}$ very close to 0 (-0.05 eV), surpassing by far the values for $\text{Ni}_{0.75}\text{Cu}_{0.25}/\text{C}$ (0.62 eV), $\text{Ni}_{0.50}\text{Cu}_{0.50}/\text{C}$ (0.38 eV), Cu/C (-0.29 eV) and Ni/C (0.86 eV) (Figure 5.8F). The relationship between the experimentally measured $C_{\text{dl}}$
and $\Delta G_{H^+}$ values of the five electrocatalysts is shown in Figure 5.8G. For $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$, the smallest value of $\Delta G_{H^+}$ together with the largest $C_{dl}$ determines the observed optimized HER activity. We have also calculated the hydrogen turn over frequency (TOF) for all of the electrocatalysts to further investigate their intrinsic HER performance. The TOF value for $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ is several times higher than for the others studied. The experimental TOFs were found to be 0.62, 0.28, 0.10, 0.061 and 0.056 s$^{-1}$ for $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$, $\text{Ni}_{0.75}\text{Cu}_{0.25}/\text{C}$, $\text{Ni}_{0.50}\text{Cu}_{0.50}/\text{C}$, $\text{Ni}/\text{C}$ and $\text{Cu}/\text{C}$ at -0.15 V, respectively (Table 5.3). To gain further insight on the nature of the catalytically active sites of the nanoalloys, the number of hydrogen molecules evolved per second per active site were carefully plotted against the potential for each catalyst and $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ electrocatalyst showed better performance than the others (Figure 5.8H). The higher performance of $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ can be directly linked to the pronounced interfacial lattice mismatch of its crystal structure which downshifts the d-band and enhances the interaction with the H reactive intermediates decreasing the $\Delta G_{H^+}$ values and promoting overall HER activity. The calculated higher mass activity and specific activity values for $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ also shows its superior intrinsic activity toward the HER process (Table 5.3). Finally, $\text{Ni}_{0.25}\text{Cu}_{0.75}/\text{C}$ showed ultrahigh electrochemical stability in acidic media, maintaining 99% of the initial current applied after 20000s and surpassing the Pt/C stability under the same experimental conditions (Figure 5.8I).

5.3.4 ORR activities of Ni, Cu and bimetallic NiCu nanostructures

The ORR activity of the carbon-embedded mono and bimetallic nanoparticles was evaluated via steady-state linear sweep voltammetry (LSV) in O$_2$-saturated 0.5 M NaOH solution under static and dynamic conditions. Figure 5.9 compares the resulting voltammetric curves obtained for O$_2$-saturated and Ar-saturated solutions, displaying very well-defined ORR cathodic peaks and demonstrating that the oxygen electroreduction processes are taking place at the electrochemical
interfaces. Remarkably, Ni_{0.25}Cu_{0.75}/C exhibited a more positive oxygen electroreduction peak at 0.67 V vs RHE than those of the other studied catalysts, indicating better electrocatalytic ORR activity than the others.

Figure 5.9: CVs of the as-synthesized electrocatalysts in Ar- and O_2-saturated 0.5 M NaOH solution.

Figure 5.10A displays the ORR polarization curves for all the catalysts. Ni_{0.25}Cu_{0.75}/C shows a much higher value of the onset potential (0.95 V vs RHE) and the half-wave potential (0.80 vs RHE) than the other mono and bimetallic catalysts. The performance is comparable or even better than for many other recently reported ORR electrocatalysts. Furthermore, the Tafel plots and the ECSA normalized ORR polarization curves also confirmed the superior ORR activity of Ni_{0.25}Cu_{0.75}/C, demonstrating both the larger intrinsic activity and faster kinetics than the other systems (Figure 5.10B and Figure 5.10C). In contrast with the observed OER and HER trends, the other two bimetallic catalysts show very similar ORR performance compared with those of the monometallic catalysts (Table 5.4).
Figure 5.10: A) Polarization curves of the ORR process and B) the corresponding Tafel plots for Cu/C, Ni/C, Ni_{0.50}Cu_{0.50}/C, Ni_{0.25}Cu_{0.75}/C, Ni_{0.75}Cu_{0.25}/C and commercial Pt/C in 0.5 M NaOH at 2mV·s⁻¹. C) Polarization curves normalized by ECSA for Cu/C, Ni/C, Ni_{0.50}Cu_{0.50}/C, Ni_{0.25}Cu_{0.75}/C and Ni_{0.75}Cu_{0.25}/C. D) Rotating disk voltammogram (RDV) curves at different rotation rates for all the samples. Inset: K-L plots. E) ORR onset potential and unit cell volumes as a function of the DFT-calculated E_{0B}. F) Free energies for the ORR pathways for all catalysts. G) Relationship between C_{dl} and ΔG_{H⁺} values for all electrocatalysts. H) Mass activity (MA) and specific activity (SA) values for all the nanocatalysts. I) I-t curves for Ni_{0.25}Cu_{0.75} and its comparison with commercial Pt/C at 0.7 V vs RHE.

To gain further insights into the kinetic parameters for the ORR, rotating-disk voltammetry (RDV) measurements were performed at different rotation rates, between 250 and 2500 rpm, at a scan rate...
of 10 mV·s⁻¹ (Figure 5.10D). The onset ORR potential was found to be 0.96 V vs RHE. The inset of Figure 5.10D shows the resulting K-L plot for Ni₀.₂₅Cu₀.₇₅/C. The excellent fit confirms a first-order reaction for dissolved O₂. Using the K-L equations, the average number of electrons transferred (n) per oxygen molecule at 0.6 V vs RHE and the resulting kinetic-limiting current density (Jₖ) values were estimated to be 4.106 and 10.63 mA·cm⁻², respectively. The number of electrons exchanged per O₂ molecule with Ni₀.₂₅Cu₀.₇₅/C is close to 4, indicating that the electrochemical reaction follows the most efficient electron pathway. Additionally, the difference of anodic and cathodic current densities as a function of scan rates was plotted for all the samples. As it is shown in the OER section, Ni₀.₂₅Cu₀.₇₅/C displays the larger Cₐl value in the alkaline media and therefore, it possesses the largest number of ORR active sites. The electrocatalytic performance can be tuned by varying the oxygen binding energy (EₒB) which constitutes a good descriptor of the catalytic efficiency of a large portfolio of reactions. Considering the Sabatier rule, very strong binding energies lead to surface oxidation, which lowers the catalytic activity, while very weak binding energies give rise to a fast desorption of the oxygen from the active site. Consequently, optimized ORR activity requires moderate EₒB values, balancing both the surface oxidation and desorption processes at the same time. To obtain a better understanding of the superior ORR activity of Ni₀.₂₅Cu₀.₇₅/C, we have plotted the onset potential and unit cell volume values as a function of the DFT-calculated oxygen binding energy values (EₒB) (Figure 5.10E). Among all, Ni₀.₂₅Cu₀.₇₅/C exhibits an optimum oxygen binding energy for electroreduction which is the midway value between the oxygen binding energies for the pure metallic nanoparticles. The lowest unit cell volume value of Ni₀.₂₅Cu₀.₇₅/C reflects that the lattice contraction and therefore, the high strain energy strongly helps to improve the ORR catalytic rates and thereby, reducing the binding energy of oxygen based adsorbates, such as O⁺ and OH⁺, increases the electron transfer
rates at the catalytically active surface sites.\textsuperscript{58, 59} Our DFT calculations showed a good agreement with the experimental results. In detail, a significant reduction of the Gibb’s free energies for the O*, OH* and OOH* intermediate catalytic species was observed (Figure 5.10F). \(\text{Ni}_{0.25}\text{Cu}_{0.75}/C\) exhibited a lower \(\eta_{\text{ORR}}\) value (0.87 eV) than those for \(\text{Ni}_{0.75}\text{Cu}_{0.25}/C\) (1.23 eV), \(\text{Ni}_{0.50}\text{Cu}_{0.50}/C\) (0.96 eV), \(\text{Cu}/C\) (3.52 eV) and \(\text{Ni}/C\) (1.32 eV) (Figure 5.10G) as well as the \(C_{\text{dl}}\) of \(\text{Ni}_{0.25}\text{Cu}_{0.75}/C\) is better than for all catalysts, indicating that the electrochemical performance is optimized for this Ni:Cu ratio. The calculated mass activity and specific activity values for the electrocatalysts are presented in Figure 5.10H. Like for the OER and HER processes, the TOF, mass activity and specific activity of the electrocatalysts were calculated at 0.75 V vs RHE (Table 5.4) and it was found that \(\text{Ni}_{0.25}\text{Cu}_{0.75}/C\) exhibits the best intrinsic activity toward the ORR process. Finally, \(\text{Ni}_{0.25}\text{Cu}_{0.75}/C\) showed an excellent long-term electrochemical stability compare to commercial Pt/C, keeping 91% of the initial current applied after 20000s (Figure 5.10I).

5.4 CONCLUSION

In summary, we report the facile synthesis of tri-functional bimetallic Ni:Cu nanoparticles encapsulated in carbon that allows for the systematic control of the structure and the electronic properties and produce an effective catalyst for HER, OER and ORR reactions. The Ni:Cu ratio was varied to control the structural and electronic properties of the bimetallic nanoparticles. Experimentally and theoretically, it was established that the local distortion of the crystalline lattice at the bimetallic nanostructured surfaces were associated to the downshift of the d-band and the lowering of the binding energies of the intermediate reactive species, which in turn, increase the electron transfer rates of the catalytically active surface sites and improves the overall reaction rates. The DFT-calculated binding energy values were used as desirable parameters to describe the trifunctional electrocatalytic efficiency of the bimetallic nanoalloys. Thus, the nanocomposite
Ni$_{0.25}$Cu$_{0.75}$/C, which exhibits a near-optimal binding energy for HER, OER and ORR reactions, shows an impressive trifunctional catalytic activity that outperforms commercial Pt and RuO$_2$ catalysts. Our findings provide in-depth insights to directly correlate the structure–catalytic function relationships of carbon-encapsulated NiCu bimetallic nanostructures, thus paving the way towards the rational design of low-cost and scalable multifunctional catalytic nanosystems.

5.5 SUPPORTING INFORMATION

5.5.1 Computational methods

To investigate the catalytic activities of the NiCu alloys, five specific compositions were selected and studied in this project in accordance with the experiments. Overpotentials during the process of HER, OER and ORR were determined through first-principles calculations by calculating the Gibbs free energy of H*, OH* and OOH* on the surfaces of different catalysts. These first-principles calculations were executed on the basis of DFT and were performed using the Vienna ab initio simulation package (VASP)\textsuperscript{51, s2}. The core electrons were treated using projected augmented wave (PAW) pseudopotentials\textsuperscript{s3}, while the exchange correlation energies were evaluated by the formulations of Perdew–Burke–Ernzerhof (PBE) and ultra-soft potentials within the generalized gradient approximation (GGA)\textsuperscript{54, s5}. The cut-off energy for the plane wave was set to be 400 eV, which was found to be sufficient for convergence of the adsorption energies. The FCC structures for each NiCu alloys (Cu, Ni$_{0.25}$Cu$_{0.75}$, Ni$_{0.50}$Cu$_{0.50}$, Ni$_{0.75}$Cu$_{0.25}$ and Ni) were generated according to the experiment observation and tested with the VASP calculations. After relaxation the alloys showed a steady FCC structure, which matches the experimental observation. To simulate the free surface, a slab model with $2 \times 2 \times 2$ supercells of the five alloys was employed. A relatively large vacuum gap of 20 Å was set in the slab model to prevent its interaction with the periodic image of the lower layer. The bottom lattice of the model was fixed at the ground-state
bulk distances, while the top lattice was set to be free to move in all directions. k-point meshes of $5 \times 3 \times 1$ were found to be sufficient to give a self-consistent field (SCF) convergence criterion of $1 \times 10^{-5}$ eV. For each structure, atomic positions were relaxed first to reach their equilibrium. Thereafter, the adsorbate ion was placed on the top of the active sites (on the relaxed free surface) at a certain distance to calculate the total formation energy. The internal energy of the isolated adsorbates was also calculated. The adsorption energy $E_{ad}$ was then calculated using Eq S1.$^{6,7}$

$$E_{ad} = E_{sub+adatom} - E_{sub} - E_{adatom}$$  \hspace{1cm} (S1)

Where $E_{sub+adatom}$, $E_{sub}$, and $E_{adatom}$ refer to the total energy of the NiCu alloy and adsorbate, the energy of the NiCu substrate and the energy of the isolated adsorbate, respectively. Based on this definition, the more negative value of $E_{ad}$ represents a higher thermodynamic stability of the system. The Gibbs free energy difference $\Delta G$ was then calculated to describe the catalytic property by additional calculations. For HER, the Gibbs free energy difference $\Delta G_H$ is $^{6,7}$

$$\Delta G_H = E_{ad-H} - \Delta E_{ZPE} - T\Delta S_H$$  \hspace{1cm} (S2)

Where $E_{ad-H}$ refers to the adsorption energy of H* (* denotes the uncertain ion state) on the NiCu surface. $\Delta E_{ZPE}$ refers to the difference of zero-point energy, which can be obtained from vibration frequency calculations. $T$ is temperature and $\Delta S_H$ is the difference of entropy for the adsorbate, here is described as half of $S_H$, which is known thermodynamic properties for each adsorbate.

For OER and ORR, the Gibbs free energy difference $\Delta G$ also contains electron transfer and can be described as$^{6,7}$

$$\Delta G = E_{ad} - \Delta E_{ZPE} - T\Delta S + \Delta G_U + \Delta G_{pH}$$  \hspace{1cm} (S3)
Where $\Delta G_U = -eU$, and $U$ refers to the potential based on the standard hydrogen electrode. $\Delta G_{pH}$ represents the Gibbs free energy corrected by the $H^+$ concentration, $\Delta G_{pH} = -kTln10 \times pH$. For the four OER processes, the free energy changes can be described as $^6, ^7$

$$\Delta G_1 = \Delta G_{OH*} \quad \Delta G_2 = \Delta G_{O*} - \Delta G_{OH*} \quad \Delta G_3 = \Delta G_{OOH*} - \Delta G_{O*} \quad \Delta G_4 = 4.92 - \Delta G_{OOH*} \quad (S4)$$

$$\Delta G_a = \Delta G_{OOH*} - 4.92 \quad \Delta G_b = \Delta G_{O*} - \Delta G_{OOH*} \quad \Delta G_c = \Delta G_{OH*} - \Delta G_{O*} \quad \Delta G_d = -\Delta G_{OH*} \quad (S5)$$

The subscript numbers and letters in Eq. (S4) and (S5) indicate the free energy changes during OER and ORR, respectively. To evaluate the catalytic performance, the overpotential ($\eta$) of OER and ORR processes can be obtained by the following equations $^6, ^7$

$$\eta_{OER} = \max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\} - 1.23 \quad (S6)$$

$$\eta_{ORR} = \max\{\Delta G_a, \Delta G_b, \Delta G_c, \Delta G_d\} + 1.23 \quad (S7)$$

5.5.2 Lattice constant for the prepared electrocatalysts

The lattice constants for the Cu/C, Ni/C, Ni$_{0.50}$Cu$_{0.50}$/C, Ni$_{0.75}$Cu$_{0.25}$/C and Ni$_{0.25}$Cu$_{0.75}$/C electrocatalysts can be calculated according to the relationship between the d-spacing and lattice constants for a face centered cubic (FCC) crystal system:

$$d_{hkl} = \frac{\lambda}{2\sin(\theta_{hkl})} = \left[\frac{h^2 + k^2 + l^2 + a^2}{a^2}\right]^{-1/2}$$

Solving the above equation for the (111) peak gives the lattice constants as shown in Table 5.1. The lattice constants for the bimetallic electrocatalysts are in between of the monometallics.
Table 5.1: (111) peak positions and lattice constants for Cu/C, Ni/C, Ni$_{0.50}$Cu$_{0.50}$/C, Ni$_{0.75}$Cu$_{0.25}$/C and Ni$_{0.25}$Cu$_{0.75}$/C as determined by the XRD.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\theta_{111}$ [°]</th>
<th>a [Å]</th>
<th>Unit cell volume [Å$^3$]</th>
<th>Atoms per unit cell</th>
<th># Surface sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/C</td>
<td>43.40</td>
<td>3.607</td>
<td>46.93</td>
<td>4</td>
<td>$1.94 \times 10^{15}$</td>
</tr>
<tr>
<td>Ni/C</td>
<td>44.50</td>
<td>3.522</td>
<td>43.68</td>
<td>4</td>
<td>$2.03 \times 10^{15}$</td>
</tr>
<tr>
<td>Ni$<em>{0.50}$Cu$</em>{0.50}$/C</td>
<td>43.8</td>
<td>3.575</td>
<td>45.69</td>
<td>4</td>
<td>$1.97 \times 10^{15}$</td>
</tr>
<tr>
<td>Ni$<em>{0.75}$Cu$</em>{0.25}$/C</td>
<td>44.05</td>
<td>3.556</td>
<td>44.97</td>
<td>4</td>
<td>$1.99 \times 10^{15}$</td>
</tr>
<tr>
<td>Ni$<em>{0.25}$Cu$</em>{0.75}$/C</td>
<td>44.17</td>
<td>3.547</td>
<td>44.62</td>
<td>4</td>
<td>$2.00 \times 10^{15}$</td>
</tr>
</tbody>
</table>

5.5.3 Turnover frequency (TOF) calculations

To calculate the per-site turnover frequency, we have used the following formula as reported by Jaramillo et al.$^{8}$

$$\text{TOF} = \frac{\# \text{number of total hydrogen turnover per cm}^2}{\# \text{number of active sites per cm}^2} = \frac{\# H_2 \times |j|}{\text{active sites}}$$

The total number of hydrogen turnovers ($\#H_2$) was calculated from the current density according to the following equation.

$$\#H_2 = \left( j \frac{\text{mA}}{\text{cm}^2} \right) \left( \frac{1 \text{ Cs}^{-1}}{1000 \text{ mA}} \right) \left( \frac{1 \text{ mol e}^-}{96485.3 \text{ C}} \right) \left( \frac{1 \text{ mol H}_2}{2 \text{ mol e}^-} \right) \left( \frac{6.022 \times 10^{23} \text{ H}_2 \text{ molecules}}{1 \text{ mol H}_2} \right)$$

$$= 3.12 \times 10^{15} \text{ H}_2/\text{s per cm}^2$$

$$\#O_2 = \left( j \frac{\text{mA}}{\text{cm}^2} \right) \left( \frac{1 \text{ Cs}^{-1}}{1000 \text{ mA}} \right) \left( \frac{1 \text{ mol e}^-}{96485.3 \text{ C}} \right) \left( \frac{1 \text{ mol O}_2}{4 \text{ mol e}^-} \right) \left( \frac{6.022 \times 10^{23} \text{ O}_2 \text{ molecules}}{1 \text{ mol O}_2} \right)$$

$$= 1.56 \times 10^{15} \text{ O}_2/\text{s per cm}^2$$

$$\#H_2O = \left( j \frac{\text{mA}}{\text{cm}^2} \right) \left( \frac{1 \text{ Cs}^{-1}}{1000 \text{ mA}} \right) \left( \frac{1 \text{ mol e}^-}{96485.3 \text{ C}} \right) \left( \frac{1 \text{ mol H}_2O}{4 \text{ mol e}^-} \right) \left( \frac{6.022 \times 10^{23} \text{ H}_2O \text{ molecules}}{1 \text{ mol H}_2O} \right)$$

$$= 1.56 \times 10^{15} \text{ H}_2O/\text{s per cm}^2$$
As the exact hydrogen binding sites are unknown, we predictably estimate the total number of surface sites or active sites by using the following equation. A similar approach was applied to estimate the TOF for Ni\textsubscript{2}P and CoP\textsuperscript{59,S10}

# number of active sites per real surface area (here calculated for Ni\textsubscript{0.25}Cu\textsubscript{0.75}/C):

\[
\text{# number of active sites} = \left( \frac{\text{number of atoms/unit cell}}{\text{unit cell volume/unit cell}} \right)^2
\]

\[
= \left( \frac{4 \text{ atoms/unit cell}}{44.62 \text{ Å}^3/\text{unit cell}} \right)^2
\]

\[
= 2.00 \times 10^{15} \text{ atoms cm}^{-2}
\]

We have demonstrated the TOF calculations for the best Ni\textsubscript{0.25}Cu\textsubscript{0.75}/C electrocatalyst in case of HER, OER and ORR processes. The other TOF values for the other electrocatalysts were also calculated accordingly.

For HER process: The current density at an overpotential of 0.15 V (vs RHE) is 5.76 mA cm\textsuperscript{-2} for the Ni\textsubscript{0.25}Cu\textsubscript{0.75}/C electrocatalyst.

\[
\text{TOF} = \frac{3.12 \times 10^{15} \text{ H}_2/\text{s cm}^2 \text{ per mA cm}^2 \times 20 \text{ mA cm}^2}{2.00 \times 10^{15} \text{ sites cm}^{-2}} = 8.98 \text{ s}^{-1}
\]

For OER process: The current density at an overpotential of 1.65 V (vs RHE) is 12.40 mA cm\textsuperscript{-2} for the Ni\textsubscript{0.25}Cu\textsubscript{0.75}/C electrocatalyst.

\[
\text{TOF} = \frac{1.56 \times 10^{15} \text{ O}_2/\text{s cm}^2 \text{ per mA cm}^2 \times 12.40 \text{ mA cm}^2}{2.00 \times 10^{15} \text{ sites cm}^{-2}} = 9.67 \text{ s}^{-1}
\]

For ORR process: The current density at an overpotential of 0.75 V (vs RHE) is 0.80 mA cm\textsuperscript{-2} for the Ni\textsubscript{0.25}Cu\textsubscript{0.75}/C electrocatalyst.

\[
\text{TOF} = \frac{1.56 \times 10^{15} \text{ H}_2\text{O}/\text{s cm}^2 \text{ per mA cm}^2 \times 0.80 \text{ mA cm}^2}{2.00 \times 10^{15} \text{ sites cm}^{-2}} = 0.62 \text{ s}^{-1}
\]

Finally, the plot of current density can be converted into a TOF plot based on the following equation:
For HER Process:

\[ \text{TOF} = \frac{(3.12 \times 10^{15}) \times |j|}{\# \text{ number of active sites} \times A_{ECSA}} \]

For OER Process:

\[ \text{TOF} = \frac{(1.56 \times 10^{15}) \times |j|}{\# \text{ number of active sites} \times A_{ECSA}} \]

Table 5.2: Comparison of OER electrocatalytic performance of Cu/C, Ni/C, Ni\text{0.50Cu0.50}/C, Ni\text{0.75Cu0.25}/C and Ni\text{0.25Cu0.75}/C electrocatalysts in 0.5 M NaOH solution.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Onset Potential (V vs RHE)</th>
<th>(\eta_{10}) (mV vs RHE)</th>
<th>Tafel slope (mV/dec)</th>
<th>Mass Activity (mA/mg)</th>
<th>Specific Activity (mA/cm²)</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/C</td>
<td>1.64</td>
<td>(/)</td>
<td>147</td>
<td>4.69</td>
<td>0.03</td>
<td>0.53</td>
</tr>
<tr>
<td>Ni/C</td>
<td>1.62</td>
<td>(/)</td>
<td>144</td>
<td>6.51</td>
<td>0.05</td>
<td>0.72</td>
</tr>
<tr>
<td>Ni\text{0.50Cu0.50}/C</td>
<td>1.52</td>
<td>480</td>
<td>113</td>
<td>36.72</td>
<td>0.23</td>
<td>4.09</td>
</tr>
<tr>
<td>Ni\text{0.75Cu0.25}/C</td>
<td>1.49</td>
<td>470</td>
<td>93</td>
<td>43.77</td>
<td>0.25</td>
<td>4.82</td>
</tr>
<tr>
<td>Ni\text{0.25Cu0.75}/C</td>
<td>1.44</td>
<td>400</td>
<td>80</td>
<td>86.8</td>
<td>0.36</td>
<td>9.67</td>
</tr>
</tbody>
</table>
Table 5.3: Comparison of HER electrocatalytic performance of Cu/C, Ni/C, Ni$_{0.50}$Cu$_{0.50}$/C, Ni$_{0.75}$Cu$_{0.25}$/C and Ni$_{0.25}$Cu$_{0.75}$/C electrocatalysts in 0.5 M H$_2$SO$_4$ solution.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Onset Potential (mV)</th>
<th>$\eta_{10}$ (mV)</th>
<th>Tafel slope (mV/dec)</th>
<th>Mass Activity (mA/mg)</th>
<th>Specific Activity (mA/cm$^2$)</th>
<th>TOF (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/C</td>
<td>401</td>
<td>471</td>
<td>179</td>
<td>2.90</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>Ni/C</td>
<td>367</td>
<td>437</td>
<td>106</td>
<td>10.50</td>
<td>0.05</td>
<td>0.27</td>
</tr>
<tr>
<td>Ni$<em>{0.50}$Cu$</em>{0.50}$/C</td>
<td>327</td>
<td>400</td>
<td>125</td>
<td>24.71</td>
<td>0.10</td>
<td>0.33</td>
</tr>
<tr>
<td>Ni$<em>{0.75}$Cu$</em>{0.25}$/C</td>
<td>243</td>
<td>334</td>
<td>114</td>
<td>87.64</td>
<td>0.16</td>
<td>0.52</td>
</tr>
<tr>
<td>Ni$<em>{0.25}$Cu$</em>{0.75}$/C</td>
<td>75</td>
<td>186</td>
<td>84</td>
<td>641.20</td>
<td>0.79</td>
<td>8.98</td>
</tr>
</tbody>
</table>

Table 5.4: Comparison of ORR electrocatalytic performance of Cu/C, Ni/C, Ni$_{0.50}$Cu$_{0.50}$/C, Ni$_{0.75}$Cu$_{0.25}$/C and Ni$_{0.25}$Cu$_{0.75}$/C electrocatalysts in 0.5 M NaOH solution.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Onset Potential (V)</th>
<th>$E_{1/2}$ (V)</th>
<th>Tafel slope (mV/dec)</th>
<th>Mass Activity (mA/mg)</th>
<th>Specific Activity (mA/cm$^2$)</th>
<th>TOF (s$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>Cu/C</td>
<td>0.78</td>
<td>0.43</td>
<td>125</td>
<td>0.48</td>
<td>0.003</td>
<td>0.056</td>
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<tr>
<td>Ni/C</td>
<td>0.78</td>
<td>0.56</td>
<td>122</td>
<td>0.56</td>
<td>0.004</td>
<td>0.061</td>
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<tr>
<td>Ni$<em>{0.50}$Cu$</em>{0.50}$/C</td>
<td>0.81</td>
<td>0.60</td>
<td>120</td>
<td>0.84</td>
<td>0.006</td>
<td>0.10</td>
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<tr>
<td>Ni$<em>{0.75}$Cu$</em>{0.25}$/C</td>
<td>0.86</td>
<td>0.75</td>
<td>80</td>
<td>2.45</td>
<td>0.015</td>
<td>0.28</td>
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<tr>
<td>Ni$<em>{0.25}$Cu$</em>{0.75}$/C</td>
<td>0.95</td>
<td>0.80</td>
<td>51</td>
<td>5.60</td>
<td>0.023</td>
<td>0.62</td>
</tr>
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</table>
Table 5.5: The obtained C(dl), ECSA and RF values for different electrocatalysts in HER and OER conditions.

<table>
<thead>
<tr>
<th>Electrocatalytic Process</th>
<th>Catalyst</th>
<th>C(dl) (mF·cm⁻²)</th>
<th>ECSA (cm²)</th>
<th>RF</th>
</tr>
</thead>
<tbody>
<tr>
<td>HER</td>
<td>Cu/C</td>
<td>1.07</td>
<td>30.57</td>
<td>436.71</td>
</tr>
<tr>
<td></td>
<td>Ni/C</td>
<td>1.13</td>
<td>32.28</td>
<td>461.14</td>
</tr>
<tr>
<td></td>
<td>Ni₀.₅Cu₀.₅/C</td>
<td>1.24</td>
<td>35.42</td>
<td>506</td>
</tr>
<tr>
<td></td>
<td>Ni₀.₇₅Cu₀.₂₅/C</td>
<td>2.71</td>
<td>77.42</td>
<td>1106</td>
</tr>
<tr>
<td></td>
<td>Ni₀.₂₅Cu₀.₇₅/C</td>
<td>4.05</td>
<td>115.71</td>
<td>1653</td>
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<tr>
<td>OER</td>
<td>Cu/C</td>
<td>0.78</td>
<td>19.5</td>
<td>278.57</td>
</tr>
<tr>
<td></td>
<td>Ni/C</td>
<td>0.80</td>
<td>20</td>
<td>285.71</td>
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<tr>
<td></td>
<td>Ni₀.₅Cu₀.₅/C</td>
<td>0.87</td>
<td>21.75</td>
<td>310.71</td>
</tr>
<tr>
<td></td>
<td>Ni₀.₇₅Cu₀.₂₅/C</td>
<td>0.98</td>
<td>24.5</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td>Ni₀.₂₅Cu₀.₇₅/C</td>
<td>1.4</td>
<td>35</td>
<td>500</td>
</tr>
</tbody>
</table>

References


52. Sneed, B. T.; Young, A. P.; Tsung, C.-K., Building up strain in colloidal metal nanoparticle catalysts. Nanoscale 2015, 7 (29), 12248-12265.

Chapter 6: Tuning the intermolecular electron transfer of low dimensional and metal-free BCN/C₆₀ electrocatalysts via interfacial defects for efficient hydrogen and oxygen electrochemistry

6.1 INTRODUCTION

Low-dimensional catalytic materials have recently impacted the scientific community as promising functional building blocks to construct highly efficient supramolecular nanoscale structures for water electrocatalysis.¹,² A wide portfolio of heterostructures can be obtained from the non-covalent integration of 0D, 1D and 2D nanomaterials into 0D-1D, 0D-2D, 1D-2D and 2D-2D hybrids to achieve sustainable alternatives for advanced electrocatalytic systems.³ The electronic structures and catalytic performances of supramolecular nanoassemblies have been starting to be tailored by controlling the interfacial interactions between their components, thus paving the way towards a new generation of tunable molecular electrocatalysts.⁴,⁵ Among them, the non-covalent heterostructures based on metal-free carbon nanomaterials are gaining special interest due to their unique physicochemical properties such as large surface areas, excellent electronic and mechanical properties as well as their affordable prices,⁶ which allow them to compete with the traditional noble metal-based electrocatalysts. In addition, noble metal-based electrocatalysts often undergo several problems associated with their high prices, susceptibility to CO poisoning, low durability and selectivity, which obstruct their applications for fuel cell technologies.⁶ Therefore, it is of utmost interest to develop highly stable and durable metal-free carbon-based electrocatalysts with higher electrochemical activities for a sustainable future. Remarkably, some new non-metal-based catalysts have exhibited excellent activities for oxygen and/or hydrogen electrochemistry under a broad range of pH, outperforming by far the catalytic activity and the long-term electrochemical stability properties of conventional benchmark
catalysts, including Pt and RuO$_2$. For instance, experimental and theoretical studies have confirmed that the high catalytic activities of low-dimensional heterostructures such as 0D-1D graphene quantum dots/graphene nanoribbons and 1D-2D CNT/graphene are ascribed to the efficient intramolecular charge transfer processes between their intimately contacted components, which result in abundant and highly accessible catalytic active sites. Among the most promising metal-free 2D-platforms to fabricate supramolecular hybrid electrocatalytic nanomaterials, boron carbon nitride nanosheets (BCN NSs) have the desirable physicochemical properties of both 2D hexagonal boron nitride (h-BN) and graphene. They can also act as high-performance nanoplatforms for energy-related purposes due to their unique electrical conductivity, mechanical and chemical stability and the synergistic N and B heteropolar bonding contribution, which can increase the electroactivity rates. Up to now, BCN nanostructures have achieved notable results in oxygen reduction (ORR) and hydrogen evolution (HER) reactions, delivering excellent yields in both alkaline and acid solutions.

Despite these remarkable results, the electrocatalytic performance of BCN nanosheets and other emerging non-metal 2D nanomaterials have not been improved yet because their electronic, physical and chemical properties are confined in a 2D structure and the number of catalytic centers as well as their intrinsic performances cannot be easily tailored, thus limiting their further applications for electrocatalysis. Therefore, the interface engineering of 2D-nanostructures with other LD architectures could expand their potential to develop new and novel nano-electrocatalytic systems. In this sense, the short range interfacial interactions of two LD materials can promote a plenty of high-speed electron pathways and a simultaneous electronic coupling, thus speeding up the ET processes at the interface as well as optimizing the energy adsorption states of the intermediate catalytic species. Buckminsterfullerene ($C_{60}$) is a 0D carbon structure that exhibits
extraordinary electron-accepting properties and high-affinity to construct supramolecular assemblies, thus becoming strong candidates to build efficient multifunctional metal-free hybrid electrocatalysts.\textsuperscript{1, 20-22} The integration of C\textsubscript{60} molecules into the BCN network could generate new tunable interfacial active sites as a consequence of the electronic flow between both LD materials, thus boosting the electrocatalytic properties of the assembled materials compared with their individual components.

To the best of our knowledge, no report of supramolecular boron carbon nitride and fullerene-based nanoheterostructures for high-performance electrocatalysis has been published. In this work, we fabricated a novel class of supramolecular metal-free and low dimensional 0D-2D nanohybrid formed by zero-dimensional C\textsubscript{60} molecules and two-dimensional BCN nanosheets. The 0D-2D nanohybrids were constructed by varying the F/BCN weight ratios (5\% F/BCN, 10\%F/BCN, 20\%F/BCN and 30\% F/BCN) to form non-metallic multifunctional electrocatalysts for HER, HOR, OER and ORR reactions that exhibit better electrocatalytic properties compared to their individual components. The multifunctional electrocatalytic activity of F/BCN nanoassemblies was finely tuned with the local structural defects at the 0D-2D interfaces. The fullerene/BCN interfacial interactions induced slight distortions on the planar sp\textsuperscript{2} BCN surfaces, allowing the electronic coupling between the N and B atoms with the fullerenes and the formation of interfacial catalytic sites. Importantly, XPS and Raman experiments also demonstrated that the effectiveness of the electronic coupling depends on the weight percentages of the fullerene molecules, which markedly influence the intrinsic catalytic activity of the interfacial catalytic sites and in turn, the overall multifunctional electrocatalytic performance of the 0D-2D catalysts. This report provides a deep insight on the structure/catalytic function of C\textsubscript{60}-BCN via a thorough combination of theory and experiment.
6.2 MATERIALS AND METHODS

6.2.1 Materials

All reagents were purchased and used as received without any further purification. Polyethylene glycol (PEG), boric acid (H₃BO₃), urea, fullerene (C₆₀/F), ethanol, isopropyl alcohol (IPA), sodium hydroxide, sulfuric acid, phosphate-buffered saline (PBS), Nafion solution (5 wt%), Pt/C (20%) and ruthenium oxide (RuO₂) were purchased from Sigma-Aldrich. Deionized water (DW, 18 MΩ/cm) was obtained from the Milli-Q® instrument.

6.2.2 Synthesis of F/BCN electrocatalysts

Initially, the boron carbon nitride nanosheet precursors were prepared to obtain the desired F/BCN electrocatalysts. Urea (10 g), boric acid (0.3 g) and PEG-2000 (2 g) were first dissolved in 60 mL of water in a 100 mL beaker under continuous stirring until a transparent solution was observed. The solution was then dried in an oven at 80 ºC for 12 h. Subsequently, the obtained solid was carbonized at 900 ºC with a 5 ºC/min for 4 h under an argon atmosphere. The black powder (BCN NSs) was collected after the tubular furnace cooled down to room temperature. For making the F/BCN electrocatalysts, 50 mg of BCN NSs powder were placed in a beaker andmixed with 20 mL of IPA and sonicated for 30 min. Considering that the IPA is soluble in toluene, a fullerene solution in toluene (from 5 to 30 wt%) was then added slowly to the BCN NSs solution using a bath sonicator for 30 min to form the F/BCN nanohybrids. The nanohybrids were then collected by centrifugation followed by washing with toluene and water several times and then dried at 70 ºC for overnight in a vacuum oven.

6.2.3 Electrochemical Measurements

The electrochemical measurements were done using a three-electrode system on an electrochemical workstation. A glassy carbon, graphite rod and Ag/AgCl were used as the
working, counter and reference electrodes, respectively. To prepare the catalyst ink for the working electrode, 1 mg of the F/BCN nanohybrids and 30 µL of Nafion solution (5% wt) were dispersed in 1 mL of ethanol. The slurry was then bath sonicated for 30 min to form a homogenous ink. Afterward, 10 µL of the catalyst ink was deposited on the working electrode and dried in air. All electrodes were made by depositing the same amount of catalyst ink on the working electrode using the same methodology. Linear sweep voltammetry (LSV) measurements were carried out at a scan rate of 2 mV·s⁻¹ in an electrolyte solution (0.5 M H₂SO₄ for HER and HOR processes, 0.5 M NaOH for OER and ORR processes). The mass activity (MA), specific activity (SA) and turnover frequency (TOF) values were calculated at -0.4 V, 1.7 V and 0.65 V for the HER, OER and ORR processes, respectively. The overall water splitting experiments including the fabrication of carbon cloth electrodes were conducted following a previously reported method. All the voltage values were referenced to the reversible hydrogen electrode (RHE) using the following equation:

\[ E_{RHE} = E_{Ag/AgCl} + 0.197 \text{V} + 0.059 \text{pH} \]  

Afterward, the Tafel equation was used to calculate the Tafel slope to investigate the electrocatalytic performances as well as the kinetics of the HER/OER/ORR processes:

\[ \eta = a + b \log j \]  

where \( j \), \( \eta \), \( a \) and \( b \) are the current density, overpotential, transfer coefficient and Tafel slope, respectively.

A glassy carbon disc (5 mm in diameter, Pine Instruments Company) was used as the working electrode in the rotating disc electrode (RDE) experiments. All electrochemical measurements were conducted within a potential range from 0.1 to −0.60 V vs Ag/AgCl at a scan
rate of 10 mV·s\(^{-1}\). All potentials were referenced to the RHE. The kinetic parameters were assessed by using the Koutecky-Levich (K-L) equations\(^{24,25}\)

\[
\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B \omega^{1/2}} + \frac{1}{J_K}
\]

(3)

\[
B = 0.20 nF C_0 D_0^{2/3} v^{-1/6}
\]

(4)

Where \(J, J_K\) and \(J_L\) are the measured, kinetic- and diffusion-limiting current densities, respectively; \(n\) is the transferred number of electrons for the ORR process, \(\omega\) is the angular velocity, \(F\) is the Faraday constant, \(C_0\) is the bulk concentration of oxygen (1.2x10\(^{-6}\) mol·cm\(^{-3}\)), \(v\) is the kinematic viscosity of the electrolyte (0.01 cm\(^2\)·s\(^{-1}\)) and \(D_0\) represent the oxygen diffusion coefficient that exhibit a value of 1.9·10\(^{-5}\) cm\(^2\)·s\(^{-1}\).

6.3 RESULTS AND DISCUSSION

6.3.1 Structural and morphological characterization of F/BCN electrocatalysts

In a typical synthetic process, a F/toluene solution was gently injected into a BCN NSs/IPA solution under constant bath sonication. This formed a dark brown interface in between the two liquid phases, indicating the formation of the F/BCN nanohybrids. The diffusion of both components from their respective solutions lead to the formation of the interface. The attachment of fullerene molecules onto the BCN NSs surfaces occur via a p-p stacking interaction. Finally, the fullerene decorated BCN NSs can be obtained by centrifugation of the solution. The schematic diagram for the synthesis of F/BCN nanohybrids is presented in Figure 6.1A.

The BCN NSs and F/BCN nanohybrid samples were characterized by X-ray powder diffraction (XRD) and the results are presented in Figure 6.1B. The XRD pattern of BCN NSs displayed two characteristic bands at around 25° and 44°, which typically represent the 002 and 101 interlayer reflections of the BCN, respectively.\(^{26}\)
On the other hand, the XRD pattern of F/BCN nanohybrids showed several diffraction peaks at around 10.83, 17.72, 20.76, 21.70, 27.56, 28.23, 30.94 and 32.86°, that correspond to the (111), (220), (311), (222), (331), (420), (422) and (511) diffraction planes of F, respectively, in addition to showing the diffraction pattern of BCN as well.4,27 Upon the interaction of F with BCN NSs, the BCN diffraction peak (002) is slightly shifted to ~25.5°. The XRD spectra of all F/BCN nanohybrids in Figure 6.1B showed a higher degree of crystallization, suggesting a good charge mobility as well as electrochemical stability. The XRD patterns demonstrated that the fullerenes had been successfully incorporated onto the BCN NSs surface. Raman spectroscopy is a non-
destructive and fast technique that can provide insightful information about the lattice and electronic structures of carbon-based nanomaterials. Raman spectra of the BCN NSs, pristine F and F/BCN nanohybrids are presented in Figure 6.2.

Figure 6.2: Raman spectra of the as-synthesized electrocatalysts [the peaks inside the black box correspond to the pentagonal pinch mode $A_g (2)$ of fullerene molecule].

The BCN NSs display two sharp peaks at around 1345 and 1588 cm$^{-1}$ for the D and G bands, respectively. Generally, the D-band reflects the defects or lattice distortion of the carbons, while the G-band represents the graphitic and crystallization degree of the carbon-based materials. The Raman spectra of F shows a sharp peak at around 1466 cm$^{-1}$, which is characteristic for the fullerene molecule due to the pentagonal pinch mode $A_g (2)$. On the other hand, the F/BCN nanohybrids showed the presence of all three Raman bands (D and G-band for BCN NSs and pentagonal pinch $A_g (2)$ mode for fullerene) with a slight shift, indicating the successful synthesis of F/BCN hybrids. For instance, the G band for BCN NSs shifts from 1588 to 1598 cm$^{-1}$ for the 10% F/BCN hybrid, demonstrating a charge transfer from the BCN NSs to the fullerene. The intensity ratio of the D to G-band ($I_D/I_G$) was also calculated and found to be 0.971, 1.014, 1.046, 0.996 and 0.994 for the BCN, 5% F/BCN, 10% F/BCN, 20% F/BCN and 30% F/BCN, respectively. While the upshift of the peak positions supports the charge transfer process from
BCN NSs to the electron-accepting F, the increase in the I_D/I_G values for F/BCN nanohybrids demonstrates that the nanosheet structure became a little more disordered.\textsuperscript{4} Interestingly, the 10\% F/BCN nanohybrid displayed the highest I_D/I_G value among all the nanohybrids, indicating the presence of more structural defects, as well as the shift in G band is also higher, suggesting that the charge transfer process is more favored, which could lead to better electrocatalytic performance.\textsuperscript{4, 24} Based on the findings from the Raman analysis, it was confirmed that F was successfully attached to the BCN NSs and charge-transfer occurred between the BCN NSs and the fullerene molecules.

X-ray photoelectron spectroscopic (XPS) measurements were conducted to verify the intermolecular charge transfer process between the BCN NSs and fullerene molecules that was observed by the Raman analysis as well as to elucidate the chemical compositions. The results are presented in Figure 6.1(C-F). As expected, it was found that the 10\% F/BCN nanohybrid contained B, C, N and O elements with sharp XPS bands (Figure 6.1C). The XPS analysis also clearly confirmed the absence of any metal content in the 10\% F/BCN sample, demonstrating the metal-free nature of the sample. To further elucidate the chemical nature of the 10\% F/BCN nanohybrid, the high-resolution XPS spectra of B, C and N were inspected. As seen in Figure 6.1D, the high-resolution B 1s spectra could be deconvoluted into three different peaks for B-N, B-C and B-O bonds.\textsuperscript{19, 30} Furthermore, the deconvolution of the C 1s band shows four types of peaks indicating the presence of B-C, C-N, sp\textsuperscript{2} (C=C) and O-C=O (Figure 6.1E).\textsuperscript{19, 30-32} The higher content of sp\textsuperscript{2} (C=C) suggests that the C=C bonds dominate for the BCN NSs conjugated framework. Moreover, the high-resolution N 1s spectra were deconvoluted into four peaks that correspond to the graphitic N, pyrrolic N, pyridinic N and C=N−B (Figure 6.1F).\textsuperscript{31, 33} Remarkably, there is a very significant content of pyridinic N and C=N−B, inferring that a higher number of ORR electroactive sites exist.
in the 10% F/BCN hybrids. The peak position of C 1s XPS spectra for F/BCN hybrids showed a negative shift to lower binding energies (B.E.) as compared to the C 1s spectra of pure fullerene, indicating the existence of intermolecular charge transfer processes from the BCN NSs to F (Figure 6.1G). The shift of the XPS band towards the lower B.E. values demonstrates the progressive distortion of the \( \text{sp}^2 \) BCN planar structure, which increases the electronic coupling between F and BCN NSs at the same time. Notably, the negative shift of the C 1s spectra (284.63 eV to 284.33 eV) for the 10% F/BCN hybrid is higher than for the other samples, indicating that the intermolecular charge transfer process is more pronounced for the 10% F/BCN hybrid, which can improve its electrocatalytic activity. This observed intermolecular charge transfer trend is also in good agreement with the findings from the Raman analysis.

The UV-Vis spectra of F and 10% F/BCN were also obtained and the results are presented in Figure 6.3. The UV-vis spectrum of F displayed a characteristic band at around 328 nm, which is usually results from the pi-pi electronic transitions. The red shift in the band located at around 328 nm is associated with the interactions between F and the other molecules, and therefore this band is a key indicator for the interactions of F with aromatic rings. The pi-pi stacking of F and BCN NSs likely delocalizes the pi-electron system and thereby reduces the required energy for the electronic transitions. The band at 328 nm for F shifts to 335 nm for 10% F/BCN, demonstrating that the F is successfully attached to the BCN nanosheets and the pi-pi interactions significantly facilitate the formation of F/BCN nanohybrids. Scanning transmission electron microscopic (STEM) analyses were conducted to further investigate the microstructure of the BCN NSs and F/BCN nanohybrids and the images are presented in Figure 6.4(A-E). BCN NSs display a smooth and sheet-like structure without particles on their surfaces (Figure 6.4A).
Figure 6.3: UV-vis spectra of F and 10% F/BCN.

By contrast, the morphological analysis of the 5% F/BCN and 10% F/BCN nanohybrids in Figure 6.4(B-C) reveals that some fullerene molecules are uniformly and well-dispersed on the surface of BCN NSs. As indicated by the yellow arrows in Figure 6.4(B-C), the F molecules with sizes ~0.9 nm are distributed on the BCN nanosheet layers. There were no apparent differences in the F size when the F concentration was increased from 5 to 10%, which could be due to the fact that changing of F concentration from 5% to 10% might not facilitate fullerene aggregation.36 Furthermore, the F-decorated BCN nanosheets prepared at higher F concentrations (20% and 30%) showed big clusters of fullerene molecules on the BCN nanosheet surfaces (indicated by the yellow arrow) with broader size distributions, compared to the ones prepared at lower concentrations (5 wt% and 10 wt%), as seen in Figure 6.4(D-E). The increase in the agglomerated fullerene domains for the 20% F/BCN and 30% F/BCN composites should have resulted from the higher F concentration, that tends to create larger seeds for the nanoparticle growth.36, 37
Figure 6.4: A-E) STEM images of BCN NSs, 5% F/BCN, 10% F/BCN, 20% F/BCN and 30% F/BCN nanohybrids, respectively; F-K) high-angle annular dark field (HAADF)-STEM image and elemental mapping of 10% F/BCN, showing the presence of B, C, N and O.

On the other hand, the F/BCN composites with lower F concentrations (5% and 10%) displayed single or few-layered structures that likely result from the attached fullerene molecules, which serve as spacers and can effectively prevent the BCN nanosheets from restacking and agglomeration during the processing in solution. However, agglomerated or multi-layered structured BCN NSs were observed in the case of higher F containing nanohybrids (20% and 30%).
where clusters of F molecules formed on the BCN surfaces cannot effectively prevent the BCN NSs from restacking or agglomeration as seen in Figure 6.4(D-E), thus can impact the electrocatalytic performances negatively. The STEM-EDS elemental mapping verified the presence of all of the expected elements (B, C, N and O) and also showed that all the elements are distributed evenly on the nanosheets, as seen in Figure 6.4(F-K).

6.3.2 Hydrogen evolution and oxidation reaction performance of F/BCN electrocatalysts

We explored the catalytic function of the F/BCN nanohybrids for hydrogen evolution and oxidation reactions using a combination of experimental and theoretical techniques to obtain a comprehensive understanding of the correlation between the structural properties of the hybrids, particularly the interfacial 0D-2D interactions and their electrocatalytic performances. The LSV polarization curves of the HER process in 0.5 M H₂SO₄ solution were recorded for F, BCN, 5% F/BCN, 10% F/BCN, 20% F/BCN and 30% F/BCN as well as for the Pt/C benchmark and the results are shown in Figure 6.5A. Notably, the incorporation of the fullerene molecules on the top of BCN NSs resulted in the formation of very active electrocatalysts with higher electrocatalytic rates that exceed the catalytic activity of their individual components, thus suggesting that the interfacial interactions enhance the HER electrocatalytic activity of the low-dimensional nanohybrids. While the onset potential for F and BCN NSs were estimated to be -0.529 and -0.394 V vs RHE, respectively, the nanohybrid structures achieved enhanced HER
Figure 6.5: A) Representative HER LSVs for F, BCN, 5% F/BCN, 10% F/BCN, 20% F/BCN, 30% F/BCN and commercial Pt/C at 2 mV·s⁻¹ in 0.5 M H₂SO₄; B) the corresponding Tafel plots; C) free energy changes (ΔG°ₚ) of H adsorption on F, BCN and their nanohybrids; D) the Volcano plots of onset potential vs ΔG°ₚ for the hybrid catalysts; E) differences of anodic and cathodic current densities vs scan rates of the catalysts at 0.2 V vs RHE; F) ECSA normalized HER LSV curves for F/BCN nanohybrids; G) MA and SA trends for F, BCN and their hybrids; H) steady-state polarization curves for F, BCN and their nanohybrids for HOR in H₂-saturated 0.5 M H₂SO₄; I) chronoamperometric plots of 10% F/BCN for HER and HOR (inset) at -0.35 V and 0.09 V vs RHE, respectively.

Onset potentials of -0.144 V, -0.042 V, -0.276 V and -0.342 V vs RHE, for 5% F/BCN, 10% F/BCN, 20% F/BCN and 30% F/BCN, respectively. To investigate the kinetics of the HER process, we calculated the Tafel slopes for each catalyst using the Tafel equation (equation 2) from the respective LSV polarization curves in Figure 6.5A. The Tafel slopes showed the same
electrocatalytic trend (Figure 6.5B). The hybrids resulted in lower Tafel slopes (153 mV/dec, 87 mV/dec, 164 mV/dec and 177 mV/dec for 5% F/BCN, 10% F/BCN, 20% F/BCN and 30% F/BCN, respectively) compared with those for F (275 mV/dec) and BCN NSs (250 mV/dec), indicating that the fullerene/BCN interfaces improve the electrokinetics of the HER process as well. Lower Tafel slopes indicate better HER kinetics, thus, the 10% F/BCN nanohybrid displayed the best HER kinetics among the systems studied (Figure 6.5B). The mechanism of the F/BCN nanohybrid mediated HER processes in acidic media can be described by three possible steps. The first step is known as the Volmer step, in which a hydrogen atom is adsorbed on the catalyst surface.\(^{24}\)

\[
\text{H}_3\text{O}^+ + e^- + \text{F/BCN} \rightarrow \text{F/BCN-H}\text{ads} + \text{H}_2\text{O} \quad (5)
\]

The Volmer step is followed either by the Heyrovsky step (electrochemical desorption)

\[
\text{F/BCN-H}\text{ads} + e^- + \text{H}^+ \rightarrow \text{F/BCN} + \text{H}_2 \quad (6)
\]

or Tafel step (chemical desorption)

\[
2\text{F/BCN-H}\text{ads} \rightarrow 2\text{F/BCN} + \text{H}_2 \quad (7)
\]

The theoretical Tafel slope of Tafel, Heyrovsky and Volmer reactions are 30, 40 and 120 mV/dec, respectively (Table 6.1).\(^{25}\) The obtained Tafel slope for 10% F/BCN suggests that the F/BCN mediated HER reaction follows a Volmer–Heyrovsky mechanism, with the Heyrovsky step being the rate-determining.

The superior catalytic performances of the hybrid supramolecular architectures can be ascribed to the interfacial synergism between the components that promote the intermolecular electron transfer (ET) from the 2D BCN sheets to the electron-accepting fullerenes, thus leading to a net negative charge density on the fullerene cages and thereby, favoring the proton adsorption step and the overall HER activity.\(^4\) The lone pair electrons on the N atoms interact with the vacant 2pz orbitals of the B atoms on the BCN framework, which inhibits electronic conjugation with the
π-systems. The distortion of the planar sp² BCN network induced by the fullerene interactions slightly elongate the B-N distances, which enhance the electronic coupling of the N lone pair electrons with the π clouds delocalized around the fullerene structure, thus allowing an effective electronic coupling between the BCN and fullerene molecule. As a result, the electrons gathering at the fullerene surfaces creates very active interfacial catalytic sites that can optimize the energy adsorption states of the intermediate catalytic species, thus enhancing the electrocatalytic activity. As stated in the characterization section using the ID/IG ratios, the number of structural defects follows the trend 10% F/BCN>5% F/BCN>20% F/BCN>30% F/BCN, which matches perfectly with both the XPS shifts to lower binding energies and the electrocatalytic rates, indicating that the interfacial defects on the catalysts regulates the efficiency of the ET process as well as the HER catalytic rates. Furthermore, the 5% F/BCN and 10% F/BCN catalysts, which are by far the best catalytic nanomaterials, show a very well-dispersed fullerene distribution pattern on the BCN surfaces (see STEM pictures). The uniform fullerene distribution hinders the restacking of the BCN NSs, providing more exposed active sites as well as higher electronic conductivity throughout the nanosheet network. It can favor both the distortion of the heteroatom groups of the sp² carbon framework and the intermolecular charge-transfer rates, giving rise to ultra-active catalytic spots at the F/BCN electrochemical interfaces. In contrast, the aggregation of fullerenes for the 20% and 30% F/BCN hybrid samples allows the restacking of the BCN NSs, thus reducing the number of exposed active sites, surface defects and ET processes, and thereby, resulting in a lower catalytic activity for the HER process. Besides, the accessibility of the protons to the active sites of the aggregated fullerene/BCN interfaces would be strongly impeded, thus decreasing the overall catalytic activity. It is also worth to note that the 10% F/BCN nanohybrid surpassed by far the electrocatalytic activity of the 5% F/BCN, showing an onset potential of -0.042 V vs RHE and
a $\eta_{10}$ of 222 mV, which places it between the most efficient metal-free carbon-based low-dimensional HER catalysts reported to date. We believe that the optimal interfacial interactions for the 10% F/BCN hybrid provide higher structural defects that trigger an effective intramolecular ET and, therefore, more efficient active sites for HER.\textsuperscript{39}

To gain further insights into the activity of the F/BCN hybrids, we employed density functional theory (DFT) calculations to obtain the $\Delta G_{\text{H}}^*$ values at the different F/BCN interfaces, which is an excellent descriptor to measure how the catalyst surfaces can thermodynamically impact the HER electrocatalysis. For the HER, in principle, the free energy of hydrogen adsorption ($\Delta G_{\text{H}}^*$) for an ideal catalyst should be zero.\textsuperscript{24} As we can see from Figure 6.5C, the value of $\Delta G_{\text{H}}^*(0.03 \text{ eV})$ for 10% F/BCN is the closest to zero, in agreement with the best HER performance. As the amount of F increases, the binding strength of the H on the active sites becomes stronger, which promotes slower kinetics for the catalysts. The Volcano catalytic trends (Figure 6.5D) also showed that the 10% F/BCN nanocatalyst is located at the maximum of the peak, reinforcing that this catalyst shows the most efficient catalytic rates. The electrochemical active surface area (ECSA) of the nanohybrids were further calculated using the double layer capacitance methodology to verify the HER performance (Figure 6.5E and Figure 6.6).\textsuperscript{39} The cyclic voltametric measurements were carried out at different scan rates (5, 10, 20, 30, 40 and 50 mV/s) and potentials ranging from 0.1 to 0.3 V vs. RHE. The difference between the anodic and cathodic currents at the non-faradaic region of the CV curves were plotted against the scan rates (mV/s) to obtain the $C_{\text{dl}}$ (mF·cm$^2$) values. The $C_{\text{dl}}$ for 10% F/BCN (5.55 mF·cm$^2$) was the largest value among all the catalysts as well as the ECSA (138.75 cm$^2$) and the RF (1982) (Table 6.3). The higher ECSA of 10% F/BCN demonstrates the existence of more available active sites on its surface, which is also responsible for the pronounced HER activity.\textsuperscript{23} The current densities were
also normalized by the measured ECSAs to investigate the intrinsic catalytic activity and it was clear that the 10% F/BCN displayed the best performance in terms of onset potential and \( \eta_{10} \) (Figure 6.5F). The LSVs were then normalized by the TOF and the 10% F/BCN nanohybrid still exhibited the best performance.

Figure 6.6: (A-F) Cyclic voltammograms of F, BCN, 5% F/BCN, 10% F/BCN, 20% F/BCN and 30% F/BCN electrocatalysts in the region of 0.1-0.3 V vs RHE in HER condition, respectively.

Additionally, the higher turnover frequency (2.63), mass activity (137.97) and specific activity (0.14) values confirmed the best intrinsic catalytic properties of 10% F/BCN nanohybrid (Figure 6.5G and Table 6.1). As expected, the factors influencing the remarkable HER activity also played a crucial role towards the hydrogen oxidation reaction (HOR). Figure 6.5H compares the steady-state polarization curves of the F, BCN and their nanohybrids in a \( \text{H}_2 \) saturated 0.5 M \( \text{H}_2\text{SO}_4 \) solution. Similar to HER, the electrocatalytic HOR performance follows the same order of 10% F/BCN>5% F/BCN>20% F/BCN, being the 10% F/BCN best for HOR reaction as well.
Particularly, the 10% F/BCN catalyst produced the largest current density value at 0.1 V (1.47 mA·cm⁻²). These findings are in good agreement with the theoretical ΔG\text{H}^\ddagger value of -0.03 eV (as the HOR is the reverse of the HER), which reinforces that 10% F/BCN is the most active HOR catalyst.\textsuperscript{40, 41} Stability is also a key factor for evaluating the performance of electrocatalysts towards the HER and HOR processes for practical applications.\textsuperscript{40, 41}

Table 6.1: Comparison of HER electrocatalytic performance of F, BCN, 5% F/BCN, 10% F/BCN, 20% F/BCN and 30% F/BCN electrocatalysts in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Onset Potential (mV)</th>
<th>η\textsubscript{10} (mV)</th>
<th>Tafel slope (mV/dec)</th>
<th>Mass Activity (mA/mg)</th>
<th>Specific Activity (mA/cm\textsuperscript{2})</th>
<th>TOF (s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>529</td>
<td>/</td>
<td>275</td>
<td>1.05</td>
<td>0.016</td>
<td>0.027</td>
</tr>
<tr>
<td>BCN</td>
<td>394</td>
<td>/</td>
<td>250</td>
<td>2.17</td>
<td>0.015</td>
<td>0.052</td>
</tr>
<tr>
<td>5% F/BCN</td>
<td>144</td>
<td>437</td>
<td>153</td>
<td>43.4</td>
<td>0.05</td>
<td>0.92</td>
</tr>
<tr>
<td>10% F/BCN</td>
<td>42</td>
<td>222</td>
<td>87</td>
<td>137.97</td>
<td>0.14</td>
<td>2.63</td>
</tr>
<tr>
<td>20% F/BCN</td>
<td>276</td>
<td>541</td>
<td>164</td>
<td>19.67</td>
<td>0.03</td>
<td>0.44</td>
</tr>
<tr>
<td>30% F/BCN</td>
<td>342</td>
<td>/</td>
<td>177</td>
<td>6.51</td>
<td>0.013</td>
<td>0.16</td>
</tr>
</tbody>
</table>

As seen in Figure 6.5I, the 10% F/BCN electrocatalyst displayed very long-term stability for the HER reaction with the current density remaining almost unchanged after 12 h of operation and showed even better electrochemical stability performance that the benchmark Pt/C. The 10% F/BCN electrocatalyst also exhibited similar long-term stability during the HOR reaction (Figure 6.5I: inset).
6.3.3 Oxygen evolution reaction performance of F/BCN electrocatalysts

The water oxidation electrocatalytic activity of the F/BCN hybrids was then evaluated in alkaline media (0.5 M NaOH) using a standard three-electrode setup. The individual components (F and BCN) and a commercial RuO₂ catalyst were also studied and compared with the hybrids. Figure 6.7A displays the linear sweep voltammetry curves of the electrocatalysts at a scan rate of 2 mV·s⁻¹. The dotted lines in Figure 6.7A indicate the overpotentials required to reach the current density of 10 mA·cm⁻², which is used as a crucial figure of merit for OER catalytic materials. Among all the studied materials, only 5% F/BCN, 10% F/BCN and the RuO₂ benchmark catalyst achieved a η₁₀ value. The 10% F/BCN dramatically surpassed the performances of all the materials tested. While the 10% F/BCN hybrid requires 390 mV to reach the current density of 10 mA·cm⁻², the benchmark RuO₂ catalyst requires 410 mV. The remarkable catalytic activity and kinetics were further reflected by the Tafel slopes. As shown in Figure 6.7B, the 10% F/BCN composite showed the lowest Tafel slope of 79 mV/dec, indicating the superior OER kinetics on the catalytic surfaces. In summary, this new electrocatalyst is comparable with the state-of-the-art non-metallic hybrid catalysts and it is also comparable to the more kinetically active candidates for the OER process.

The outstanding catalytic properties of 10% F/BCN can be understood on the basis of the unique electronic flow at the interfacial regions. As was described in the HER section, the interfacial interactions and defects are strongly connected with the intermolecular ET at the 0D-2D interfaces. For the 10% F/BCN hybrid, the distorted heteroatom motifs that are in contact with the fullerenes activate a very strong unidirectional electronic coupling from the lone pair electrons of the nitrogen atoms to the F cages, thus generating positive charges at the N atoms that can behave as highly efficient active sites for oxygen electrochemistry.
Figure 6.7: A) OER LSV polarization curves for F, BCN, 5% F/BCN, 10% F/BCN, 20% F/BCN, 30% F/BCN and RuO$_2$ benchmark catalyst at 2mV·s$^{-1}$ in 0.5 M NaOH; B) their respective Tafel plots; C) differences of anodic and cathodic current densities vs scan rates at 1.2 V vs RHE; D) LSV polarization curves normalized by ECSA for the F/BCN catalysts; E) comparison of intrinsic OER catalytic activities in terms of MA and SA; F) OER LSVs normalized by the TOF for all F/BCN nanohybrids; G) changes in Gibbs free energy of each elementary reaction step toward OER for both BCN and LD hybrids; H) the volcano plots of $\eta$$_{OER}$ vs $\Delta$G$_{O}$; I) chronoamperometric measurement of 10% F/BCN at 1.70 vs RHE and the comparison of LSV curve before and after 1000 CV cycles (inset).

In order to demonstrate the effectiveness of 10% F/BCN hybrid in alkaline media (OER condition), we performed electrochemical double layer capacitance measurements (Figure 6.7C and Figure 6.8). Figure 6.7C displays the $\Delta$j vs scan rate plot of the catalysts obtained at 1.2 V vs RHE.
From these plots, the double layer capacitances (C_{dl}) at the electrochemical interfaces as well as the ECSA and RF were calculated. Importantly, the 10% F/BCN catalyst delivered values of 4.61 mF·cm^{-2}, 115 cm² and 1646 for C_{dl}, ECSA and RF, respectively, which are much higher than those of the other F/BCN hybrids. These results demonstrate that the remarkable ET from the interfacial N atoms to the fullerenes induce the formation of the highest number of electrochemically active sites for OER. To unravel the intrinsic catalytic activity, the LSV of the catalysts were normalized by the corresponding ECSA values (Figure 6.7D). The 10% F/BCN catalyst still exhibits the lowest OER onset potential value (1.46 V vs RHE), indicating that its interfacial active sites initiate the water oxidation process more efficiently than the catalytic centers of the other hybrids. The improved SA and MA values of the 10% F/BCN are additional indicators that verify its superior intrinsic OER catalytic activity (Figure 6.7E and Table 6.2). The turnover frequency of 10% F/BCN at 1.7 V was estimated to be 1.14, which is two times better than the second-best electrocatalyst (5% F/BCN), revealing that the number of oxygen molecules produced by each catalytic center is optimal for the 10% F/BCN. The higher intrinsic catalytic performances of the 10% F/BCN nanomaterials were further confirmed by the TOF normalized current density vs potential plots (Figure 6.7F).

In-depth insights were obtained from the Gibbs free energy diagrams of the 0D-2D catalysts (Figure 6.7G). It is important to point out that the third step (*O→*OOH) is the rate-limiting step for the OER process for all the F/BCN composites. We found that the local interactions as well as the pronounced intermolecular ET between the fullerenes and the BCN NSs for the 10% F/BCN system decrease the uphill energy states towards the formation of catalytic intermediates, thus facilitating water oxidation.
In this regard, the O*, OH* and OOH* intermediate catalytic species exhibited the most energetically favourable ΔG values, which are 4.22, 2.3 and 1.8 eV, respectively, as well as a desirable rate-limiting potential of 0.69 eV, which is the lowest value among all the catalysts. This is attributed to the moderate interaction between the reaction intermediates and the 10% F/BCN, leading to the best catalytic activity for the OER process. It is also worth pointing out that the 10% F/BCN nanohybrid is located at the top of the Volcano curves, confirming the previous findings (Figure 6.7H). The durability of the 10% F/BCN catalyst was investigated for the OER process by performing one thousand CV cycles at 50 mV/s. A LSV measurement was carried out right after the CV measurements and compared with the initial LSV measurement to examine the durability (Figure 6.7I: inset). It was observed that the current density change between the two LSVs was insignificant, demonstrating the excellent durable nature of the catalyst. Chronoamperometric measurements were further conducted to confirm the stability of 10%
F/BCN for 12 h. Interestingly, the 10% F/BCN catalyst retained \( \sim 99.5\% \) of the current density even after 12 h of operation, revealing its remarkable long-term stability features (Figure 6.7I).

Table 6.2: Comparison of OER electrocatalytic performance of F, BCN, 5% F/BCN, 10% F/BCN, 20% F/BCN and 30% F/BCN electrocatalysts in 0.5 M NaOH solution.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Onset Potential (V)</th>
<th>( \eta_{10} ) (mV vs RHE)</th>
<th>Tafel slope (mV/dec)</th>
<th>Mass Activity (mA/mg)</th>
<th>Specific Activity (mA/cm²)</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>1.69</td>
<td>/</td>
<td>219</td>
<td>2.45</td>
<td>0.022</td>
<td>0.032</td>
</tr>
<tr>
<td>BCN</td>
<td>1.62</td>
<td>/</td>
<td>210</td>
<td>3.92</td>
<td>0.063</td>
<td>0.047</td>
</tr>
<tr>
<td>5% F/BCN</td>
<td>1.50</td>
<td>502</td>
<td>120</td>
<td>51.38</td>
<td>0.078</td>
<td>0.55</td>
</tr>
<tr>
<td>10% F/BCN</td>
<td>1.45</td>
<td>390</td>
<td>79</td>
<td>119.49</td>
<td>0.15</td>
<td>1.14</td>
</tr>
<tr>
<td>20% F/BCN</td>
<td>1.55</td>
<td>/</td>
<td>140</td>
<td>33.88</td>
<td>0.075</td>
<td>0.38</td>
</tr>
<tr>
<td>30% F/BCN</td>
<td>1.58</td>
<td>/</td>
<td>178</td>
<td>15.61</td>
<td>0.051</td>
<td>0.19</td>
</tr>
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</table>

6.3.4 Oxygen reduction reaction performance of F/BCN electrocatalysts

The electrochemical properties of the F/BCN catalysts towards the ORR reaction were also studied. Initially, cyclic voltammetric (CV) measurements were conducted in a conventional three-electrode electrochemical cell in an O₂- or N₂-saturated 0.5 M NaOH solution at 50 mV·s⁻¹. Figure 6.9 depicts a well-defined characteristic oxygen reduction peak for the 10% F/BCN hybrid at \( \sim 0.70 \) V vs RHE in an O₂-saturated NaOH solution. This peak is also observed for the other F/BCN catalysts, but at lower potential values, indicating their lower catalytic activities for the electroreduction of oxygen.²⁴, ⁴³ The ORR LSV polarization curves (Figure 6.10A) show that the 10% F/BCN exhibits an excellent ORR performance with an onset potential of 0.92 V, a half-wave
potential of 0.79 V vs RHE and a Tafel slope of 87 mV·dec⁻¹ (Figure 6.10B), which surpass the values exhibited by the other 0D-2D catalysts and are comparable to those of the state-of-the-art metal free carbon-based electrocatalysts reported to date. The ORR kinetics of the 10% F/BCN catalyst was further explored using linear sweep voltammetry at different rotational speeds from 200 rpm to 1500 rpm (Figure 6.10C). The corresponding Koutecky-Levich (K-L) plots revealed important insights of the kinetics of the interfacial redox reactions at the catalytic surfaces of 10% F/BCN.⁴⁴,⁴⁵ The linearity of the K-L plots of 10% F/BCN (Figure 6.10D) clearly establishes a first-order reaction kinetic process.⁴⁶,⁴⁷ Furthermore, they show a very efficient 4-electron reduction pathway since the calculated electron transfer number is 3.85 per O₂ molecule.⁴⁸

Figure 6.9: CV measurements of the as-synthesized electrocatalysts in Ar- and O₂-saturated solutions.
The remarkable ORR electrocatalytic properties of 10% F/BCN is associated with the positively charged N active sites at the 0D-2D interfaces, which were previously explained. Additionally, the large number of pyridinic nitrogen atoms in the BCN nanosheet network (20.25%) of 10% F/BCN
nanohybrid facilitates the oxygen adsorption by providing more Lewis base sites and reducing the energy barriers.\textsuperscript{19}

We also cannot rule out the influence of the B-C-N edge groups on the improved catalytic activity.\textsuperscript{49} To investigate the intrinsic catalytic activity of the electrocatalysts, we have calculated the MA, SA, TOF and the results are presented in Figure 6.10E and Table 6.4. The 10\% F/BCN hybrid exhibit the highest values. Furthermore, 10\% F/BCN displays the best onset potential as well as a higher current density than the other hybrids after normalizing the ORR LSV polarization curves by their respective ECSAs (Figure 6.10F), indicating that this hybrid exhibits the greatest catalytic performance per active unit toward the ORR process. The Gibb’s free energy diagrams for all the hybrids were calculated to obtain mechanistic insights of the ORR electrocatalytic performance of the 0D-2D hybrids (Figure 6.10G). It is important to note that the third step (*O→*OH) is the rate-limiting step for the ORR process for all the F/BCN catalysts.\textsuperscript{50, 51} Noticeably, the 10\% F/BCN shows the lowest rate-limiting potential (0.81 eV), thus decreasing the energy barrier for the rate-determining catalytic step, which, in turn, increase the reaction rates. Also, the 10\% F/BCN heterostructure reached the top of the volcano plot, indicating its superior catalytic performance (Figure 6.10H). Considering the possibility of practical applications, we tested the durability of 10\% F/BCN for the ORR reaction using the same methodology mentioned above in the OER section (Figure 6.10I: inset). The LSVs that were measured at the initial time and after CV measurements, were plotted together and compared. There were very small changes in the onset potential and current density, indicating excellent durability. Additionally, 10\% F/BCN nanohybrid also demonstrated remarkable stability for the ORR process with respect to the benchmark Pt/C as seen in Figure 6.10I, making it an excellent candidate for practical applications.
6.3.5 Overall water splitting application of 10% F/BCN electrocatalyst

Taking into consideration the remarkable HER and OER performances of the 10% F/BCN, a two-electrode configuration water electrolyser was setup to study the overall water splitting reaction in a NaOH electrolyte (0.5 M), where the 10% F/BCN catalyst was loaded on carbon cloth to perform as both the anode and cathode. As Figure 6.11A depicts, the 10% F/BCN||10% F/BCN requires only a cell potential of 1.62 V to reach a current density of 10 mA·cm$^{-2}$. Remarkably, the electrocatalytic performance of the 10% F/BCN||10% F/BCN electrolyser is comparable and competitive with recently reported water splitting devices.$^{52-56}$

Figure 6.11: A) LSV curve of the overall water splitting process using 10% F/BCN as both cathode and anode in a 0.5 M NaOH solution. Inset in A) shows the digital photograph for producing O$_2$ (anode) and H$_2$ (cathode) bubbles on the 10% F/BCN modified carbon cloth electrodes; B) Chronoamperometric measurements of 10% F/BCN for H$_2$O electrolysis at 1.61 V for 20 h.

The inset in Figure 6.11A shows the digital image of the carbon cloth electrodes of the water splitting device. Many bubbles appear on the carbon cloths, demonstrating the effectiveness of the assembled overall water splitting system. Finally, the electrochemical stability of the 10% F/BCN catalyst was also investigated by conducting chronoamperometric measurements at 1.61 V (Figure 6.11B) and the current densities remain fairly stable (only 9% of the initial current lost) during the measurement period (i.e. 20 h), indicative of very good stability.
6.4 CONCLUSION

In summary, we report a new family of supramolecular F/BCN nanohybrid materials that exhibit tetrafunctional high-performance electrocatalysis for HER, HOR, OER and ORR, as well the ability to serve as dual-purpose electrode for a single-cell device for water electrolysis. Using a combination of theory and experiment, we demonstrated that the metal-free 10% F/BCN nanohybrid material comprises a synergistic arrangement of the components that form a supramolecular interface with catalytic properties that exceed the performance of existing commercial metal-based catalysts. The low-manufacturing costs and the facile scalable synthesis of the new supramolecular material will pave the way to a new metal-free electrocatalysts for hydrogen and oxygen electrochemistry and related reactions that may have applications in emerging water treatment and energy storage technologies.
### 6.5 Supporting Information

Table 6.3: The obtained $C_{dl}$, ECSA and RF values for F, BCN, 5% F/BCN, 10% F/BCN, 20% F/BCN and 30% F/BCN electrocatalysts in HER and OER conditions.

<table>
<thead>
<tr>
<th>Electrocatalytic Process</th>
<th>Catalyst</th>
<th>$C_{dl}$ (mF·cm$^{-2}$)</th>
<th>ECSA (cm$^2$)</th>
<th>RF</th>
</tr>
</thead>
<tbody>
<tr>
<td>HER</td>
<td>F</td>
<td>0.37</td>
<td>9.25</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>BCN</td>
<td>0.79</td>
<td>19.75</td>
<td>282</td>
</tr>
<tr>
<td></td>
<td>5% F/BCN</td>
<td>4.76</td>
<td>119.00</td>
<td>1700</td>
</tr>
<tr>
<td></td>
<td>10% F/BCN</td>
<td>5.55</td>
<td>138.75</td>
<td>1982</td>
</tr>
<tr>
<td></td>
<td>20% F/BCN</td>
<td>3.29</td>
<td>82.25</td>
<td>1175</td>
</tr>
<tr>
<td></td>
<td>30% F/BCN</td>
<td>2.89</td>
<td>72.25</td>
<td>1032</td>
</tr>
<tr>
<td>OER</td>
<td>F</td>
<td>0.22</td>
<td>5.50</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>BCN</td>
<td>1.01</td>
<td>25.25</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>5% F/BCN</td>
<td>3.79</td>
<td>94.75</td>
<td>1353</td>
</tr>
<tr>
<td></td>
<td>10% F/BCN</td>
<td>4.61</td>
<td>115.25</td>
<td>1646</td>
</tr>
<tr>
<td></td>
<td>20% F/BCN</td>
<td>2.56</td>
<td>64.00</td>
<td>914</td>
</tr>
<tr>
<td></td>
<td>30% F/BCN</td>
<td>1.76</td>
<td>44.00</td>
<td>628</td>
</tr>
</tbody>
</table>
Table 6.4: Comparison of ORR electrocatalytic performance of F, BCN, 5% F/BCN, 10% F/BCN, 20% F/BCN and 30% F/BCN electrocatalysts in 0.5 M NaOH solution.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Onset Potential (V)</th>
<th>E_{1/2} (V)</th>
<th>Tafel slope (mV/dec)</th>
<th>Mass Activity (mA/mg)</th>
<th>Specific Activity (mA/cm², ×10⁻³)</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.63</td>
<td>0.53</td>
<td>215</td>
<td>0.07</td>
<td>1.79</td>
<td>0.0009</td>
</tr>
<tr>
<td>BCN</td>
<td>0.68</td>
<td>0.60</td>
<td>179</td>
<td>0.20</td>
<td>1.12</td>
<td>0.002</td>
</tr>
<tr>
<td>5% F/BCN</td>
<td>0.85</td>
<td>0.71</td>
<td>95</td>
<td>3.03</td>
<td>4.57</td>
<td>0.032</td>
</tr>
<tr>
<td>10% F/BCN</td>
<td>0.92</td>
<td>0.79</td>
<td>82</td>
<td>5.59</td>
<td>6.92</td>
<td>0.053</td>
</tr>
<tr>
<td>20% F/BCN</td>
<td>0.80</td>
<td>0.66</td>
<td>190</td>
<td>1.56</td>
<td>3.49</td>
<td>0.017</td>
</tr>
<tr>
<td>30% F/BCN</td>
<td>0.74</td>
<td>0.64</td>
<td>197</td>
<td>0.78</td>
<td>2.52</td>
<td>0.010</td>
</tr>
</tbody>
</table>

References


43. Shao, M.; Chang, Q.; Dodelet, J.-P.; Chenitz, R., Recent advances in electrocatalysts for oxygen reduction reaction. Chem. Rev. 2016, 116 (6), 3594-3657.


Chapter 7: Controlling the Interfacial Charge Polarization of MOF-derived 0D-2D vdW Architectures as a Unique Strategy for Bifunctional Oxygen Electrocatalysis

7.1 INTRODUCTION

The discovery of efficient energy materials from inexpensive nature sources is currently leading the path towards the development of a sustainable future. Along with the increasing endeavors to build green energy technologies, the oxygen electrode reactions, including oxygen evolution/reduction, have sparked special attention as crucial steps of renewable-energy devices. Currently, Pt-group metals such as Pt, Ir or Ru are the state-of-the-art electrocatalysts for OER and ORR. Nonetheless, the high cost and restricted availability of precious metals have significantly blocked their practical applications. As a result, there is an increasing interest to design highly active bifunctional electrocatalysts from earth-abundant materials.

Over the last decade, notable efforts have been dedicated to develop highly efficient bifunctional OER/ORR electrocatalysts using non-precious metal-based materials. Among them, transition metal oxides (TMOs) represent desirable candidates because of their low-cost and easy fabrication. Nonetheless, their poor electrical conductivities and lack of OER stability have limited their practical applications to achieve low overpotential bifunctional catalysts towards the fabrication of electrochemical devices. To achieve this goal, the integration of TMOs into low-dimensional carbon networks has been successfully accomplished. The synergistic interfacial interactions of TMOs-carbon heterostructures have appeared as an incredibly attractive strategy to improve the overall electrocatalytic rates via boosting the number of accessible catalytic sites as well as the electron transfer across the interfacial surfaces. For instance, the synergetic chemical coupling effects between Co₃O₄ and graphene nanosheets gave rise to unprecedented bifunctional hybrids that exhibited Pt-like catalytic activities and even surpassed the commercial Pt in terms of
stability and durability.\textsuperscript{21} Furthermore, advanced bifunctional catalysts were obtained from the covalent attachment of CoO\textsubscript{x} NPs rich in oxygen vacancies to B,N-decorated graphene layers via strong Co-N-C bonds.\textsuperscript{22} The superior bifunctional catalytic activity was attributed to i) the improved electron transfer (ET) due to the Co-N-C bonds, (ii) the co-doping with two elements with remarkable electronegativity differences, such B and N, activates adjacent carbon atoms by the so-called synergistic coupling towards the efficient capture of oxygen molecules and (iii) the large number of catalytic active sites generated by the oxygen vacancies of CoO\textsubscript{x} NPs. Among other examples of TMO-energy related heterostructure materials, the effective 0D-2D interfacial interactions between ZrO\textsubscript{2}-based nanoparticles and reduced graphene oxide (rGO) nanosheets have been used to build highly porous interconnected composite nanomaterials for supercapacitor applications.\textsuperscript{23} Remarkably, the ZrO\textsubscript{2} addition into the rGO network created incredibly favorable conditions to increase the mechanical stability and, in turn, the long-term electrochemical durability properties of the resulting architectures.

Despite all the current advances, the influence of the underlying interfacial chemistry of TMOs NPs/carbon-based LD materials and their implication for the fabrication of highly efficient energy-related electrochemical devices have remained poorly explored. Particularly, disentangling the factors that control the oxygen electrochemistry at engineered interfaces represents an essential step towards the rational design of bifunctional OER/ORR catalysts, and, in turn, water-splitting and zinc-air battery electrochemical devices.\textsuperscript{24-26} Hence, we investigate the non-covalent interfacial interactions of 0D-2D vdW ZrO\textsubscript{2} NPs/B-, N- and B, N-doped carbon nanosheets (denoted as C/ZrO\textsubscript{2}, BC/ZrO\textsubscript{2}, CN/ZrO\textsubscript{2} and BCN/ZrO\textsubscript{2}) using a framework of experimental and theoretical techniques. The main hypothesis driving this work was that the successive incorporation of B, N and both of them into the carbon network could tailor the charge polarization
properties of the resulting hybrids, thus deviating the electrons from the Zr metal centers and optimizing both the electronic densities at the electrochemical interfaces and the bifunctional OER/ORR catalytic activity of the LD heterostructures. The remarkable electronic polarization of the interfacial Zr metallic centers at the BCN/ZrO₂ interfaces provides ultra-efficient active sites for both OER and ORR, giving rise to a new class of bifunctional 0D-2D heterostructure catalysts.

Scheme 7.1: Synthesis and application of C, BC, CN or BCN/ZrO₂ nanohybrids for the water splitting and zinc-air battery devices.

7.2 MATERIALS AND METHODS

7.2.1 Materials

Boric acid (H₃BO₃), polyethylene glycol (PEG), zirconium chloride, terephthalic acid, Nafion solution (5 wt%), sulfuric acid, sodium hydroxide, ethanol, ruthenium oxide, Pt/C and urea were purchased from Sigma Aldrich. All chemicals were used as received without any further purification. Deionized water from a Millipore sigma instrument was used in all experiments.
7.2.2 Synthesis of UiO-66 MOF

For synthesis of UiO-66 MOF, a typical amount of zirconium chloride (1.576 g) and terephthalic acid (3.413 g) was dissolved in 30 mL water and 30 mL DMF, respectively under stirring for 30 min. Afterward, the salt solution was mixed with the organic linker solution in a glass reactor under constant stirring for 15 min. Subsequently, the solution mixture was kept in an oven for 24 h at 100 °C. Once the solution was reached to the room temperature, it was washed with DMF and water for several times by centrifugation process and the resultant white solid crystal was dried at 85 °C in air.

7.2.3 Synthesis of C/ZrO₂ nanohybrid

For the synthesis of C/ZrO₂ nanohybrids, 1 g of UiO-66 MOF was carbonized at 900 °C for four hours under an inert/argon atmosphere. Once the furnace was reached to the room temperature, the black powder of C/ZrO₂ nanohybrid was taken out from the furnace and stored for further use.

7.2.4 Synthesis of ZrO₂ nanoparticles

For the synthesis of ZrO₂ nanoparticles, 1 g of UiO-66 MOF sample was calcined at 700 °C for two hours under an air atmosphere and afterwards, the sample was collected and stored in a glass vial for further use.

7.2.5 Synthesis of BCN/ZrO₂ nanohybrid

For the synthesis of BCN/ZrO₂ nanohybrids, 0.065 g of UiO-66 MOF, PEG-2000 (0.5 g), urea (5 g) and boric acid (0.15 g) were dissolved in 60 mL of water under constant stirring and further dried in a vacuum oven at 90 °C for 12 h and then carbonized at 900 °C for four hours under an argon atmosphere. Consequently, black powder of BCN/ZrO₂ product was achieved.
7.2.6 Synthesis of BCN nanosheet, CN/ZrO2 and BC/ZrO2 nanohybrids

To investigate the effect of reagents on the synthesis process, BCN, CN/ZrO2 and BC/ZrO2 were also prepared. For BCN nanosheets, PEG-2000 (0.5 g), urea (5 g) and boric acid (0.15 g) were dissolved in 60 mL of water. For CN/ZrO2, 0.065 g of UiO-66 nanocrystals, PEG-2000 (0.5 g) and urea (5 g) were dissolved in 60 mL of water. For BC/ZrO2, 0.065 g of UiO-66 nanocrystals, PEG-2000 (0.5 g) and boric acid (0.15 g) were dissolved in 60 mL of water. All of the three (BCN, CN/ZrO2 and BC/ZrO2) precursor solutions were then stirred, dried and carbonized as aforementioned method. The resultant products were denoted as BCN, CN/ZrO2 and BC/ZrO2.

7.2.7 Electrochemical Measurements

The electrochemical experiments were performed in a three-electrode electrochemical setup on a CHI660A electrochemical workstation in 0.1M KOH electrolyte solution. The catalyst ink was made by homogenously dispersing 1 mg of catalyst into 30 μL of Nafion solution and 970 μL of ethanol. Afterward, a certain amount of catalyst ink was drop casted onto the working electrode (loading ~ 0.141 mg/cm²) and dried in air. The catalyst-loaded glassy carbon electrode (working electrode area: 0.07 cm²) and glassy carbon rotating disk electrode (RDE) (working electrode area: 0.196 cm²) were used as the working electrode for the OER and ORR processes, respectively, while an Ag/AgCl (saturated in KCl solution) electrode and a graphite rod electrode were used as the reference and counter electrode, respectively for both processes. All the measurements were performed at room temperature. Linear sweep voltammetry (LSV) curves were obtained at 0.1M KOH solution and O2-saturated 0.1M KOH solution for the OER and ORR processes, respectively. All the obtained voltages were referenced to the reversible hydrogen electrode (RHE) according to the following equation:\footnote{7}

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{V} + 0.059 \text{pH} \]
Afterward, the Tafel equation was utilized to obtain the Tafel slope to inspect the electrocatalytic kinetic performances of the OER and ORR processes,\(^7\)

\[
\eta = a + b \log j
\]

where \(\eta\), \(j\), \(a\) and \(b\) are the overpotential, current density, transfer coefficient and Tafel slope, respectively. The electrochemical active surface area (ECSA) of the prepared nanohybrids was calculated using cyclic voltammetry method by following our previous work. The ECSA was then estimated by using the following equation.\(^7\)

\[
ECSA = \frac{C_{dl}}{C_s}
\]

The roughness factors (RF) were also estimated by using the following equation.\(^7\)

\[
RF = \frac{ECSA}{\text{geometric area of the electrode}}
\]

RDE LSVs of the nanoheterostructures were recorded at different rotational speeds from 200 to 1600 rpm with a scan rate of 10 mV s\(^{-1}\) in the potential range of 0.2 to -0.7 V vs. Ag/AgCl. The electron transfer number (n) of the as-synthesized samples was evaluated by the Koutecky-Levich method.\(^7\)

\[
\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{B \omega^{1/2}} + \frac{1}{J_K}
\]

\[
B = 0.2 nF D_0^{2/3} \theta^{-1/6} C_0
\]

where \(n\) is the number for transferred-electrons, \(\omega\) is the rotation speed recorded in rpm, \(F\) is the Faraday’s constant (96487 C\(\cdot\)mol\(^{-1}\)), \(D_0\) is the bulk concentration of O\(_2\), \(\nu\) is the kinematic viscosity, \(C_0\) is the solubility of the gas in the electrolyte. For 0.1M KOH solutions, \(D_0 = 1.9 \times 10^{-5}\) cm\(^2\) s\(^{-1}\), \(\nu = 8.7 \times 10^{-3}\) cm\(^2\) s\(^{-1}\), and \(C_0 = 1.22 \times 10^{-6}\) mol cm\(^{-3}\).
The overall water splitting experiments were executed in a two-electrode system in a 1 M KOH electrolyte solution, the BCN/ZrO₂ electrocatalyst was loaded on two 1×1 cm carbon cloth by drop coating (loading amount: ~ 1 mg/cm²). The Zn–air battery experiments were tested in 6M KOH with 0.2M Zn(CH₃COO)₂ electrolyte solution and a polished zinc plate was utilized as the anode. The air cathode was prepared by drop casting the electrocatalyst (BCN/ZrO₂ or Pt/C) ink onto carbon cloth with a loading amount of 1 mg/cm².

7.3 RESULTS AND DISCUSSION

7.3.1 Structural and morphological characterization of ZrO₂-based electrocatalysts

The synthesis scheme of the Zr-MOF as well as ZrO₂-based nanohybrids is illustrated in Scheme 7.1. During the synthesis process, the terephthalic acid (organic linker) was used as the C source, whereas, the boric acid, urea and ZrCl₄ were used as B, N and Zr sources, respectively. Firstly, the MOF precursor was synthesized by a facile solution-phase method and finally, carbonized to form BCN/ZrO₂ nanohybrid. At first, the XRD measurement of the prepared samples was executed to investigate the crystalline structures. The XRD pattern of the pristine UiO-66 MOF exhibited narrow peaks with higher crystallinity, matched well with the previously reported literatures (Figure 7.1A). Typically, ZrO₂ involves three different crystalline phases such as cubic, monoclinic and tetragonal. The ZrO₂ obtained by calcining UiO-66 MOF at 900 °C are predominantly of tetragonal phase with diffraction patterns at 30.20 (101), 35.3 (002), 50.37 (112), 60.24 (211), and 63.06 ° (202). Similar peaks were also found in the nanohybrids. Notably, BCN/ZrO₂ showed an additional peak at ~25° that corresponds to the 002 interlayer reflections of the BCN nanosheets, confirming the successful synthesis of BCN/ZrO₂ nanohybrid. The Raman spectra of the nanohybrids exhibited the well-defined peaks belongs to the defective and graphitic bands of the carbon materials (Figure 7.1B). The D, G and 2D bands of all the nanohybrids
appeared at 1330, 1594 and 2600 cm$^{-1}$, respectively, with difference intensity ratios. The D band is usually ascribed to the structural defects on the graphitic plane, whereas the G band is corresponding to the E$_{2g}$ vibrational mode of the graphitic carbon. The D and G bands represent the defective sp$^3$ carbons and sp$^2$ carbons present in the carbon layer of the nanohybrid, respectively. The intensity ratio (I$_D$/I$_G$) was also calculated to get more insights about the structural defects created on the nanohybrids. The role of different dopants on defect creation and graphitization is evaluated by comparing the I$_D$/I$_G$ values. Among them, BCN/ZrO$_2$ showed a higher I$_D$/I$_G$ value of 1.1, demonstrating that the presence of higher structural defects on the BCN/ZrO$_2$ surface, which was caused by the incorporation of B and N atoms. It is well known that structural defects can offer more active sites for different electrochemical processes, thus improving the electrocatalytic properties of the nanohybrids. The incorporation of boron and nitrogen heteroatoms into the carbon network could also improve the conductivity and facilitate the electron transport during the electrochemical reactions.

Furthermore, the valence state and composition data of the nanohybrids were collected by XPS. The XPS spectra of Zr-MOF and BCN/ZrO$_2$ nanohybrid clearly demonstrated that the MOF is mainly consisted of C, O and Zr, whereas, the BCN/ZrO$_2$ nanohybrid is consisted of B, C, N, O and Zr (Figure 7.6). Additional extra peaks of B and N were observed in the BCN/ZrO$_2$, suggesting that B and N were doped effectively. The incorporation of boron and nitrogen dopants in BCN/ZrO$_2$ electrocatalysts could improve the conductivity significantly to facilitate the electron transport process during the electrochemical reactions.
To further inspect the nature of the chemical bonding that is present in the as-synthesized BCN/ZrO$_2$ electrocatalyst, high-resolution XPS spectra of all elements were measured (Figure 7.1C-F and Figure 7.7). The deconvolution of B 1s of BCN/ZrO$_2$ showed two peaks demonstrating the presence of B–N–C and B–O bands (Figure 7.1C).$^{35}$ The C 1s spectra could be deconvoluted into three peaks for $sp^2$–C, C–O/C=N and C–N bands (Figure 7.1D).$^{36}$ The N 1s XPS band was deconvoluted into four peaks corresponding to C–N–B, pyridinic N, pyrrolic N and graphitic N bands (Figure 7.1E).$^{30}$ Remarkably, the relative deconvoluted peak area clearly shows that the
BCN/ZrO₂ was dominated by the pyridinic N. The pyridinic nitrogen was found to be preferentially located at the edges of the carbon layers. Higher amount of pyridinic N has been proposed to greatly facilitates the ORR electrocatalytic activity. Additionally, the Zr 3d spectra is mainly composed of two main peaks that are corresponding to the Zr 3d₃/₂ and Zr 3d₅/₂ bands (Figure 7.1F). The high-resolution O1s spectra depicts three kind of oxygen bands: Zr-O, Zr-OH and C-OH, which were located at 530.3 eV, 531.4 eV and 533.1 eV, respectively (Figure 7.7).

The morphological analysis of the as-synthesized nanohybrids was deeply investigated using transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) techniques. It was found that the UiO-66 MOF has an octahedral morphology with a diameter of ~200 nm, whereas, the MOF derived ZrO₂ nanoparticles showed spherical type morphology having a particle size of ~20-30 nm (Figure 7.1G and Figure 7.8A). The ZrO₂ NPs are embedded on the graphitic-like carbon nanoplatforms in case of all the C/ZrO₂, BC/ZrO₂, CN/ZrO₂ and BCN/ZrO₂ nanohybrids (Figure 7.1H-J and Figure 7.8B). Such graphitic frameworks could facilitate the efficient electron transport essential for effective electrocatalysis. Remarkably, the particle size of ZrO₂ NPs was decreased due to the incorporation of different dopants (B, N and B/N) in the graphitic carbon framework. The ZrO₂ NPs in the C/ZrO₂ nanohybrid showed a particle size of ~15-20 nm, whereas the particle size of ZrO₂ NPs was decreased to ~2-3 nm in the BCN/ZrO₂ nanohybrid. It is well-documented that the electrocatalytic processes over a metal catalyst are size-dependent. Hence, the smallest nanosized BCN/ZrO₂ hybrid among others can provide lots of accessible active sites, yielding higher electrocatalytic rates. The interplanar distance was found to be 0.325 nm which corresponds to the (121) lattice plane of tetragonal ZrO₂. This result is consistent with the results obtained from the XRD analysis. The MOF as well as the MOF-derived nanohybrids was further inspected using
HAADF-STEM (Figure 7.1K and Figure 7.9-7.14) analysis. As seen, the newly developed nanohybrids shrank clearly from the original morphology because of the decomposition of the MOF during the pyrolysis process, suggesting that the UiO-66 MOF acts as a precursor as well as a self-sacrificing template for the construction of the nanohybrids. It is clear from the elemental mapping image of BCN/ZrO$_2$ nanohybrid that B, C, N, O and Zr were uniformly dispersed over the entire sheet structure (Figure 7.1K), which was also verified by the EDS-scan line profile of the BCN/ZrO$_2$ (Figure 7.14). The STEM-EDS mapping images of the other nanohybrids also confirmed the presence of all expected elements in all samples (Figure 7.9-7.14).

### 7.3.2 OER performance of ZrO$_2$-based electrocatalysts

The OER activity of the vdW ZrO$_2$-based heterostructures was deeply investigated in 0.1 M KOH using a standard three-electrode setup. Figure 7.2 (A-B) represents the iR-corrected LSVs and the corresponding Tafel plots of Zr-MOF, BCN, ZrO$_2$, C/ZrO$_2$, BC/ZrO$_2$, CN/ZrO$_2$, BCN/ZrO$_2$ and commercial RuO$_2$ catalysts. The C/ZrO$_2$, BC/ZrO$_2$, CN/ZrO$_2$, BCN/ZrO$_2$ hybrids significantly outperformed the catalytic activity of BCN, Zr-MOF and ZrO$_2$, indicating that the interfacial 0D-2D assembly of ZrO$_2$ NPs and C, BC, CN and BCN 2D networks accomplish a crucial role towards the OER catalytic rates. Noticeably, the OER activity of the heterostructures was markedly influenced by the heteroatom doping into the carbon network. While C/ZrO$_2$, BC/ZrO$_2$, and CN/ZrO$_2$ nanohybrids rendered $\eta_{10}$ and Tafel slope values of 449 mV and 170 mV·dec$^{-1}$, 409 mV and 140 mV·dec$^{-1}$, and 372 mV and 120 mV·dec$^{-1}$, respectively; BCN/ZrO$_2$ catalysts exhibited 301 mV and 75 mV·dec$^{-1}$. Thus, the catalytic activities of the hybrids follow this trend: BCN/ZrO$_2$ > BC/ZrO$_2$ > CN/ZrO$_2$ > C/ZrO$_2$, which suggests that the 0D-2D electrochemical interface is tuning the OER catalytic performance of the inorganic hybrids in terms of both thermodynamics and kinetics.
Figure 7.2: OER electrocatalytic performance of the vdW 0D-2D C/ZrO₂, BC/ZrO₂, CN/ZrO₂ and BCN/ZrO₂ heterostructures in 0.1 M KOH. A) iR-corrected OER LSVs for Zr-MOF, BCN, ZrO₂ NPs, C/ZrO₂, BC/ZrO₂, CN/ZrO₂, BCN/ZrO₂ and RuO₂ benchmark catalysts and B) their corresponding Tafel plots. C) η₁₀ values for the BCN/ZrO₂ and the top-ranked metal-based LD catalysts. D) differences of anodic and cathodic current densities vs scan rates at 1.2 V vs RHE. E) ECSA-normalized OER LSV curves for C/ZrO₂, BC/ZrO₂, CN/ZrO₂ and BCN/ZrO₂ nanohybrids. F) Chronoamperometric measurements of BCN/ZrO₂ and RuO₂ for OER process at 1.7 V vs RHE.

Remarkably, BCN/ZnO₂ catalysts surpassed the catalytic activity of commercial RuO₂, exhibiting a compelling η₁₀ value that is comparable with those of the recent top-ranked metal-based LD carbon electrocatalysts (Figure 7.2C). The electrochemically active surface area (ECSA) represents an effective methodology to estimate the relative activity of electrocatalysts, which, in turn, is proportional to its electrochemical double-layer capacitance (Cₐl). The electrochemical double layer capacitance values of the heterostructures were evaluated from 1.10 to 1.30 V vs RHE in a 0.1 M KOH solution at different scan rates (5, 10, 20, 30, 40 and 50 mV/s) in a non-faradaic region. The difference between the anodic and cathodic current densities at 1.20 V vs RHE were
plotted against the scan rate and the corresponding slopes represent the double layer capacitance values of the corresponding catalysts (Figure 7.15). The BCN/ZrO$_2$ heterostructures showed the largest $C_{dl}$ value of 7.36 mA·cm$^{-2}$ compared with those of the CN/ZrO$_2$ (5.34 mA·cm$^{-2}$), BC/ZrO$_2$ (3.55 mA·cm$^{-2}$) and C/ZrO$_2$ (3.42 mA·cm$^{-2}$) (Figure 7.2D). The calculated ECSA values for BCN/ZrO$_2$, CN/ZrO$_2$, BC/ZrO$_2$ and C/ZrO$_2$ are 184 cm$^2$, 134 cm$^2$, 89 cm$^2$ and 86 cm$^2$, respectively, while the RF values for the nanohybrid catalysts were 2628, 1907, 1267 and 1221, respectively. The results reflect the strong relationship between the incorporation of different heteroatoms into the 2D networks and the number of catalytically active sites. We believe that the functionalization of 2D carbon networks with B and N, which exhibit reverse electronegativity to that of carbon, could drastically enhance the number of efficient electrocatalytic active sites for OER, which intrinsically enhances the catalytic activity.$^{31, 34}$ Additionally, the synergistic electrostatic interactions between B and N heteroatoms and the interfacial Zr atoms could facilitate the charge polarization at the electrochemical interfaces, thus creating very effective interfacial active sites, which optimize the $\Delta G$ states of the intermediate catalytic species and improve the overall OER performance. It should be specially noted that the mass activity and specific activity values of the BCN/ZrO$_2$ heterostructure are 89.95 mA·mg$^{-1}$ and 0.29 mA·cm$^{-2}$, respectively, surpassing at least twice times the values obtained for CN/ZrO$_2$ and demonstrating the superior intrinsic catalytic nature of the OER active sites formed by the non-covalent interactions of BCN layers and ZrO$_2$ NPs (Figure 7.16-7.17). Importantly, these results were further verified by the ECSA-normalized OER LSVs of the as-synthesized catalysts (Figure 7.2E). Finally, the BCN/ZrO$_2$ shows a negligible decay (3%) in current density after 24h, exhibiting better long-term stability properties than the benchmark RuO$_2$ catalysts (Figure 7.2F).
7.3.3 ORR performance of ZrO2-based electrocatalysts

The catalytic activity of non-covalent ZrO2-based nanohybrids toward the ORR was initially explored by cyclic voltammetry measurements in 0.1 M KOH solution. Notably, the reduction peak potential of BCN/ZrO2 (0.78 V) largely outperformed the values obtained for CN/ZrO2 (0.68 V), BC/ZrO2 (0.64 V) and C/ZrO2 (0.50 V), thus revealing that BCN/ZrO2 possesses greater ORR activity (Figure 7.3A). Rotation rate-dependent experiments were carried out to quantify the ORR activity of all the hybrid electrocatalysts. The LSVs were recorded first at 1600 rpm rotation speed in O2-saturated 0.1 M KOH electrolyte as shown in Figure 7.3B. Notably, the nanohybrid catalysts largely surpassed the catalytic performance of the individual component catalysts, thus indicating the key influence of the 0D-2D interfaces on the oxygen electrocatalysis. Remarkably, the ORR polarization curves also verify the exceptional ORR performance of BCN/ZrO2 catalyst (Figure 7.3B), which delivered a $E_{\text{onset}}$ of 0.98 V vs RHE, a $E_{1/2}$ of 0.85 V vs RHE and a high limiting current density of 5.6 mA·cm$^{-2}$ at 0.3 V vs RHE, thus outperforming the catalytic rates of all the studied catalysts. Furthermore, the obtained electrocatalytic parameters are comparable to those values reported for the top-ranked metal-based LD catalysts (Figure 7.3C). We believe that the singular electronegativity differences of the B and N atom into the BCN nanosheets induces an effective charge polarization of the electronic clouds of the interfacial Zr atoms, thus promoting the formation of highly active interfacial catalytic sites for ORR process. Interestingly, the BCN/ZrO2 electrocatalyst (90 mV/dec) shows a lower Tafel slope that is comparable to the benchmark Pt/C (85 mV/dec), demonstrating the impressive electrokinetic properties of the BCN/ZrO2 interfaces. The comparable Tafel slopes for BCN/ZrO2 (90 mV/dec) and Pt/C (85 mV/dec) imply that the transfer of the first electron might be the rate-limiting step in the ORR mechanism (Figure 7.18).40
Figure 7.3: ORR electrocatalytic performance of the vdW 0D-2D C/ZrO₂, BC/ZrO₂, CN/ZrO₂ and BCN/ZrO₂ heterostructures in 0.1 M KOH. A) CV curves in N₂-saturated (dotted lines) and O₂-saturated (solid lines) 0.1 M KOH solutions for C/ZrO₂, BC/ZrO₂, CN/ZrO₂ and BCN/ZrO₂ nanohybrids. B) iR-corrected ORR polarization curves of all as-prepared catalysts at 1600 rpm. C) Onset and half-wave potential values for BCN/ZrO₂ and the state-of-the-art ORR metal-based LD catalysts. D) LSVs of BCN/ZrO₂ at different rotation speeds [the inset displays the corresponding K-L plots]. E) Calculated electron transfer numbers and kinetic current densities of the 0D-2D catalysts. F) Chronoamperometric measurements of BCN/ZrO₂ and Pt/C for ORR process at 0.7 V vs RHE. G) LSV curves of the overall water-splitting system using BCN/ZrO₂ catalyst as both anode and cathode in a 1 M KOH electrolyte solution. H) Bifunctional catalytic activity of BCN/ZrO₂ toward both OER and ORR processes. I) Discharge polarization curves and the corresponding power densities for Zn-air batteries using BCN/ZrO₂ or Pt/C as cathodes.
The dynamic ORR features of the ZrO$_2$-based carbon heterostructures were also investigated at different rotation speeds to get valuable insights about the kinetic of the interfacial redox reactions under different 2D-platforms (Figure 7.3D and Figure 7.19). The linearity of the K-L plots derived from the corresponding LSVs reflects the first-order reaction kinetics with respect to the concentration of dissolved oxygen.$^{41}$ Additionally, the K-L plots of ZrO$_2$-based carbon nanomaterials reflect the superior ORR activity of BCN/ZrO$_2$ catalyst, exhibiting an electron transfer number ($n$) of 4 at 0.5 V vs RHE and kinetic current density ($j_k$) of 22.92 mA·cm$^{-2}$, better than those of C/ZrO$_2$ (1.5 and 7 mA·cm$^{-2}$), BC/ZrO$_2$ (2.84 and 12 mA·cm$^{-2}$) and CN/ZrO$_2$ (3.40 and 15.5 mA·cm$^{-2}$) (Figure 7.3E). Additionally, the higher onset potential and $E_{1/2}$ values in the ECSA normalized LSVs together with the higher mass activity and specific activity display the superior intrinsic catalytic activity of the BCN/ZrO$_2$ nanocatalyst (Figure 7.20-7.22). Bearing in mind that the electrochemical interfaces of the ZrO$_2$-based carbon heterostructures provide the most active ORR catalytic centers, it is reasonable to think that the larger intrinsic catalytic activity of the BCN/ZrO$_2$ is owed to the highly favored interfacial charge density redistribution. It creates ultra-active catalytic spots with locally concentrated charged density, which influence the adsorption energies of the intermediate catalytic species, thus boosting the overall ORR electrochemical performance. In addition, the BCN/ZrO$_2$ catalysts showed excellent electrochemical long-term stability properties in alkaline media, keeping 96% of the initial current applied after 24 h and beating the stability of Pt/C under the same experimental conditions (Figure 7.3F).

**7.3.4 Overall water splitting performance of BCN/ZrO$_2$ electrocatalyst**

Finally, the BCN/ZrO$_2$ catalysts was used in the water electrolyzer and zinc-air battery devices to investigate their practical applicability and the results showed impressive performances
compared to the benchmark Pt/C and RuO₂ (Figure 7.3G-I and Figure 7.23-25). As both the HER and OER processes take place together in the water splitting device, we have investigated the HER performance of the best BCN/ZrO₂ electrocatalyst at first and the results are presented in Figure 7.23. Interestingly, the BCN/ZrO₂ delivered an excellent η₁₀ of 165 mV, demonstrating that the BCN/ZrO₂ nanohybrid could be potentially used in the water splitting device. Taking into consideration the remarkable performance of the BCN/ZrO₂ electrocatalyst for HER and OER processes, we have constructed a two-electrode configuration water splitting device in 1 M KOH electrolyte solution, where the BCN/ZrO₂ catalyst deposited on carbon cloth was used as cathode and anode at the same time and Pt/C||RuO₂ was also used as the control. As seen in Figure 7.3G, the BCN/ZrO₂ || BCN/ZrO₂ needs only a cell potential of 1.58 V to reach a current density of 10 mA/cm², which is even better than the benchmark Pt/C||RuO₂ (1.61 V) in the similar experimental conditions. Besides, the durability of the BCN/ZrO₂ catalyst was also tested by chronoamperometric measurements at 1.58 V (Figure 7.24), where the current densities nearly remain stable for the BCN/ZrO₂ catalyst during the experimental period (i.e. 50 h), revealing its outstanding stability.

7.3.5 Zinc-air battery performance of BCN/ZrO₂ electrocatalyst

Furthermore, inspired by the remarkable performance in both OER and ORR conditions, the BCN/ZrO₂ electrocatalyst was also used as the air cathode to construct a Zn-air battery device. The Zn-air battery device was fabricated with a zinc plate as the anode, 6.0 M KOH containing 0.2 M of Zn(CH₃COO)₂ solution as the electrolyte and the electrocatalyst deposited on the carbon cloth as the air cathode. Initially, to evaluate the overall OER/ORR bifunctional activity of BCN/ZrO₂ catalyst, we compared the overvoltage between the OER and ORR (∆E = η₁₀ − E₁/₂), where η₁₀ is the OER overpotential at a current density of 10 mA/cm² and E₁/₂ is the ORR half-
wave potential. The ΔE value of 0.72 V in 0.1 M KOH reflect the excellent bifunctional activity, which is comparable with recently reported bifunctional electrocatalysts (Figure 7.3H), demonstrating its potential application in the Zn-air battery. In this direction, the calculated power density values were found to be 153 and 129 mW/cm² for the BCN/ZrO₂ and Pt/C electrocatalysts, confirming its superior performance than Pt/C for the Zr-air battery applications in the same experimental conditions (Figure 7.3I). Then the battery was operated for 100 h at a current density of 10 mA/cm² to investigate the stability performance of the BCN/ZrO₂ air cathode and the BCN/ZrO₂ battery exhibited a much smaller voltage decrease over the 100 h operation period (Figure 7.25), demonstrating the applicability of BCN/ZrO₂ electrodes in Zn–air batteries.

7.3.6 Experimental and theoretical insights towards OER and ORR mechanism

To disentangle the extraordinary bifunctional electrocatalytic performance of BCN/ZrO₂, we have interrogated the electronic states of the nanohybrids by XPS. Figure 7.4A shows a notable shift to higher binding energies (BE) of Zr 3d band for the nanoheterostructures that follow the trend BCN/ZrO₂>CN/ZrO₂>BC/ZrO₂>C/ZrO₂, indicating that BCN/ZrO₂ interfaces exhibit the lowest screening of electrons in the outer electronic layer of Zr interfacial atoms. Interestingly, the positive shifts in the BE of the catalysts correspond to their bifunctional catalytic performances.

Nonetheless, the sp² C=C (at ≈ 284.7 eV) XPS bands of all the catalysts maintained the same BE value, demonstrating that the electronic structures of the 2D-platforms (C, BC, NC and BCN) remained unchanged (Figure 7.4B). These findings strongly suggest two crucial points: (i) the electrons of Zr interfacial atoms were not transferred to the 2D platforms, rather they were displaced to the interface and (ii) the larger deviation of Zr outer electrons was produced in the BCN/ZrO₂ interface. As shown, the acute electrostatic interactions of the ZrO₂ NPs with the positively charged B and negatively charged N atoms of the BCN network have enabled the
polarization of the outer electrons of Zr interfacial atoms, thus giving rise to a superior electronic polarization at the interface (Figure 7.4C). Therefore, the positively charged Zr atoms would favor the adsorption of OH\(^{-}\) catalytic species, thus benefiting the OER; while the polarized electronic cloud would be favorable for ORR\(^{42}\), which might notably decrease the uphill energy states of the intermediate catalytic species, thus providing ultra-active catalytic sites for bifunctional OER/ORR electrocatalysis. To support this explanation and gain theoretical insights into the enhanced bifunctional catalytic activity of BCN/ZrO\(_2\), DFT calculations were carried out (Figure 7.5A-D). We calculated the OER and ORR free-energy diagrams for the nanohybrids, following

\[
\begin{align*}
\text{OH}^- + {}^* & \longrightarrow {}^*\text{OH} + e^- \quad \text{(R1, OER)} \\
{}^*\text{OH} + \text{OH}^- & \longrightarrow {}^*\text{O} + \text{H}_2\text{O} + e^- \quad \text{(R2, OER)} \\
{}^*\text{O} + \text{OH}^- & \longrightarrow {}^*\text{OOH} + e^- \quad \text{(R3, OER)} \\
{}^*\text{OOH} + \text{OH}^- & \longrightarrow \text{O}_2 + \text{H}_2\text{O} + e^- \quad \text{(R4, OER)} \\
{}^*\text{OH} + e^- & \longrightarrow \text{OH}^- + {}^* \quad \text{(R4, ORR)}
\end{align*}
\]

the widely accepted 4-electron pathway in alkaline conditions at both top and interfacial sites.\(^{43,44}\)

It is worth noting that BCN/ZrO\(_2\) shows more favorable energetic barriers among all the nanoheterostructures. Specifically, the ΔG values for OER/ORR rate-limiting steps show a notable improvement at interfacial catalytic sites compared to the top ones, thus demonstrating the key influence of the interfacial charge polarization on the electrocatalytic activity.

A notable change in the ΔG value of the rate-limiting catalytic steps from the top site to the interfacial site of the BCN/ZrO\(_2\) was observed. The ΔG was reduced from 0.92 to 0.72 eV, demonstrating the key role of the synergistic couple effect of B and N on the electronic polarization of the interfacial Zr atoms to give rise to highly active OER catalytic centers as shown in Figure 7.5 (A-B).
Furthermore, a similar behavior was detected for both the top and interfacial ORR catalytic sites. The $\Delta G$ values of the rate-determining steps of top and interfacial sites decreased from 0.90 to 0.71 V as seen in Figure 7.5 (C-D). These findings provide valuable insights into the key function of the interfacial charge polarization to control the binding strength of the reaction intermediates, thus improving the catalytic activity for both OER and ORR processes.
Figure 7.5: Free-energy diagrams for the optimized as-synthesized electrocatalysts under alkaline conditions during the (A-B) OER and (C-D) ORR processes at both top and interfacial sites, respectively.

7.4 CONCLUSION

In summary, an innovative bottom-up strategy using a Zr-MOF has been successfully developed to synthesize a new family of vdW 0D-2D heterostructures formed by ZrO$_2$ NPs anchored on B and/or N doped LD carbon nanoplatforms. We have introduced a new electron polarization approach to regulate the interfacial microenvironment of 0D-2D metal oxide/heteroatoms-doped LD carbon materials for highly efficient multifunctional electrocatalysis. The synergistic couple effect of B and N led to a notable charge redistribution at the 0D-2D interfaces, which can greatly boost the adsorption-desorption catalytic steps of the oxygenated intermediates and, in turn, the bifunctional OER/ORR activity. It is worth noting that
this work represents the first example of a non-covalent assembly of B, N co-doped carbon network and TMO NPs as very efficient bifunctional electrocatalysts.

7.5 SUPPORTING INFORMATION

Figure 7.6: A-B) XPS survey spectra of Zr-MOF and BCN/ZrO₂ nanohybrid, respectively.

Figure 7.7: High resolution XPS O1s band for the BCN/ZrO₂ nanohybrid.
Figure 7.8: Typical TEM image of A) ZrO$_2$ NPs and B) STEM image of BC/ZrO$_2$ nanohybrid. The obtained TEM image of ZrO$_2$ NPs revealed that the NPs are not embedded on any kind of carbon matrix, whereas, the STEM image of BC/ZrO$_2$ revealed that the ZrO$_2$ NPs are embedded on the porous carbon matrix.

Figure 7.9: High-angle annular dark field (HAADF)-STEM image and elemental mapping of UiO-66 MOF, showing the presence of C, O and Zr as well as they are evenly distributed.
Figure 7.10: High-angle annular dark field (HAADF)-STEM image and elemental mapping of C/ZrO$_2$ nanohybrid, showing the presence of C, O and Zr and also, all the elements are well distributed in the carbon matrix.

Figure 7.11: High-angle annular dark field (HAADF)-STEM image and elemental mapping of BC/ZrO$_2$ nanohybrid, showing the presence of B, C, O and Zr and all the elements are evenly distributed throughout the nanoplatform.
Figure 7.12: High-angle annular dark field (HAADF)-STEM image and elemental mapping of CN/ZrO$_2$ nanohybrid, showing the presence of C, N, O and Zr as well as they are well distributed throughout the carbon matrix.

Figure 7.13: EDS-scan line profile of the marked area (inset) of UiO-66 MOF crystal, revealing the presence of C, O and Zr elements.
Figure 7.14: EDS-scan line profile of the marked area (inset) of BCN/ZrO$_2$ nanohybrid, revealing the presence of B, C, N, O and Zr elements.

Figure 7.15: A-G) Cyclic voltammograms of UiO-66 MOF, BCN nanosheet, ZrO$_2$ NPs, C/ZrO$_2$, BC/ZrO$_2$, CN/ZrO$_2$ and BCN/ZrO$_2$ nanohybrids in the region of 1.10-1.30 V vs RHE, respectively.
Figure 7.16: Mass activity values from the OER LSV curves of C/ZrO₂, BC/ZrO₂, CN/ZrO₂ and BCN/ZrO₂ nanohybrids at 1.60 V in 0.1 KOH solution.

Figure 7.17: Specific activity values from the OER LSV curves of C/ZrO₂, BC/ZrO₂, CN/ZrO₂ and BCN/ZrO₂ nanohybrids at 1.60 V in 0.1 KOH solution.
Figure 7.18: Tafel plots of the as-synthesized electrocatalysts for the ORR process.
Figure 7.19: RDE-LSV ORR polarization curves of A) C/ZrO₂, C) BC/ZrO₂ and E) CN/ZrO₂ heterostructures and B), D) and F) their corresponding K-L plots at 0.5 V vs RHE, respectively.
Figure 7.20: ECSA-normalized ORR LSV curves for C/ZrO₂, BC/ZrO₂, CN/ZrO₂ and BCN/ZrO₂ nanohybrids at 1600 rpm. The normalized ORR LSV curves display the superior intrinsic catalytic performance of the BCN/ZrO₂ heterostructure, which still exhibiting the highest onset potential.

Figure 7.21: Mass activity values from the ORR LSV curves of C/ZrO₂, BC/ZrO₂, CN/ZrO₂ and BCN/ZrO₂ nanohybrids at 0.75 V vs RHE.
Figure 7.22: Specific activity values from the ORR LSV curves of C/ZrO$_2$, BC/ZrO$_2$, CN/ZrO$_2$ and BCN/ZrO$_2$ nanohybrids at 0.75 V vs RHE.

![Bar graph showing specific activity values for different nanohybrids.]

Figure 7.23: HER performance of the BCN/ZrO$_2$ nanohybrid in 0.5M H$_2$SO$_4$ electrolyte solution.

![Graph showing HER performance.]

The graph illustrates the current density ($j$) in mA/cm$^2$ as a function of the voltage ($E$) in V vs RHE, demonstrating the HER performance of the BCN/ZrO$_2$ nanohybrid in a 0.5M H$_2$SO$_4$ electrolyte solution.
Figure 7.24: Chronoamperometric measurements of BCN/ZrO₂ nanohybrid for water electrolysis at 1.58 V for 50 h. The I-t plots display the excellent long-term stability properties of BCN/ZrO₂ catalyst for a water splitting device.

Figure 7.25: Discharge curve at a current density of 10 mA·cm⁻² using BCN/ZrO₂ nanohybrid as an air cathode for the Zinc-air battery, demonstrating good stability performance over a 100 h operating period.

References


Chapter 8: Conclusions and Future Directions

A facile and novel synthetic method for making functionalized carbon materials through waste biomass conversion was developed in this study. The functionalized carbon material (SCW-SO$_3$H) was synthesized through introducing sulfonic acid polar functionalities over the polymeric biomass (cellulose and lignin) of the spent coffee waste. They were successfully used as low-cost adsorbents for removing different organic (methylene blue and tetracycline) and inorganic pollutants (chromium) from water. The exceptionally higher sorption capacity of these functionalized carbon materials for the three pollutants makes it a good candidate for commercial wastewater treatment applications. SCW-SO$_3$H could be also used to remove other pollutants such as methyl orange, arsenic, cadmium, lead, mercury, etc. This developed biomass conversion method can be extended to functionalize any kind of waste biomass source, which then could be potentially used for removing different water contaminants. This developed method not only makes the highly efficient adsorbent materials for wastewater treatment, but also it can clean the environment at the same time while utilizing the waste biomass from the environment.

A facile and green synthetic methodology was developed to prepare nickel and copper-based metal organic frameworks (MOFs) and finally utilized them as a sacrificial template to make nickel and copper nanoparticles embedded on porous carbon matrix via carbonization method. These carbon-based metal nanoparticles were used as a catalyst for the catalytic reduction of organic pollutants such as methylene blue, methyl orange and 4-nitrophenol in presence of sodium borohydride. These developed carbon-based nanoparticles could be further used for the catalytic reduction of heavy metal ions such as chromium, arsenic etc. Also, the proposed synthetic method here could also be used to other MOFs such as Zn-MOF, Zr-MOF, Mn-MOF, Cr-MOF, Ti-MOF etc. and subsequently, the corresponding metal nanoparticles on carbon matrix via carbonization
method. These newly proposed materials could be used as Fenton catalyst, photocatalyst and
electrocatalysts for different reactions.

A low cost, facile and green method was developed based on the tissue paper template for
making transition metal based nanocatalysts that were encapsulated on hierarchically porous
carbon network. These nanocatalysts were used as a Fenton like catalyst for the advanced oxidation
water treatment process to remove different organic pollutants via peroxymonosulfate activation.
Catalytic studies revealed that the newly developed nanocatalysts could be potentially used for
practical water treatment technologies in the resource limited areas. These nanocatalysts
(Co/Ni/Fe) were also magnetic in nature and could be potentially used in the magnetic
hyperthermia cancer treatment. Finally, this developed synthetic method reported in this
dissertation can be extended to make a broad range of mono or bimetallic nanoparticles, metal
oxide nanoparticles, mixed metal oxide nanoparticles etc. and these nanoparticles could be
employed in different catalytic reactions.

The development of a sustainable and cost-effective route to synthesize trifunctional
bimetallic Ni-Cu nanocatalysts was effectively achieved. The connection between the
microstructural properties and the ORR, HER and OER multifunctional activity of bimetallic non-
precious nanoparticles with different Ni:Cu surface ratios was also comprehensively explored.
These findings open the pathway to explore the d-band center variations in the local structural
microdefects of bimetallic surface nanodomains as a new catalytic descriptor for multifunctional
electrocatalysis. This work also establishes the basis for the rational design of the new generation
of low-cost and scalable multifunctional bimetallic catalysts.

A new class of 0D-2D van der Waals (vdW) heterostructure catalyst formed by the
supramolecular interaction of $C_{60}$ molecules and BCN nanosheets was successfully developed.
The distribution pattern of different amounts of fullerene molecules at the top of 2D-BCN nanosheets was experimentally and theoretically associated with both the interfacial structural defects and the efficiency of the intermolecular electron transfer (ET) function of BCN/C₆₀ interfaces, which strongly regulate the catalytic rates for hydrogen and oxygen electrochemistry. The unique synergistic arrangement of C₆₀ and BCN into the hybrid nanostructure at the metal-free 10% F/ BCN material boosts the interfacial ET and creates multifunctional active sites, establishing a new chapter in the development of metal-free nanohybrids for multifunctional catalysis. These results provide an in-depth understanding about the relationship between low-dimensional nanostructures and their catalytic activities.

For the first time, we use a new electron polarization strategy to regulate the interfacial microenvironment of 0D-2D vdW TMO NPs/heteroatoms-doped low-dimensional carbon materials for efficient bifunctional electrocatalysis. It was discovered that the synergistic couple effect of B and N led to a notable charge redistribution at the 0D-2D interfaces, which can greatly boost the adsorption-desorption catalytic steps of the oxygenated intermediates and, in turn, the OER/ORR catalytic activity. Briefly, the proposed route will serve as a useful tool for the fabrication of TMO-based heterostructures with better catalytic properties.
Appendix

Characterization Techniques

X-ray diffraction (XRD) experiments were performed on a Bruker D8 Discover X-ray Diffractometer. The elemental analysis and color mapping were performed using Energy dispersive spectroscopy (EDS) equipped with the SEM instrument (model: Hitachi S-4800). Transmission electron microscopic (TEM) analysis was carried out on a Hitachi H-7650 microscope to further investigate the morphology and microstructure of the electrocatalysts. Scanning transmission electron microscopic (STEM) analysis was performed on a JEOL ARM200 equipped with a JEOL windowless EDS detector spectrometer for spectral mapping and imaging. The chemical valence and surface elements of the electrocatalysts were detected using X-ray photoelectron spectroscopy (XPS) on a PHI VersaProbe II Scanning XPS Microprobe with scanning monochromatic X-ray Al Kα radiation as the excitation source (200 μm area analyzed, 52.8 W, 15 kV, 1486.6 eV), and a charge neutralizer. Thermal gravimetric analysis (TGA) was performed under a continuous nitrogen flow and at a heating rate of 10 °C/min on a Mettler Toledo thermogravimetric apparatus. Raman spectra of the electrocatalysts were collected using a DXR Smart Raman instrument. Brunauer–Emmett–Teller surface area (BET) and pore volume experiments were carried out using a Micromeritics Surface Area and Porosity Analyzer (ASAP-2020). The magnetic properties of the nanocatalyst at room temperature were measured by means of Versalab. Vibrating sample magnetometer (VSM) from Quan-tum Design in the magnetic field range of −3 T to 3 T. A UV-Vis spectrophotometer (Model: Agilent Cary 50 Conc) was used to measure the absorbance of the pollutant solution as well as to study the kinetics of the catalytic reduction reaction.

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Vita

Md Ariful Ahsan was born and raised in Mymensingh, Bangladesh. He received his B.Sc. in Applied Chemistry and Chemical Engineering from the University of Dhaka, Bangladesh, in 2012. Later, he obtained a graduate teaching assistant scholarship from the Tuskegee University, USA, to pursue his M.Sc. in Chemistry in the same year. During his M.Sc. study in Chemistry, he received a prestigious Alabama GRSP EPSCoR fellowship for his outstanding graduate research work. After completing his M.Sc. degree, he joined the University of Texas at El Paso to pursue his Ph.D. degree in Chemistry in Fall 2015 and right after, he started to work with Prof. Noveron. While working with Dr. Noveron, he was engaged with so many projects and these projects led him to publish more than 40 research articles in peer-reviewed prestigious scientific journals. His research interests mainly lie in the synthesis of multifunctional carbon-based nanocatalysts and their potential applications in wastewater treatment and energy conversion technologies. He is also serving as a reviewer for more than twenty scientific journals. He served as a judge in different scientific symposiums, conferences and presentations during his Ph.D. study. During his stay at UTEP, Ahsan also had the privilege to teach many undergraduate students as a teaching assistant for analytical chemistry, organic chemistry and general chemistry. He also had experience in mentoring undergraduate students, high school students, and high school teachers at different research projects in Dr. Noveron’s lab. He has published several first-author articles, which are co-authored by undergraduate students. He received Matthew and Wanda Diethelm /Coca-Cola Endowed Scholarship Fund and Research Award from the College of Science Dean’s Office during his Ph.D. study for his outstanding research work. He loves to play cricket, watch movies and travel with family during his leisure period.

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