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**XXXVII CICLO DEL DOTTORATO DI RICERCA IN
NANOTECNOLOGIE**

**EXPLORING THE USE OF CARBON-BASED
NANOCATALYSTS FOR SUSTAINABLE PROCESSES**

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Abstract

In recent years, new schemes for the industrial system, from energy production to chemical synthesis, have been at the core of research. Elevated waste gaseous emissions into the atmosphere and the consequent global warming are seriously threatening our quality of life, putting at risk future livability on the planet. Intervention to reduce emission and move to circular economy with low environmental impact is the most urgent priority at global governmental level. In this landscape, alternative processes are widely investigated, with a focus on electrocatalytic and photocatalytic approaches, where renewable resources can be the main driving force. Alongside the adoption of more sustainable energy sources, the choice of raw materials itself represents a central topic. In fact, industrial catalysts are mainly based on expensive and scarce elements, often accompanied by supply risks. One of the most effective solutions consists in the use of earth-abundant carbon-based materials to substitute, partially or entirely, traditional catalysts. While considerable research efforts have been directed toward these metal-free materials, there is still much to uncover in this field.

In this thesis, electrocatalytic and photocatalytic processes have been investigated, exploiting the use of carbon-based nanostructures (CNSs) and their coupling with non-precious metal-based catalysts through diverse approaches. Thanks to the high adaptability of CNSs, the dissertation explores various catalytic applications for the sustainable production of chemicals. In particular, different catalytic systems are proposed: (a) a defective carbon nitride photocatalyst in combination with a homogeneous nickel complex to drive dual photocatalysis for the efficient production of value-added organic molecules under visible light irradiation; (b) functionalized carbon nanohorns (CNHs) integrated with a Bi-based catalyst to enhance the electrocatalytic properties for CO₂ conversion into formic acid, developing a highly effective nanohybrid material with reduced Bi loading; and (c) novel metal-free N-doped carbon materials derived from hyper-crosslinked polymer to study hydrogen peroxide electrosynthesis, investigating the relationship between the structural, compositional, and textural properties of these catalysts with their electrocatalytic behavior, activity, and selectivity. Within all these research lines, the structural tuning and versatility of the investigated carbon-based materials are defined based on their task-specificity, from the introduction of suitable functional groups onto the CN surface to enhance effective interaction with the Ni counterpart, to the exploitation of the unique morphology of CNHs for a tight contact with the inorganic Bi-based catalyst, and the tuning of graphitization and nitrogen doping

of ORR electrocatalysts.

These studies, though still distant from real industrial applications, provide new fundamental insights for future exploitation, underscoring the potential of carbon-based catalysts as main actors in the transition to sustainable catalysis.

Riassunto

Negli ultimi anni, l'identificazione di nuove direzioni per il settore industriale, dalla produzione di energia alla sintesi di prodotti chimici, sono al centro della ricerca. Le elevate emissioni di inquinanti nell'atmosfera e il conseguente riscaldamento globale minacciano la qualità della nostra vita, e quindi la necessità di un cambiamento è cruciale. In questo contesto, al giorno d'oggi vengono ampiamente studiati processi alternativi, in particolare approcci elettrocatalitici e fotocatalitici, in cui le risorse rinnovabili possono costituire la sorgente d'energia principale. Oltre all'utilizzo di fonti energetiche più sostenibili, la stessa scelta delle materie prime rappresenta un tema fondamentale. Infatti, i catalizzatori industriali si basano principalmente su elementi scarsi e costosi, spesso soggetti a rischi di approvvigionamento legati a situazioni socio-economiche sfavorevoli. Una delle soluzioni più efficaci consiste nell'impiego di materiali a base di carbonio per sostituire, parzialmente o totalmente, i catalizzatori tradizionali che fanno affidamento su metalli. Sebbene numerosi studi siano stati dedicati a questi materiali carboniosi, vi è ancora molto da investigare e approfondire in questo campo.

In questa tesi sono stati studiati processi elettrocatalitici e fotocatalitici, sfruttando l'uso di materiali a base di carbonio e il loro accoppiamento con catalizzatori contenenti metalli non preziosi attraverso vari approcci. Grazie all'elevata adattabilità e modulabilità strutturale dei materiali a base di carbonio, la tesi esplora diverse applicazioni catalitiche per una produzione sostenibile di prodotti chimici. In particolare, sono stati proposti diversi sistemi catalitici: (a) un fotocatalizzatore di nitrato di carbonio modificato, in combinazione con un complesso omogeneo di nichel per guidare una fotocatalisi duale nella produzione di importanti molecole organiche sotto irradiazione di luce blu; (b) nanocorni di carbonio funzionalizzati ed integrati con un catalizzatore a base di bismuto al fine di migliorare le proprietà elettrocatalitiche per la conversione di CO_2 in acido formico, sviluppando un materiale nanoibrido altamente efficace con un ridotto carico di Bi; e (c) nuovi materiali a base di carbonio N-dopato derivati da polimeri iper-reticolati, per studiare l'elettrosintesi di perossido di idrogeno senza l'utilizzo di metalli, indagando la relazione tra le proprietà strutturali, composizionali e testurali di questi catalizzatori con il loro comportamento elettrocatalitico, attività e selettività. All'interno di questi progetti, la modulazione strutturale e la versatilità dei materiali a base di carbonio studiati sono sfruttate per introdurre gruppi funzionali adeguati sulla superficie del nitrato di carbonio migliorando l'interazione con il nichel, per sfruttare la morfologia unica dei nanocorni di carbonio che favorisce un contatto stretto con

il catalizzatore inorganico a base di bismuto, e per ottimizzare la grafitizzazione e il dopaggio con azoto degli elettrocatalizzatori per la reazione di riduzione dell'ossigeno.

Questi studi, sebbene ancora lontani da reali applicazioni industriali, evidenziano il potenziale dei catalizzatori a base di carbonio come alternative sostenibili, ponendo solide basi per futuri sistemi catalitici.

Chapter 1

Introduction

Modern scientific and technological advancements have been a decisive factor for improving the quality of human life, in relation to health, comfort, and productivity. Yet, these gains have deepened our reliance on finite, environmentally costly energy and resources. Fossil fuels have long dominated the energetic schemes, leading to massive greenhouse gas emissions and air pollution. Today, however, we stand at a crossroads. The socio-economic and environmental landscape urgently demands a rapid shift towards the implementation of a circular economy, while abandoning the unsustainable current trajectory of the linear economy. Addressing these challenges requires a commitment to sustainable development, which the United Nations famously defines as *meeting the needs of the present without compromising the ability of future generations to meet their own needs* (UN Conference on Environment and Development, Rio 1992). In this light, sustainability prioritizes resource conservation, waste reduction, and eco-innovations to reduce dependency on non-renewable materials and, consequently, lower the ecological impact. Building a near-zero carbon footprint, secure, and cost-effective energy infrastructure has become one of the defining challenges of our century.

Within this evolving landscape, catalysis emerges as a pivotal driver of change, steering society away from fossil fuel dependency toward a more circular economy. According to IUPAC, a catalyst is a substance that speeds up the rate of a reaction while leaving the overall Gibbs free energy change and thermodynamic balance of the reaction unaffected.¹ Its main function is therefore to lower the energy barrier of the rate-limiting step(s) compared to the non-catalyzed route, improving the kinetics of the process.² Reduction of the activation energy barrier is manifested not only by faster reaction rates, but it can also open preferential reaction pathways that enhance the selectivity. Overall, this results in more efficient and less energy demanding production schemes, in perfect resonance with circular economy requirements. Heterogeneous catalysis, in particular, is at the core of current chemical industry, with an estimated 85% of industrial processes involving at least one catalytic step.³ Currently, however, heterogeneous catalysis in industrial application often involves operating under extreme conditions, including high temperatures and pressures, to drive reactions at commercially viable rates.

The scientific community is increasingly focused on reducing the carbon footprint of catalytic processes and improving their environmental and economic sustainability. A key strategy involves driving catalytic reactions with renewable energy sources, such as solar and wind, to reduce reliance on fossil-derived energy. However, as shown in Figure 1.1, data from the International Energy Agency (IEA) from 1990 to 2022 reveal a persistently high dependency on fossil fuels.⁴

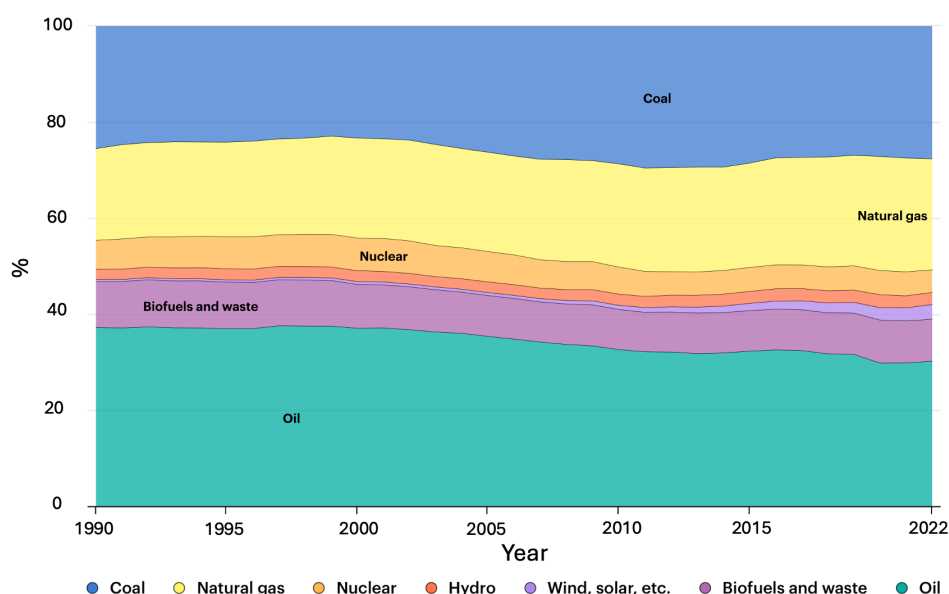


FIGURE 1.1: World's total energy supply from IEA data.⁴

In addition to cost-effectiveness, the development of modern catalysts must comply with other requisites, such as abundance of the raw materials used to prepare them, low toxicity or in general low environmental impact, and not depending on geopolitical constraints. At times, the catalytic activity of metal catalysts clashes with these requisites. For instance, palladium and platinum often offers high activity for a number of reactions, but they are costly and unevenly distributed on Earth, and therefore subject to supply vulnerabilities. It is worth noting that these aspects are frequently overlooked, and material choice often prioritizes catalytic performance without sufficient regard to issues related to scarcity, environmental impact or long-term availability. Replacing critical elements with more affordable and widely available base metals (such as iron, nickel, copper, and zinc), or, even better, with carbon-based materials, provides a cost-effective and practical alternative. Carbon-based materials, as metal-free catalysts, offer a promising path to reduce the reliance on metals in catalytic processes. While a world of catalysis entirely free from metals may still be a vision for the future, carbon-based materials present a real potential to partially replace or work alongside metal-based catalysts, significantly decreasing the need for metals.

In latest year, the integration of carbon components in catalyst formulation or even the direct use of carbon structure as metal-free catalysts has risen to great prominence as a strategy to mitigate the reliance on metals for chemical transformations. Carbon-based materials have long been integral to catalysis, with activated carbons widely recognized for their high surface area and adsorption capabilities. However, the true expansion of carbon's catalytic potential emerged with the advent of carbon nanostructures (CNSs). This breakthrough began with the Nobel Prize-winning discovery of fullerenes in 1985, followed by graphene in 2004. Along the path, several other allotropic forms with peculiar morphologies have been discovered, each featuring distinct characteristics. CNSs have opened new avenues in catalysis, paving the way for innovations that continue to push forward the boundaries of the field. The family of CNSs is in continuous expansion thanks to the better knowledge acquired throughout these years and the inventiveness in devising novel synthetic methodologies. Today, the best known CNSs (Figure 1.2), such as carbon nanotubes, graphene, carbon nanohorns, nanodiamonds, carbon dots, or the parent class of doped carbons, carbon nitrides, and porous carbons do not identify a single type of structure, but encompass materials with tailored structural variations that produce important change in the properties.⁵

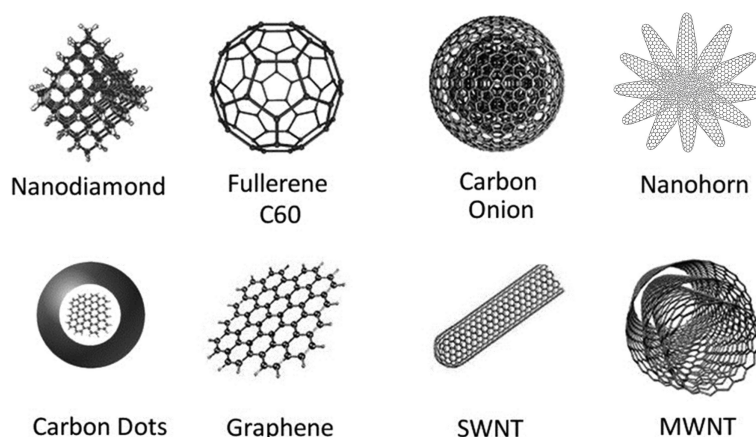


FIGURE 1.2: Representation of the most common carbon nanostructures.⁵

Most generally, synthetic approaches for CNSs are categorized as top-down or bottom-up methods. The former starts from larger carbon structures which are broken down with precise control to create desired nanoscale materials. Examples of top-down synthesis include pyrolysis method for the assembly of fullerenes and carbon nanotubes, or exfoliation of graphite to prepare graphene sheets. In contrast, bottom-up methods assemble nanoscale structures starting from small organic molecules that undergo isotropically controlled condensation phenomena and grow in size to reach nanoscale dimensions. The most popular examples is that of chemical vapor deposition (CVD) that allows for high-purity nanomaterials. Moreover, their tunability in properties through doping, surface functionalization,

and introduction of defects widen the versatility of CNSs for their use across many diverse applications,⁶ including energy storage,^{7,8} environmental purification,⁹ optoelectronics,¹⁰ biomedicine,¹¹ and catalysis.¹² In this realm of applicability exploits, the role of CNSs in electrocatalysis and photocatalysis are particularly noteworthy, especially in the context of renewable energy. A growing number of examples are available that demonstrate how integrating nanocarbon components within electrocatalytic and photocatalytic processes enables the development of cleaner and more efficient chemical solutions.

1.1 Carbon-based Materials in Electrocatalysis

One main function of CNSs in electrocatalysis is to act as an active support for metal-based catalyst (e.g. metal alloys, oxides, sulfides, nitrides), thanks to their electric conductivity. In more recent years, CNSs have been more and more frequently employed directly as catalysts, often modified by the inclusion of heteroatom dopants or functional groups.

When employed as supports, carbon materials provide a high surface area that facilitates optimal dispersion of inorganic components, enhancing the accessibility of active sites and, consequently, the efficiency of the catalytic process.¹³ Furthermore, the excellent electron mobility provided by π -conjugated systems facilitate charge transfer steps, resulting in faster reaction kinetics. Additionally, carbon-based materials are highly compatible with surface modifications or doping, allowing strong interactions with inorganic components and making them ideal platforms for hybrid catalysts involving transition metals. Consequently, these materials are recognized as ideal support structures due to their low cost, ease of functionalization, and ability to improve charge transfer at interfaces, expose more active sites, facilitate reactant diffusion, and enhance catalyst stability.¹⁴ The active role of CNSs support in electrocatalysis, namely their participation in the reaction mechanism, is well documented in several examples.^{15,16} Valenti *et al.* reported an innovative inorganic-organic composite combining multiwalled carbon nanotubes (MWCNTs) with CeO₂ nanoparticles (NPs) for the selective reduction of CO₂ to formic acid in an acidic electrolyte at remarkably low overpotential, achieving Faradaic efficiencies (FEs) up to 65% at an overpotential of -0.02 V vs RHE.¹⁷ Notably, the MWCNT scaffold in this catalytic system facilitates the electrochemical reduction of Ce⁴⁺ to Ce³⁺, as confirmed by *in situ* XPS measurements, which introduces additional oxygen vacancies within the CeO₂ phase. Both these features are crucial for the binding, activation, and conversion of CO₂ into formic acid. As shown in Figure 1.3, the mechanism occurs through the adsorption of CO₂, enhanced in presence on the nanocomposite, and subsequent formation of carbonate intermediates on the CeO₂ surface. Through a transient CeO₂-hydride species, the direct hydrogenation of these adsorbed CO₂ intermediate is promoted. This study is a powerful example in which a strategic interplay at the interface carbon/metal oxide is instrumental for promoting activity in CO₂RR.

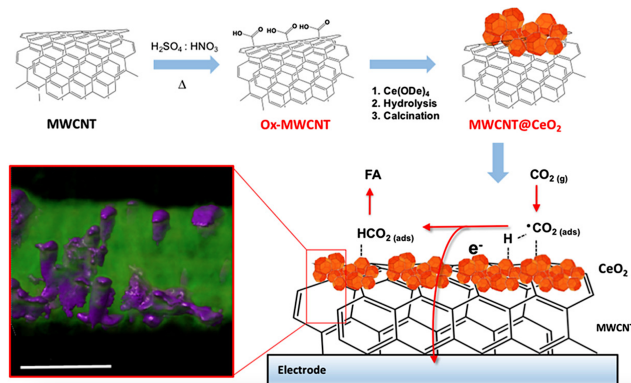


FIGURE 1.3: Schematic of MWCNT@CeO₂ synthesis involving a first oxidation step of the MWCNT scaffolds, followed by decoration with CeO₂-NPs (*top panel*); STEM tomographic reconstruction of MWCNT@CeO₂ (the region of high density corresponding to the CeO₂ is rendered with a violet mesh) and sketch of the possible mechanism of CO₂ hydrogenation to formic acid (*bottom panel*). Reprinted with permission. Copyright (2020) American Chemical Society.

Another field of research in which CNSs proved to be ideal support is that of the synthesis of single-atom catalysts (SACs). In the last few years, SACs risen to great popularity and positioned at the frontier of heterogeneous catalysis, bridging the gap between homogeneous and bulk heterogeneous systems. The isolation of single-metal atom sites on suitable supports represents an important step towards the critical industrial challenge of atom economy. The unique configuration of SACs provides high catalytic efficiency in terms of turnover frequency (TOF) and selectivity in a number of catalytic processes, but also presents significant challenges. In particular the isolated atoms have a strong tendency to aggregation due to their high surface energy, which is manifested both during their synthesis and during operative measurements.^{18,19} Interestingly, CNSs, particularly nitrogen-doped variants, are perhaps the most popular supports for SACs because they offer an optimum stabilizing environment that mitigates this aggregation.^{19–22} Nitrogen atoms in the carbon framework can coordinate with the metal atoms, forming stable sites that enhance both catalyst stability and activity.

In parallel to the roles of supporting component, carbon-based materials are also increasingly deployed as fully metal-free catalysts, offering a definite appeal in terms of cost-effectiveness whereby reliance on metals is completely avoided. Functionalization strategies (e.g. doping, introduction of surface functionalities, defect engineering) enable precise tuning of their electronic properties and introduce active sites capable of driving essential reactions, such as oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), oxygen evolution reaction (OER), with remarkable efficiency.^{12,23,24} In particular, doping with heteroatoms like nitrogen, sulfur, boron, fluorine, or phosphorus is an effective and widely

used strategy to develop versatile electrocatalysts with optimal electronic properties. The presence of the heteroatom within the graphitic lattice introduces structural defects and electronic modifications into carbon matrices, most relevantly modifying the charge density on the carbon lattice, and acting as electron-donating or electron-withdrawing groups to enhance catalytic activity by creating new active sites and improving conductivity. In 2009, a breakthrough in the field of ORR was reported by Gong and co-workers, who used of N-doped CNTs as ORR catalysts for the conversion to H_2O_2 and sparked intensive research on this subject.²⁵ This study showed that vertically aligned nitrogen-containing carbon nanotubes (VA-NCNTs) could function as efficient metal-free electrodes, offering superior electrocatalytic activity, long-term stability, and resistance to crossover effects compared to platinum-based catalysts in alkaline fuel cells. The introduction of nitrogen atoms into the carbon framework adjusts the electronic structure, increasing the positive charge density on nearby carbon atoms which proved critical for adsorption and activation of O_2 . Contemporary research has significantly expanded the scope of ORR carbon-based electrocatalysts^{23,26–29} assembling a variety of different carbon materials, ranging from simple mono-doped porous carbons, and advancing to more complex co-doping with multiple heteroatoms.^{30–33} Not only is the type of dopant atom significant, but its specific configuration within the carbon structure also plays a crucial role. This aspect has been widely recognized and became a particularly active field of research, which focus on understanding the precise correlation between activity and selectivity with the particular distribution of the classic types of N moieties such as pyrrolic, pyridinic, and graphitic nitrogen.^{34,35} It has been established quite clearly that these different nitrogen configurations influence the electronic environment and active sites in specific ways, thereby enhancing catalytic performance by modulating charge distribution, binding strength, and overall stability of the catalyst. Guo *et al.* studied model graphite catalysts to clarify the role of nitrogen doping in ORR, identifying carbon atoms adjacent to pyridinic nitrogen as highly active sites. Their observations on well-defined π -conjugated graphite models with controlled nitrogen doping demonstrate that pyridinic nitrogen creates Lewis basic sites where O_2 adsorbs, initiating the ORR.³⁶ However, there is not yet a unified framework to predict how the types of N atom distributions will behave in ORR catalysis, as many other factors, such as textural properties, conductivity, defect distributions, additional functional groups etc can also influence the mechanism. The electrocatalytic approach based on metal-free catalyst has more recently been extended to the CO_2RR process, which is more challenging from a thermodynamic point of view. Zhang *et al.* demonstrated that the combination of N-doping and a polyethylenimine (PEI) overlayer on carbon nanotubes enables effective catalysis for the reduction of CO_2 to formate in aqueous media, without the need for metal catalysts. PEI acts as a co-catalyst, significantly lowering the overpotential, increasing current density, and enhancing catalytic efficiency by stabilizing the CO_2^- intermediate and concentrating CO_2 around the CNT active sites.³⁷

In conclusion, carbon-based materials for electrocatalysis is a modern and very popular research trend of high appeal in relation to sustainable schemes for synthetic and energy related applications. Use of CNSs contributes to improved fuel efficiency, reduced emissions, lower production costs for industrial chemicals, and enhanced environmental and health monitoring. The unique versatility of carbon-based materials, as supports for inorganic elements or as active catalysts themselves, positions them as essential players in driving sustainable progress in electrocatalytic applications.

1.2 Carbon-based Materials in Photocatalysis

Using only the energy of light, photocatalysis offers a powerful approach to drive chemical reactions for environmental remediation and clean energy production, which is even more attractive (although more problematic) than electricity-powered conversions. In heterogeneous photocatalysis, when a semiconductor photocatalyst absorbs light with photon energy sufficient to overcome its band gap, electrons are excited from the valence band (VB) to the conduction band (CB), generating electron (e^-)/hole (h^+) pairs, also known as excitons (Figure 1.4). These photoexcited pairs separate into free charge carriers that migrate to the catalyst's surface, where they can participate in redox reactions, provided that the band edge potentials are suitable aligned with the redox potentials of the target reactions. If the CB potential is more negative than that of the target electron acceptor, CB electrons can be transferred to the substrate and drive its reduction reactions. Conversely, if the VB edge is more positive than the oxidation potential of an electron donor species, the photogenerated holes in the VB can oxidize the donor species.

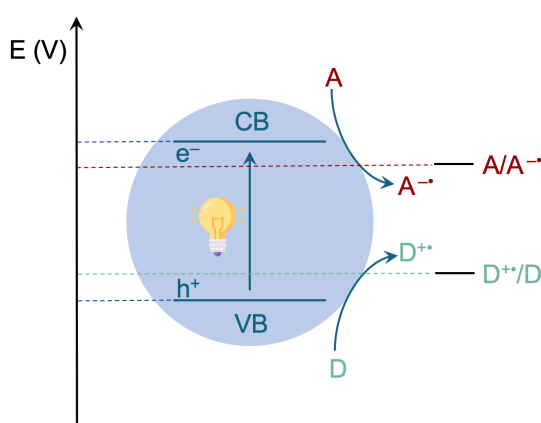


FIGURE 1.4: Schematic illustration of semiconductor photocatalysis.

In the context of photocatalysis, CNSs like graphene and CNTs like graphene and CNTs have been paired with traditional semiconductor photocatalysts to enhance photocatalytic

performance.³⁸ The rationale behind this opportunity is that thanks to their excellent conductivity of CNSs scavenge the photo-generated charges and favor charge mobility, resulting in better charge separation and reduced electron-hole recombination rates. In some report, it is proposed that they can also enable a more efficient use of the visible spectrum through heterojunction formation and band gap engineering.³⁹ As already discussed in electrocatalytic applications, several carbon-based materials are also able to function as standalone, metal-free photocatalysts. Notable examples include graphitic carbon nitride (CN),⁴⁰ carbon quantum dots (CQDs),^{41,42} covalent organic frameworks (COFs),^{43–45} and conjugated polymers (CPs).^{46–49} These materials are particularly attractive for sustainable photocatalysis, offering advantageous optical properties, chemical stability, and recyclability. Each class of carbon-based photocatalyst offers unique benefits: for instance, CN has a suitable band gap for visible light absorption, while COFs and conjugated polymers exhibit high surface areas and structural design flexibility, and are applied in many environmental and energy-related photocatalytic applications (e.g. hydrogen production, organic synthesis, CO₂ reduction). Currently, the main player in this field is undoubtedly carbon nitride, whose structure can be ideally represented by a bidimensional arrangement of cross-linked heptazine units, although the real structure considerably deviate from this representation and is far more disordered and inhomogeneous. Still, CN offers a variety of advantages such as very good chemical and thermal stability and a band gap (approximately 2.7 eV) suitable for visible light absorption and liable to facile tuning. The effectiveness of CN-based photocatalysts has already proven in a large number of experiments and for different types of photocatalytic reactions. Based on the number of publications in the last 20 years and considering that CN initial publications started only less than 15 years ago, the analysis of the projected data indicates that CN is rapidly catching up with benchmark TiO₂ semiconductors in terms of number of reports for photocatalysis (Figure 1.5).

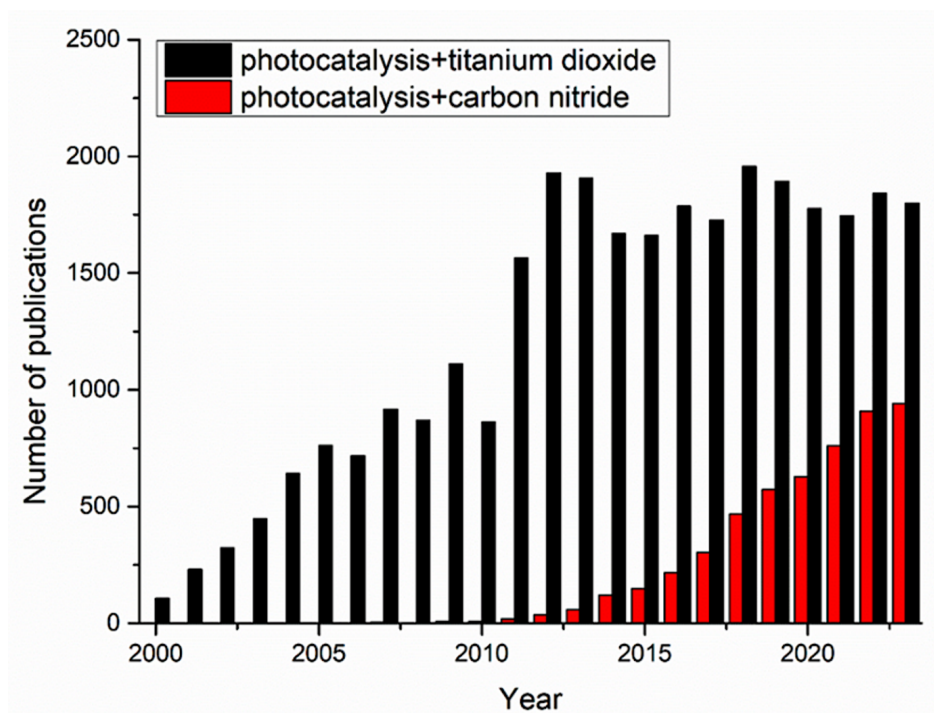


FIGURE 1.5: CN and TiO₂ publications on photocatalysis in the last 20 years.

One of the most attractive aspects is that the synthetic methodologies for CN are typically simple and inexpensive. Since the pioneering work of Antonietti and co-workers in 2009, which demonstrated the use of cyanamide-derived CN as an effective visible-light photocatalyst for hydrogen production,⁵⁰ studies and applications of this semiconductor have flourished also in relation to the new strategies for modifications of the conventional CN materials and to the fundamental mechanisms at the core of CN-catalyzed reactions. The versatility of CN is also well documented, with high efficiency achieved for several photocatalytic reactions, from water splitting, CO₂ reduction and organic synthesis, to wastewater treatment and air purification.^{40,51,52} The most known developments of CN structure include the possibility of doping, defect engineering, heterostructure formation and morphological alteration. All these modification are functional to the specific purpose. Despite all these benefits, many challenges in the use of CN are still to be resolved. In particular, the low surface area of the conventionally prepared CN implies a small number of active sites, while the typically fast recombination rates of the photogenerated e^-/h^+ pairs are detrimental for quantum efficiency. To improve the charge transfer, the interfacing with other graphitic carbon components has been widely investigated. For instance, CQDs have been implanted in CN nanotubes (CCTs), in which the charge separation and the photoelectron transfer are promoted by the tubular heterostructure in CN nanotubes, while CDs allows

an enhanced visible-light harvesting.⁵³ In 2020, Zhang and colleagues combined morphology manipulation with electronic structure engineering, reporting a hierarchical phosphorus and sulfur-doped CN mesoporous microspheres.⁵⁴ This approach resulted in enhanced visible-light absorption, electronic modulation for improved trapping centers, an increased number of active sites, improved mass transfer, and shorter diffusion pathways for charge carriers. The material demonstrated exceptional H_2 production under visible light, and the authors further coupled this process with benzyl alcohol oxidation, thereby leveraging both reductive and oxidative processes.

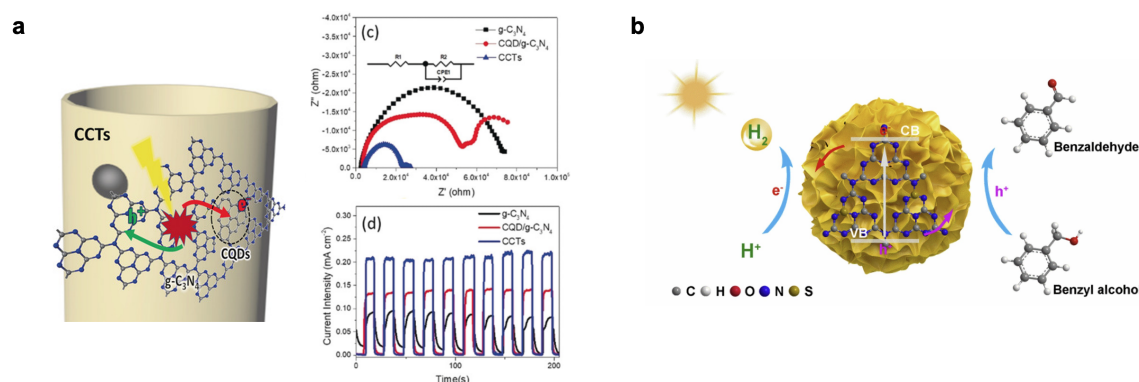


FIGURE 1.6: (a) Schematic representation of CQD/CN catalytic composite, electrochemical impedance spectra and transient photocurrent response; (b) Schematic representation of P, S-doped CN microsphere for concomitant H_2 and benzaldehyde production. Reproduced with permission.^{53,54}

A more recent trend has emerged only in latest years, where CN photocatalysts have been proposed and explored as photocatalysts in the realm of organic synthesis. This topic is currently attracting high interest in the photocatalysis community,^{55,56} and will be thoroughly addressed in the introduction of Chapter 3 of the present thesis, as it represents a central focus of my research.

1.3 Motivations and Outline of the Thesis

In the realm of catalysis, carbon-based materials offer not only efficiency and selectivity, but also the potential to harness renewable energy sources and to serve as sustainable alternatives to scarce and costly metals, paving the way for environmentally friendly and economically viable catalytic systems. The industrial production of chemicals is traditionally associated with significant waste generation and relies heavily on cost-intensive, energy-consuming processes. My research centers on exploring alternatives to these conventional methods by exploiting the properties of carbon components to foster more sustainable catalytic pathways. Specifically, my PhD project has focused on the investigation of various

catalytic processes for the production of valuable chemicals, harnessing the versatile applicability of carbon based materials. This thesis is structured in three main parts, as follows:

- **Chapter 1** explores the use of carbon nitride photocatalyst in organic synthesis, particularly for the formation of cross-coupling products by dual Ni/CN photocatalysis. A tailored modification of the photocatalyst is proposed to improve the efficiency of the photocatalytic organic reactions through an precise mode of interaction with the nickel catalyst;
- **Chapter 2** presents the development of a nanohybrid composed of a Bi-based catalyst and a carbon nanostructure, designed for the conversion of CO₂ into formic acid. The use of carbon nanohorns as support is investigated, studying the interplay between the carbon material and the inorganic counterpart;
- **Chapter 3** discusses the application of metal-free electrocatalysts based on polymeric materials for the synthesis of hydrogen peroxide. The influence of structural tunability achieved through thermal treatment is examined in relation to the resulting electrocatalytic activity.

Across all three projects, the selective exploitation of specific features inherent to carbon phases catalysts plays a central role, driving the development of innovative catalytic systems. Ultimately, the objectives of these thesis are to contribute to the understanding of how carbon-based materials, both independently and in synergy with metal catalysts, can redefine heterogeneous catalysis.

Chapter 2

Characterization Techniques

2.1 Nitrogen Physisorption

The catalytic activity of a material is intrinsically linked to its surface area, morphology and availability of active sites. However, it is not only the surface area that determines the performance. The dimension and texture of the pores play a critical role as well in catalytic processes. The ability of reactants and products to diffuse efficiently around the active sites is essential for maintaining reaction kinetics. If the pores are too narrow, the reaction may become limited by mass transport rather than the availability of active sites. Therefore, the interplay between surface area and pore structure may dictate not only the effectiveness of a reaction, but also its selectivity.

The physisorption of a gas, typically nitrogen (N_2), is a widely adopted technique for analyzing the textural properties of materials, providing valuable insights into surface area, pore volume, and pore size distribution.^{57–59} This method is particularly advantageous due to several characteristics. (a) Physisorption relies on low adsorption heat, with weak intermolecular forces, such as ion-dipole, dipole-dipole, and quadrupole interactions, promoting efficient adsorption without chemically altering the material surface. The process also allows for multilayer adsorption on surfaces, enabling estimation of the total pore volume. Additionally, it offers accessibility to the entire surface area, as it does not depend on specific site energetics, and therefore provides an accurate surface area measurement. Finally, physisorption is generally a fast process, except when diffusion limitations may arise in very small pores.

Brunauer-Emmett-Teller (BET) method is one of the most established approaches in physisorption analysis, developed to experimentally determine the amount of adsorbate needed to form a theoretical monolayer. If the area effectively occupied by each molecule is known, the total surface area can be estimated. The BET equation, which assumes the formation of a series of adsorption layers, is expressed as follows:

$$\frac{p}{n(p_0 - p)} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} \cdot \frac{p}{p_0} \quad (2.1)$$

where:

- p is the equilibrium pressure of the adsorbate gas,
- p_0 is the saturation vapor pressure at the experimental temperature,
- n is the adsorbed gas amount at p in grams,
- n_m is the amount of adsorbed gas to form a monolayer in grams,
- C is the BET constant, which depends on adsorbent-adsorbate interactions.

Typically, this equation is linear in the range of relative pressures p/p_0 between 0.05 and 0.30. From the slope and intercept, n_m and C can be derived, allowing to calculate the surface area as follows:

$$SA_{\text{BET}} = \frac{n_m a_m N_A}{MW} \quad (2.2)$$

where:

- a_m is the area occupied by a single adsorbate molecule (for N_2 at 77 K, $a_m = 0.162 \text{ nm}^2$),
- N_A is Avogadro constant,
- MW is the molar weight of the adsorbate gas.

Materials with high surface areas typically exhibit a porous structure. It is essential to distinguish between internal surface area, due to porosity, and the external surface area. The nature of the pores can be categorized as:

- **Micropores** with diameters less than 2 nm,
- **Mesopores** with diameters from 2 to 50 nm,
- **Macropores** with diameters greater than 50 nm.

The porosity of a material greatly affects the shape of its physisorption isotherm. IUPAC classifies adsorption isotherms into six types (Figure 2.1):

- **Type I** isotherms: characteristic of microporous materials with small external surfaces, where most adsorption occurs within the internal pore structure.
- **Type II** isotherms: typical of macroporous systems, with an inflection point indicating monolayer formation.
- **Type III** isotherms: uncommon and lack a B-point, suggesting weak adsorbent-adsorbate interactions.
- **Type IV** isotherms: show hysteresis loops due to capillary condensation in mesopores.
- **Type V** isotherms: exhibit a weak adsorbent-adsorbate interaction, also showing a hysteresis loop.

- **Type VI** isotherms: characterized by stepwise adsorption on a non-porous surface.

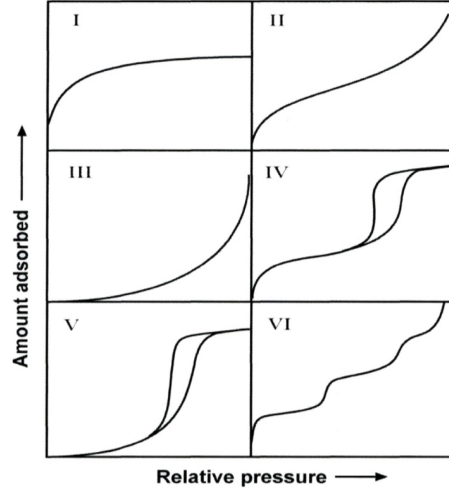


FIGURE 2.1: Types of adsorption-desorption isotherms. Reproduced with permission.⁶⁰

In the cases where only monolayer adsorption occurs, Langmuir adsorption model is more suitable. This model assumes that adsorption happens at specific surface sites, with each site accommodating only one adsorbate molecule and no additional multilayer formation. The Langmuir isotherm is given by:

$$\theta = \frac{K_L p}{1 + K_L p}$$

where:

θ is the fractional surface coverage,

K_L is the Langmuir constant, related to adsorption energy,

p is the gas pressure.

This model is particularly useful for interpreting adsorption on non-porous or microporous surfaces where the monolayer adsorption is predominant.

The Barrett-Joyner-Halenda (BJH) method is commonly applied to analyze mesoporous structures, especially for materials with type III and IV isotherms. This method estimates pore size distribution by examining capillary condensation, where gas condenses in pores at pressures below saturation (p_0), due to the curvature of the meniscus within the pore. This effect is described with the Kelvin equation:

$$\ln \left(\frac{p}{p_0} \right) = - \frac{2\gamma V_m}{R T r_c} \quad (2.3)$$

where:

- p is the gas pressure,
- p_0 is the saturation vapor pressure,
- γ is the liquid surface tension,
- V_m is the liquid molar volume,
- r_c is the effective pore radius.

The BJH method assumes pores as cylinders, and calculates the pore size by adding the thickness of the adsorbed layer to the meniscus radius from Kelvin equation. This approach generates a pore size distribution curve, which reveals insights into pore geometry and accessibility, which are crucial for catalytic applications.

2.2 Electron Microscopy

Electron microscopy is a powerful imaging technique that achieves resolutions far beyond those possible with optical microscopy, allowing observation of materials at nanometer and even atomic scales.⁶¹ Unlike optical microscopes that rely on photons, electron microscopes use high-energy electron beams as source. Electron microscopy includes techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), and scanning transmission electron microscopy (STEM), each offering unique insights based on how the electron beams interact with the sample.

2.2.1 Transmission Electron Microscopy

Transmission electron microscopy directs a high-energy electron beam through an ultrathin sample, allowing transmitted electrons to form either an image or a diffraction pattern.⁶² In a TEM microscope, the electron beam is directed to a specimen, and the electrons transmitted through the specimen are focused by lenses to be collected by a detector. A schematic representation of a typical microscope column is depicted in Figure 2.2.

A TEM instrument consists of three main systems. The illumination system includes the electron source, typically a thermoionic gun or a field emission gun (FEG), and condenser lenses that focus the electron beam. FEG sources, known for their high coherence and brightness, are particularly suited for high-resolution imaging. The specimen stage holds the sample and permits fine positioning along three spatial axes. Samples, frequently prepared on thin copper grids or carbon film supported copper grids, are introduced into an ultra-high vacuum chamber to minimize the electron scattering by gas molecules. Finally, the imaging system contains objective and projector lenses that magnify and project the transmitted electron image onto a phosphorescent screen or a charge coupled device (CCD) camera.

The contrast of image in a TEM, defined as the difference in intensity of electrons between

a point in comparison with other areas, is determined by geometry of the electron illumination, the electron scattering within the specimen and the path of transmitted electron. TEM offers various imaging modes to highlight different aspects of a sample. In Bright-Field (BF) imaging, only unscattered electrons contribute to the image, while in Dark-Field (DF) imaging, scattered electrons are used, enhancing contrast for specific crystalline regions. High-Angle Annular Dark Field (HAADF) imaging detects incoherently scattered electrons at large angles, producing Z-contrast images that reveal atomic number differences within the sample. TEM ability to provide structural, compositional, and crystallographic information makes it one of the most versatile and insightful techniques in electron microscopy.

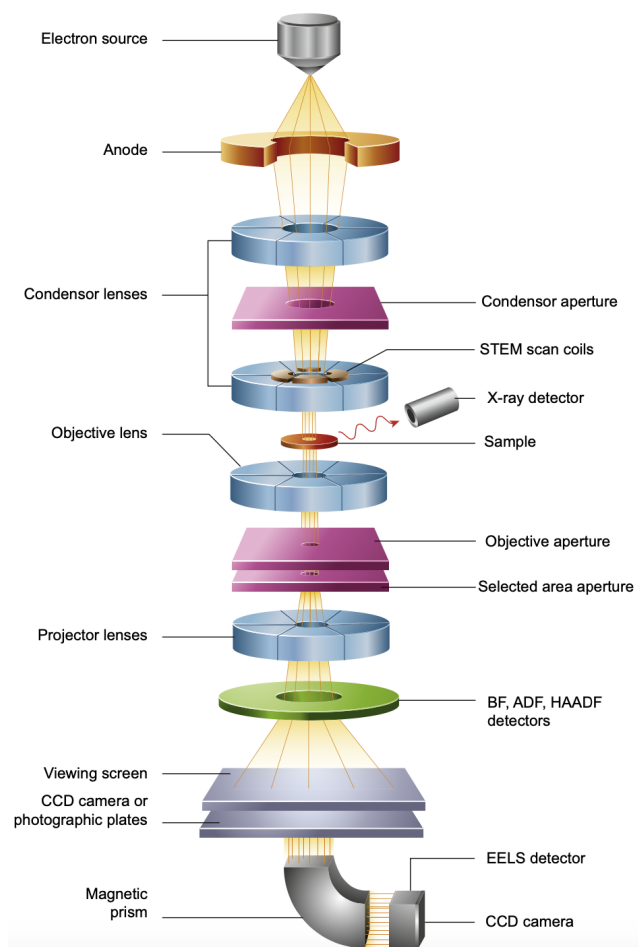


FIGURE 2.2: Schematic of the components of transmission electron microscope. Reproduced with permission.⁶³

2.2.2 Scanning Electron Microscopy

In scanning electron microscopy (SEM), a focused electron beam is directed at the sample within a vacuum chamber and scanned across its surface. As the incident electrons interact

with the sample's atoms, they scatter elastically or inelastically. In elastic scattering, electrons are deflected with negligible energy loss, generating backscattered electrons (BSE). These BSEs are highly sensitive to the atomic number of the elements in the sample, allowing for compositional contrast in the resulting images, as areas with heavier elements appear brighter.⁶³

Inelastic scattering, on the other hand, occurs when the incident electrons lose some of their kinetic energy as they interact with atoms, resulting in X-ray emission, Auger-electron emission, light emission or electron-hole pair regeneration. This process generates secondary electrons (SE), which escape from near the sample surface, providing detailed topographical information. Additionally, inelastic scattering can cause the emission of X-rays through two main mechanisms. The first is Bremsstrahlung radiation, which produces a broad spectrum of X-rays, but is less useful for the analysis. The second mechanism produces characteristic X-rays, which are generated when the primary electrons displace inner-shell electrons from atoms. As electrons from higher energy levels fill the vacancies, they emit X-rays at energies characteristic to each element, allowing for precise elemental identification.

Energy dispersive X-ray spectroscopy (EDX), often coupled with SEM or TEM, uses these characteristic X-rays for qualitative and quantitative analysis, offering detailed insights into the elemental composition of the sample.⁶⁴

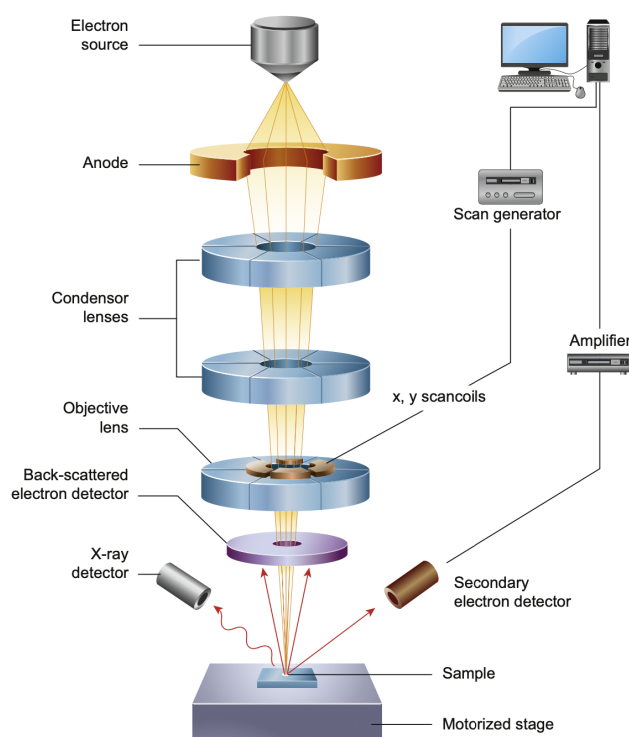


FIGURE 2.3: Schematic of the components of scanning electron microscope. Reproduced with permission.⁶³

2.3 Raman Spectroscopy

Raman spectroscopy is a powerful technique used to study lattice vibrations and molecular structures of materials. This method is based on the Raman effect, discovered by physicist C.V. Raman in 1928, where a small fraction of monochromatic light scattered by a material undergoes a change in frequency. This inelastic scattering occurs because the incident light interacts with the vibrational modes of the sample's molecules, causing a shift in the energy of the scattered photons.⁶⁵

In particular, when monochromatic light (usually a laser) strikes a sample, most of it is either transmitted or elastically scattered (Rayleigh scattering), with the scattered light retaining the same frequency as the incident light. However, a small fraction undergoes inelastic scattering (Raman scattering), resulting in a change in photon frequency due to energy transfer between the photons and molecular vibrations. This shift in frequency, known as the Raman shift, provides specific information about the vibrational modes of the sample, often reported in units of relative wavenumbers (cm^{-1}).

In Raman scattering, the frequency of scattered light can shift to lower (Stokes scattering) or higher frequencies (anti-Stokes scattering). In Stokes scattering, photons lose energy to the sample, exciting vibrational modes and shifting the scattered light to a lower frequency. In anti-Stokes scattering, photons gain energy from already excited vibrational states in the sample, resulting in a shift to a higher frequency.

The difference in energy between the incident and scattered light corresponds to the energy of specific vibrational modes in the sample, providing detailed information on chemical bonds, molecular structure, and material composition. Raman spectroscopy complements infrared (IR) spectroscopy, as it can reveal vibrational modes that are IR-inactive. This difference arises because Raman-active modes require a change in polarizability, while IR-active modes require a change in dipole moment.

Practically, Raman spectra often focus on Stokes scattering signals, which are more intense than anti-Stokes signals due to the population distribution of vibrational states governed by Boltzmann statistics. Additionally, the wavelength of the laser source significantly impacts the signal intensity, which is proportional to the fourth power of the laser frequency (λ^{-4}). Shorter wavelengths produce stronger signals, though longer wavelengths are sometimes used to avoid fluorescence interference.

2.4 X-Ray Diffraction

Powder X-ray diffraction (XRD) is a widely used technique for the structural characterization of crystalline materials. This method relies on the interaction of X-rays with the atomic planes within a crystal lattice, where X-ray photons are scattered, generating diffraction patterns that contain valuable structural information. When X-rays encounter the regularly

spaced planes in a crystal, they undergo constructive interference at specific angles, resulting in high-intensity peaks in the diffraction pattern. This phenomenon is governed by Bragg's law:

$$n\lambda = 2d \sin \theta \quad (2.4)$$

where:

- n is the order of diffraction,
- λ is the wavelength of the incident X-rays,
- d is the spacing between lattice planes,
- θ is the angle of incidence.

This diffraction pattern provides detailed structural information, allowing to determine characteristics such as unit cell dimensions, the orientation and spacing of lattice planes. Furthermore, XRD can estimate crystallite sizes (τ) by analyzing the peak broadening in the diffraction pattern using the Scherrer equation:

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (2.5)$$

where:

- K is a shape factor,
- λ is the X-ray wavelength,
- β is the peak's Full Width at Half Maximum (FWHM),
- θ is the Bragg angle;

The Scherrer equation highlights that narrower peaks correlate with larger crystallites, while broader peaks are related to smaller crystallites. However, peak broadening can also be due to other factors. Variations in peak width may arise from lattice defects, such as dislocations, grain boundaries, or even the presence of impurities, which influence the diffraction pattern independently of crystallite size. Instrumental factors can also impact β , necessitating calibration to isolate the effect of crystallite size from other variables in the analysis.

2.5 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a technique used to monitor mass changes in a sample as it is subjected to a controlled temperature program, typically involving heating at a constant rate. The sample is placed on a highly sensitive thermobalance inside a furnace, allowing precise control over temperature and atmospheric conditions. TGA can be conducted in inert atmospheres (such as nitrogen) or reactive ones (such as oxygen or hydrogen), providing insights into the thermal stability and reactivity of materials under varying conditions.⁶⁶

As the sample is heated, it may undergo processes such as decomposition, vaporization, or oxidation, leading to a loss or gain in mass, depending on interactions with the surrounding gases. The data from TGA is typically represented as a thermogravimetric (TG) curve, where mass change (either absolute or as a percentage) is plotted against temperature.

While TGA provides precise quantitative measurements of mass change, its qualitative insights are limited. The TG curve's shape and position reflect the kinetics and mechanisms of thermal events, but TGA cannot detect structural changes without mass variation or directly identify decomposition products and degradation pathways if it's not coupled with other techniques (e.g. gas chromatography).

2.6 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique based on the photoelectric effect, where an incident X-ray photon interacts with a sample, causing the ejection of an electron that escapes into a vacuum.⁶⁷ By analyzing the energies of these emitted electrons, XPS provides valuable insights into the elements present and their chemical environment. Due to the shallow escape depth of electrons (1–10 μm), XPS primarily analyzes the surface layer and nearby, making it highly effective for studying surface chemistry in catalysts.

Each element produces a characteristic pattern of core-electron binding energies in XPS spectra, enabling precise identification of atomic composition. Small shifts in binding energy, known as chemical shifts, provide detailed information on the oxidation state and type of chemical bonding within the sample. Moreover, XPS also offers quantitative insights. By examining the intensities of spectral peaks corresponding to different elements, the relative atomic concentration of each component can be estimated.

The electron binding energy (BE) is calculated using the known X-ray energy and the kinetic energy (E_k) of the emitted electron, based on the equation:

$$\text{BE} = E_p - (E_k + \phi) \quad (2.6)$$

where:

BE is the electron binding energy,

E_p is the X-ray photon energy,

E_k is the kinetic energy of the emitted electron,

ϕ is the work function of the spectrometer.

In this way, XPS provides essential data on surface composition and chemical states, facilitating insights into material properties and surface interactions.

2.7 Theoretical Introduction on Electrochemical Techniques

Electrochemical techniques are fundamental tools in the study of electrocatalysis, allowing to probe the kinetics, thermodynamics, and mechanisms of reactions at the electrode surface. In electrocatalysis, where electron transfer processes drive chemical transformations, understanding the interactions between reactants and the electrode surface is essential. This interplay, involving both charge transfer and mass transport phenomena, define a efficiency, selectivity, and stability of the electrocatalytic process.⁶⁸

The most common electrochemical techniques include *Cyclic Voltammetry (CV)*, *Linear Sweep Voltammetry (LSV)*, *Chronoamperometry (CA)*, *Electrochemical Impedance Spectroscopy (EIS)*, and *Electrochemical Surface Area (ECSA)* measurements. Each technique provides unique insights into specific aspects of the catalytic process, from electrochemically active surface area and charge transfer resistance to mass transport properties.

Electrocatalysis combines principles of electrochemistry and catalysis, enabling chemical transformations at the electrode surface through electron transfer. Electrocatalytic reactions can be divided in faradaic processes, which involve electron transfer and lead to oxidation or reduction, and non-faradaic processes, which may include adsorption or desorption at the electrode surface.

The behavior of these processes is influenced by the structure of the electrical double layer that forms at the electrode-electrolyte interface under potentiostatic control. This layer, consisting of oriented dipoles and charged species, impacts the accessibility and reactivity of the electrode surface. The double layer structure is typically divided into the inner Helmholtz plane (IHP), where ions are specifically adsorbed and interact with the electrode, and the outer Helmholtz plane (OHP), where solvated ions are held by electrostatic forces. Beyond the OHP lies the diffuse layer, where ion concentration gradually approaches bulk solution levels.

The following paragraphs provide an overview of the electrochemical techniques used within this thesis for studying electrocatalytic reactions.

2.7.1 Cyclic Voltammetry (CV)

Cyclic Voltammetry (CV) is a widely used direct current (DC) technique.⁶⁹ In CV, a triangular potential waveform is applied to the working electrode, sweeping the potential back and forth over a fixed range. During the anodic sweep, where the potential changes from V_1 to V_2 (Figure 2.4), oxidation reactions are recorded, while the reverse sweep (cathodic, from V_2 to V_1) reveals reduction processes.

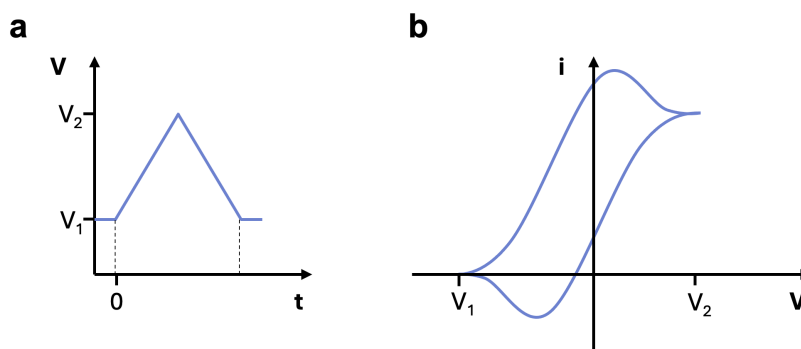


FIGURE 2.4: (a) Potential vs time waveform applied during a CV experiment; (b) resulting current vs potential plot, illustrating the corresponding CV response.

The height of the peak in CV is proportional to the amount of reactant, as well as to scan rate and diffusional properties of the electroactive species. The Randles-Sevcik equation defines how the peak current correlates with electrochemical parameters of the system, especially for reactions involving analytes that diffuse freely in solution:

$$i_p = 0.4463 n F A C \sqrt{\frac{n F \nu D}{RT}} \quad (2.7)$$

where:

- i_p is the peak current,
- n is the number of electrons transferred,
- F is the Faraday constant,
- A is the electrode surface area,
- C is the analyte concentration,
- ν is the scan rate,
- D is the diffusion coefficient,
- R is the gas constant,
- T is the temperature.

The characteristic shape of the CV curve results from the diffusion of reactive species from the bulk solution toward the electrode surface. The peak current potential (E_p) corresponds to the point at which the rate of the electrochemical reaction at the electrode-electrolyte interface balances the rate of reactant diffusion from the bulk solution to the interface. Beyond this peak potential, the reaction becomes diffusion-limited, and the current decreases as the diffusion layer is depleted of reactant species. A similar process is observed in the cathodic sweep, where reduction reactions occur. Analyzing the position, shape, and area under these peaks is essential for identifying the electrochemical processes taking place. Randles-Sevcik equation establishes a linear relationship between the peak

current and the square root of the scan rate. However, if the reactant is adsorbed on the electrode surface, the peak current no longer depends on the reactant concentration or diffusion coefficient, but on the surface coverage (Γ):

$$i_p = \frac{n^2 F^2}{4RT} A \Gamma \nu \quad (2.8)$$

In this second case, the peak current is linear to the scan rate (ν). Consequently, running a series of CVs at different scan rates allows for plotting i_p against ν , which can reveal whether the analyte is freely diffusing in the solution or adsorbed on the electrode surface.

2.7.2 Linear Sweep Voltammetry (LSV)

Linear Sweep Voltammetry (LSV) is similar to CV, but involves a single potential sweep (Figure 2.5). LSV records the current response as a function of applied potential, helping to determine parameters such as onset potential and overpotential. LSV is particularly useful in evaluating the electrocatalytic activity of materials and understanding reaction mechanism.

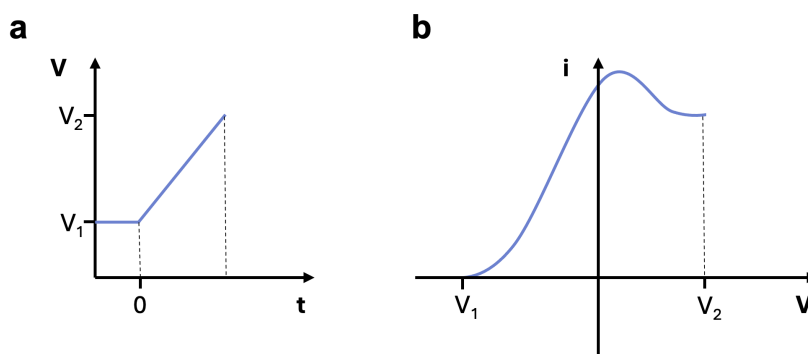


FIGURE 2.5: (a) Time-potential waveform of a LSV; (b) corresponding signal in a current-potential plot.

2.7.3 Chronoamperometry

Chronoamperometry (CA) is a technique where a constant potential is applied, and the resulting current response is recorded over time (Figure 2.6).

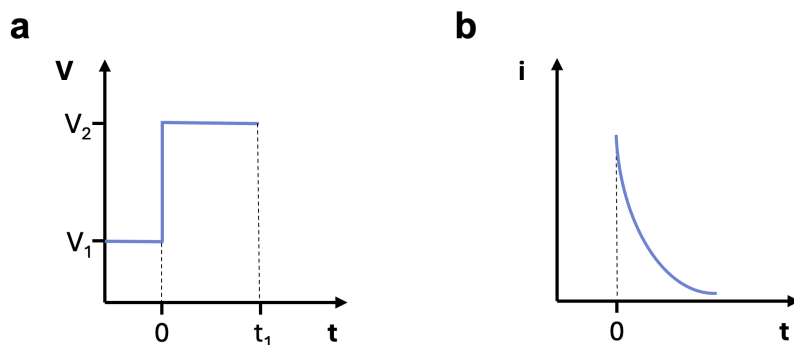


FIGURE 2.6: (a) Excitation waveform of a CA experiment; (b) response wave of CA.

CA is effective in studying mass transport and kinetic parameters in systems where the analyte diffuses toward the electrode surface. The current response in CA typically decays exponentially, following the Cottrell equation:

$$i = \frac{nFAc_j^0 D_j^{1/2}}{\pi^{1/2} t^{1/2}} \quad (2.9)$$

where:

c_j^0 is the initial concentration of analyte j ,
 D_j is the diffusion coefficient,
 F is Faraday's constant.

The current decays over time until the analyte near the electrode is consumed or reaches equilibrium. From CA data, information on the reaction kinetics and Faradaic efficiency can be obtained, providing insights into the selectivity of the reaction products.

2.7.4 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is an alternating current (AC) technique widely used to study the complex impedance behavior of electrochemical systems across a broad range of frequencies. By applying a small sinusoidal voltage perturbation to an electrochemical cell and measuring the current response, EIS provides a frequency-dependent profile of the system impedance, offering insights into electrochemical processes at the electrode-electrolyte interface.^{70,71}

EIS data are commonly displayed in Nyquist and Bode plots, which visually represent the system's impedance characteristics. In a Nyquist plot, the real component of impedance (Z_{Re}) is plotted against the imaginary component (Z_{Im}), while in a Bode plot, the impedance magnitude and phase shift are plotted as a function of frequency.

Impedance is defined as the combined effect of resistance and reactance within the system, indicating the opposition to current flow in AC circuits. An electrochemical cell can be represented by an equivalent circuit model, where each component (resistors, capacitors, and less frequently inductors) corresponds to a specific phenomenon. Understanding EIS data involves recognizing how these equivalent circuits respond to AC stimuli and what they reveal about the system electrochemical behavior.

For a better explanation, consider a simple resistor, R , connected in an AC circuit. When a sinusoidal voltage is applied across R , the resulting sinusoidal current wavefunction is in phase with the voltage, and Ohm's law ($i = V/R$) fully describes this relationship. In contrast, if the circuit contains a capacitor instead, the current and voltage are out of phase due to the capacitor's charging behavior. Initially, when the capacitor begins charging, the current is at its maximum; as the capacitor becomes fully charged, no current passes. This phase difference is conveniently expressed in complex notation. The Randles circuit, which includes a resistor coupled with a capacitor, and a resistor in parallel, is the simplest model for an electrochemical cell. When represented on a Nyquist plot, the Randles circuit generates a semicircular response (Figure 2.7). This basic model provides a foundation for analyzing EIS data in more complex electrochemical systems.

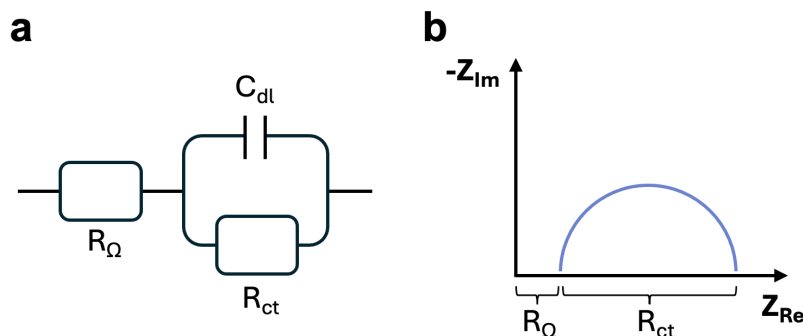


FIGURE 2.7: (a) Excitation waveform of a CA experiment; (b) response wave of CA.

Each component in the Randles circuit corresponds to a distinct aspect of the electrochemical interface. The first resistance (R_Ω) represents the solution resistance between the working and reference electrodes. This term accounts for the electrolyte intrinsic resistance and is independent of the electrode reactions. The capacitance term (C_{dl}) reflects the double-layer capacitance at the electrode surface, where ions accumulate in response to an applied bias. This capacitance is influenced by the surface area and morphology of the electrode, and thus can be useful in estimating the electrochemical surface area (ECSA) of catalytic materials, that will be described in the next section. Another key parameter in the Randles circuit is the charge transfer resistance (R_{ct}), which is associated with the electron transfer

process between the electrode and the analyte. R_{ct} can be derived from the Butler-Volmer equation:

$$R_{ct} = \frac{RT}{nFi_0} \quad (2.10)$$

where:

- R is the gas constant,
- T is the temperature,
- n is the number of electrons transferred,
- F is the Faraday constant,
- i_0 is the exchange current density.

From the Butler-Volmer equation, R_{ct} is inversely proportional to the exchange current density, i_0 , indicating that faster electron transfer kinetics correspond to lower R_{ct} values. In a typical Nyquist plot, R_{ct} appears as the diameter of the semicircle, with larger values suggesting less efficient charge transfer. However, in practice, Nyquist plots of real systems often deviate from the ideal semicircular shape due to surface roughness or heterogeneity. When the semicircle appears distorted, it indicates non-ideal capacitive behavior, which can be modeled by introducing a constant phase element (CPE) in place of the pure capacitor. The admittance (reciprocal of impedance) of a CPE, Y_{CPE} , is given by:

$$Y_{CPE} = Q_0(\omega i)^n \quad (2.11)$$

where:

- n is an exponent with values between 0 and 1,
- ω is the angular frequency,
- Q_0 is a constant,

When $n = 1$, the CPE behaves like an ideal capacitor, while for $n = 0$, it behaves as a resistor. Values of n close to 0.8 are often used to model the response of electrodes with rough or porous surfaces, where the semicircle in Nyquist plot is typically depressed.

At low frequencies, diffusion limitations become significant, leading to a diffusion-controlled response in the Nyquist plot. This effect is often modeled with a Warburg impedance, which represents semi-infinite linear diffusion toward a planar electrode surface. In the Nyquist plot, the Warburg element manifests as a line with a 45° slope, indicating that the system behavior is dominated by diffusion limitations at those frequencies.

2.7.5 Electrochemical Surface Area

Electrochemical Surface Area (ECSA) is a measure of the active surface area of an electrocatalyst, often more representative than the geometric surface area, since provides an accurate

estimate of the active sites available for catalysis. ECSA is especially valuable for understanding the real catalytic performance of a material, as it reflects the number of active sites available for electron transfer processes.

Several methods can be used to determine ECSA, with common approaches involving measurements of the double-layer capacitance through techniques like CV or EIS. These techniques typically focus on non-faradaic regions of the potential window to avoid any redox activity, ensuring that the measured capacitance is due to the double-layer charging rather than faradaic reactions. By dividing the measured double-layer capacitance by the specific capacitance of a flat surface of the same material, ECSA provides an accurate estimate of the number of accessible active sites.⁷² The experimental approach used in this thesis will be described in Section 2.7.7.

2.7.6 Rotating Ring Disk Electrode

The Rotating Ring Disk Electrode (RRDE) is a specialized electrochemical set-up designed to investigate reaction mechanisms at the electrode surface by allowing simultaneous detection of products and intermediates formed during electrochemical reactions.^{73,74} The RRDE setup consists of two electrodes arranged in concentric circles: a central disk electrode, where the primary reaction occurs thanks to the catalyst, and a surrounding ring electrode that detects species generated at the disk. This configuration enables selective and continuous analysis of reaction intermediates and products as they are transported from the disk to the ring.

The RRDE operates under controlled hydrodynamic conditions achieved by rotating the electrode at a set rotation speed. The rotation creates a laminar flow near the electrode surface, drawing electrolyte and reactants toward the disk and subsequently forcing reaction products radially across the ring. By increasing the rotation rate, the thickness of the diffusion layer decreases, enhancing the mass transport of reactants to the electrode surface.

The primary function of the RRDE setup is to facilitate the analysis of reaction mechanisms. For instance, in the oxygen reduction reaction (ORR), hydrogen peroxide (H_2O_2) and H_2O can be both formed as products (respectively through 2-electron and 4-electron pathway) at the disk and carried outward by the hydrodynamic flow to the ring (Figure 2.8). A fraction of H_2O_2 reaches the ring electrode, where it is detected through oxidation due to an appropriately set potential at the ring, while the remainder disperses into the bulk solution or undergoes chemical decomposition.

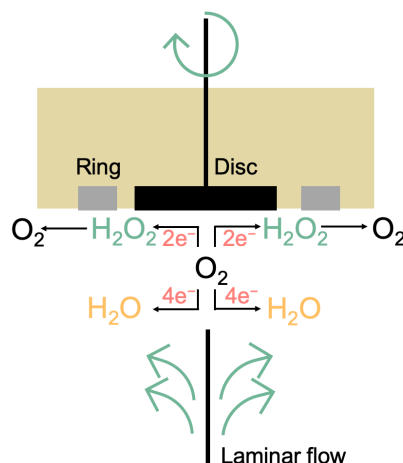
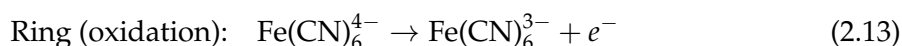
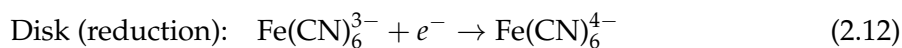


FIGURE 2.8: Schematic illustration of RRDE for ORR process.

The ability of the ring to capture these intermediates is quantified by the collection efficiency (N), which represents the fraction of species generated at the disk that subsequently reaches the ring. The collection efficiency depends primarily on the geometric properties of the RRDE, specifically the radii of the disk and ring electrodes. Typical commercial RRDE set-ups have collection efficiencies of 25%. This parameter can be determined empirically by measuring the ratio of currents at the ring and disk using a well-defined redox couple, such as ferricyanide/ferrocyanide:



Ferricyanide (Fe(CN)_6^{3-}) is reduced to ferrocyanide (Fe(CN)_6^{4-}) at the disk electrode, generating a disk current (i_d). The ferrocyanide produced at the disk is then transported to the ring electrode, where it is oxidized back to ferricyanide, producing a ring current (i_r). N is calculated from the ratio of these currents:

$$N = \frac{i_r}{i_d} \quad (2.14)$$

For reactions like ORR, the RRDE set-up enables the calculation of the number of electrons (n) and the selectivity for hydrogen peroxide production (% H_2O_2).⁷⁵ These parameters are derived from the measured i_d and i_r according to the following equations:

$$n = \frac{4 i_d}{i_r N + i_d} \quad (2.15)$$

$$\%H_2O_2 = \frac{4 - n}{2} \times 100 \quad (2.16)$$

The number of electrons provides insight into the reaction pathway, with n equal to 4 indicating full reduction of O_2 to H_2O , while values closer to 2 suggest the formation of H_2O_2 . In this project, the RRDE is utilized primarily for studying ORR process. By controlling the potential applied to both the disk and the ring (ring potential 1.4 V vs RHE), the RRDE allows for the selective detection of H_2O_2 at the ring electrode, enabling accurate quantification of its production. This approach provides a detailed understanding of the ORR pathway, as the ring current reflects the amount of H_2O_2 generated at the disk that reaches the ring.

2.7.7 Technical Details of Electrochemical Experiments

This section outlines briefly practical details common to the electrochemical studies presented throughout this thesis. For more specific experimental procedures of each study, the Experimental Sections at the end of each chapter will be more detailed.

EIS was firstly used to determine R_Ω and to verify that the electrochemical set-up was functioning correctly before each measurement. The potentials measured during LSV were manually corrected for ohmic losses estimated via EIS, and subsequently converted to the reversible hydrogen electrode (RHE) scale, when appropriate, to account for the electrolyte pH.⁷⁶ The conversions from Ag/AgCl and saturated calomel electrode (SCE) to RHE scale were performed according to the following equations:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + E_{Ag/AgCl}^\circ = E_{Ag/AgCl} + 0.059 \times pH + 0.197 \quad (2.17)$$

$$E_{RHE} = E_{SCE} + 0.059 \times pH + E_{SCE}^\circ = E_{SCE} + 0.059 \times pH + 0.241 \quad (2.18)$$

Different methodologies for ECSA calculations can be performed. In this thesis, ECSA was determined using the following equation:

$$ECSA = RF \cdot S \quad (2.19)$$

$$RF = \frac{C_{dl}(\text{catalyst})}{C_{dl}(\text{smooth electrode})} \quad (2.20)$$

In the equations, RF represents the roughness factor, defined as the ratio of the double layer capacitance (C_{dl}) of the working electrode to that of the smooth electrode (glassy

carbon electrode). S denotes the geometric surface area of the electrode. This approach accounts for the specific characteristics of the smooth electrode to provide a normalized ECSA value, allowing for a more accurate comparison of catalytic activity across different materials and electrode surfaces.

Faradaic Efficiencies (FEs) were calculated based on the concentration of the reaction products during or after CA experiments. The following formula applies to any product, whether in solution or in the gas phase:

$$\text{FE}(\%) = \frac{n_e \cdot n_p(\text{mol}) \cdot F}{|Q(\text{C})|} \times 100 \quad (2.21)$$

where:

n_e is the number of electrons exchanged in the reaction,

n_p is the amount of product in moles,

F is the Faraday constant (96485 C mol^{-1}),

Q is the absolute value of the charge obtained from the integration of the CA data.

Chapter 3

Tailoring of Carbon Nitride Structures Steers the Activity in Dual Nickel Photocatalysis

3.1 Introduction

Carbon nitrides (CNs) stand as a prominent class of metal-free semiconductors due to their optical and functional properties.⁷⁷ CNs are a family of materials characterized by a highly conjugated framework of alternating carbon-nitrogen bonds made of s-triazine or tri-s-triazine (heptazine) building blocks. The various carbon nitrides differ in condensation degree, repeat units, motifs and intermolecular packing. The most stable and most frequently investigated allotrope, the graphitic carbon nitride (g-CN), consists of repeating heptazine units connected through trigonal nitrogen bridges, forming a graphite-like layered structure with an theoretical carbon-to-nitrogen ratio of 3:4 (as indicated by the frequently used formula C_3N_4 , although in reality synthetic carbon nitride structures deviate from the theoretical stoichiometric ratio).^{78–80} The origins of carbon nitride derivatives and their precursors can be traced back to 1834, when Berzelius and Liebig identified "melon," a linear synthetic polymer composed of interconnected heptazine rings linked via secondary nitrogen atoms.⁸¹ To highlight the diversity of carbon nitride forms, Figure 3.1 provides an overview of the common CN local chemical structures, showing the main intermediates and fragments of heptazine-based and triazine-based carbon nitrides.

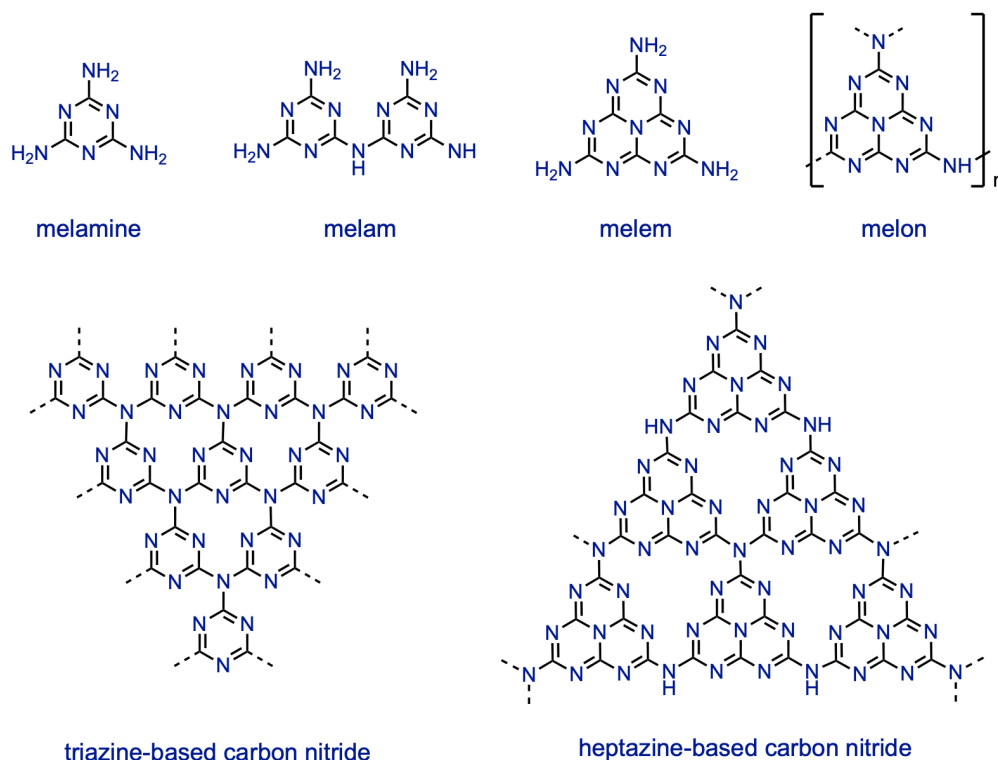


FIGURE 3.1: Structural motifs of intermediates and fully-condensed planar structures of carbon nitride.

Despite this early discovery, the structures and properties of CN subclasses remained largely unexplored until the late 20th century. Interest in their synthesis, structural features, and electronic properties grew significantly during this period, leading to their potential application in materials science and catalysis. In 2006, graphitic carbon nitride was firstly employed as a metal-free heterogeneous catalyst.^{82,83} Since then, research on CN and its application has flourished, placing it at the forefront of contemporary heterogeneous catalysis. Its success of carbon nitride in catalysis primarily originates from its semiconductor properties and visible-light absorption wavelength, with a bandgap of approximately 2.7 eV (corresponding to an absorption wavelength of around 460 nm) and with the conduction band (CB) and valence band (VB) positioned at approximately -1.1 eV and $+1.6$ eV versus the normal hydrogen electrode (NHE).⁸⁰ Additionally, carbon nitrides exhibit excellent chemical and thermal stability (up to 600°C in air) due to their high degree of condensation and layered structure.^{77,84}

From a synthetic point of view, CNs are prepared by thermal polymerization of cheap nitrogen-rich precursors, such as melamine and urea.^{85,86} This synthetic approach is convenient and easy scalable, consisting of a calcination driven in solid state. The features of carbon nitride materials can be effectively tuned by altering various factors such as the

synthetic method, the choice of precursors, and the specific polymerization conditions.⁸⁷ Consequently, material engineering to modulate CN properties represents a key step toward the achievement of a wide range of catalytic application, positioning CN-based catalysis as a highly active area of research. The applicability of CN overarches photocatalysis, organocatalysis, and electrocatalysis, being a promising catalysts for processes such as hydrogen production, water oxidation, organic synthesis, degradation of pollutants and CO₂ reduction.^{55,86,88–90}

In the last years, growing interest in visible-light photocatalysis has led to the development of a large number of photocatalytic organic reactions. In fact, implementing photocatalytic synthetic routes for the production of industrially relevant compounds matches current requirement for sustainable schemes to replace conventional industrial routes, often based on energy-demanding operating conditions with large environmental impact. Unlike conventional catalysis, photocatalysis takes advantage of light to generate reactive intermediates through mechanisms such as photoinduced electron transfer, energy transfer, or atom transfer processes. One common approach is that of photoredox catalysis, featuring the photon absorption by the catalyst (a homogeneous or heterogeneous species) which then engages in single-electron transfer (SET) processes with to produce reactive radical species under mild conditions.^{91–93} When in their excited state, these photoredox catalysts (PCs) can serve as strong oxidants, reductants, or both oxidants and reductants, enabling access to unique catalytic environments. Thus, photoredox catalysis is used to reach complex molecules, also enabling uphill processes. Light-driven organic reactions have been predominantly mediated by homogeneous molecular catalysts, typically based on transition metals, such as ruthenium or iridium complexes, and metal-free organic dyes.^{92,94,95} On the other hand, semiconductor materials can serve as alternatives molecular catalysts, offering the advantage of facilitating recovery, recycling and, consequently, potentially lower the overall costs of the chemical production process. When irradiated with photons of sufficient energy, it undergoes charge separation, resulting in the formation of electron-hole pairs that, after separation of the two charges, can be individually exploited in the reductive and oxidative steps *en-route* to the desired of organic transformations (Figure 3.2). Over the last few years, carbon nitride has been extensively investigated in organic photoredox catalysis, standing out as one of the most versatile visible-light activated photocatalyst, showing compatibility with many kinds of reactions. In particular, the collaboration between material science and organic chemistry has enabled the development of photocatalytic protocols for the sustainable production of organic compounds of industrial interest, exploiting the tunability of CN properties to specifically drive an efficient photocatalysis.⁸⁶

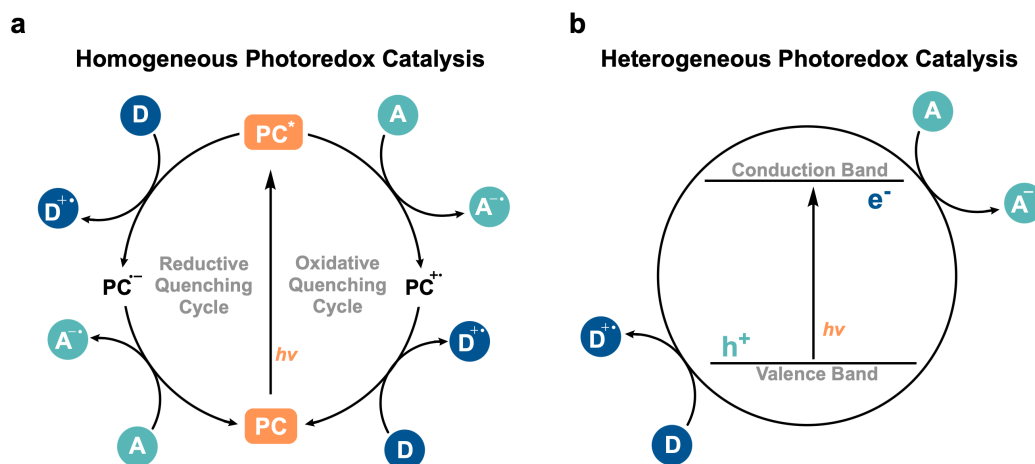


FIGURE 3.2: Schematic mechanism of homogeneous and heterogeneous photoredox catalysis.

A fascinating strategy of great utility is the accomplishment of challenging transformations, involving C–C and C–X (X = nonmetal heteroatom) couplings. These types of coupling are dominated by the use of dual metallaphotoredox catalytic approaches, for which examples in literature have been proliferating over the last decade. The approach makes use of the synergy between a photocatalyst and a homogeneous transition metal complex (TMC), interconnecting a photoredox mechanism with a non-photochemical second catalytic cycle.^{96,97} A more detailed description of this catalytic mechanism and the use of carbon nitride as photocatalytic counterpart in the dual mechanism will be discussed in the following paragraph.

3.1.1 Dual Nickel-Carbon Nitride Photocatalysis

Dual metallaphotoredox catalysis leverages the cooperative effects of two distinct catalytic components, typically a transition metal complex (such as palladium, copper, or nickel) and a photocatalyst, to unlock new reaction pathways under mild conditions. Since Sanford's pioneering work in 2011,⁹⁸ followed by independent reports from MacMillan, Doyle^{99,100} and Molander¹⁰¹, the use of photoredox catalysis in metal-mediated processes has attracted significant interest.¹⁰⁰

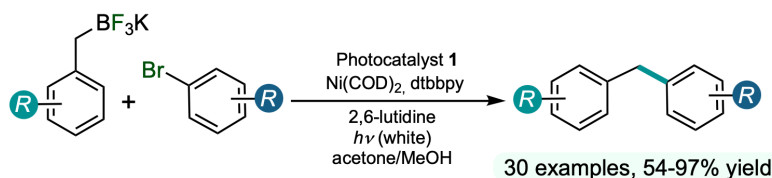
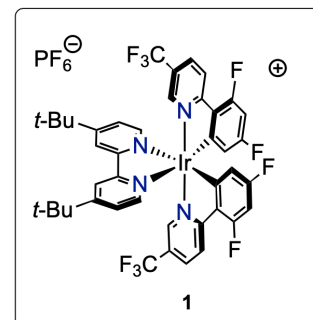
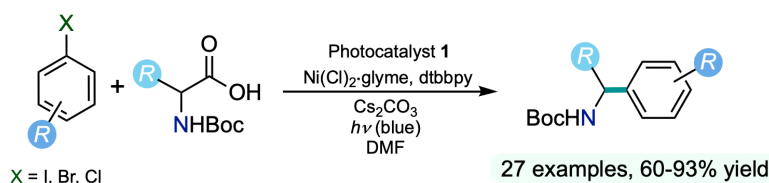
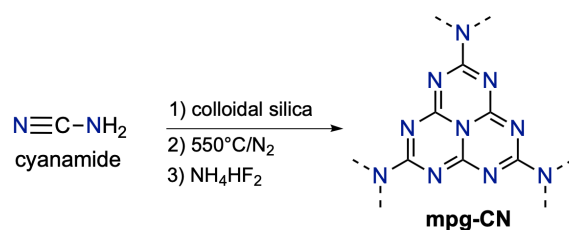
Molander, 2014**Doyle and MacMillan, 2014**

FIGURE 3.3: Dual nickel photoredox reactions, pioneered by the Molander, Doyle, and Macmillan groups in 2014.^{99–101}

A widely investigated example consists in the combination of a visible-light molecular photocatalyst with a nickel-based catalyst, affording numerous C–C and C–heteroatom couplings. It is worth noting that these synthetic steps are crucial for assembling small fragments into complex molecules and are among the most relevant processes in organic synthesis. This strategy may set the scene for implementing a more sustainable alternative to traditional transition metal-catalysed coupling reactions, which typically exploit precious metals. In particular, it could alleviate the dependence from palladium-based catalysts, that entail significant economic and environmental costs and that currently dominate this field of research.¹⁰² In comparison with palladium, nickel is a much more affordable and available metal, making it a practical alternative in terms of cost. Beyond its economic benefits, nickel also bears physical and chemical properties that can prove beneficial for several catalytic reactions. For example, Ni is more electropositive than palladium, facilitating oxidative addition with electrophiles, and it also offers flexibility due to its multiple accessible oxidation states, making it suitable for chemical transformations that require more complex synthetic pathways. Initial studies of dual Ni photoredox catalysis predominantly used Ru- or Ir-based complexes (e.g. polypyridyl complexes) as the photocatalytic component.^{103,104} These metal-based systems have been gradually replaced by more cost-effective alternatives, such as organic dyes.^{105,106} However, the advantages coming from their metal-free nature are counterbalanced by the various challenges faced such as a difficult recovery and recyclability. To address these drawbacks, in recent years there has been a definite shift towards the employment of heterogeneous photoredox catalysts based on semiconductors, which offer a large number of benefits like simple preparation, low cost, excellent optoelectronic properties, and improved stability and recyclability. Thus, in this case, the dual

photocatalysis involves the use of a homogeneous Ni complex and heterogeneous photocatalyst, following a semi-heterogeneous mechanism. A wide range of materials, including transition metal oxides and dichalcogenides, semiconductor quantum dots (QDs) and metal-organic frameworks (MOFs), have been successfully utilized to enable C–heteroatoms coupling reactions.¹⁰⁶ Among the diverse semiconductors explored, g-CN and its derivatives stand out as some of the most studied semiconductors on account of their low toxicity and cost-effectiveness. Despite today CN are the most prominent class of photocatalysts, their rise is only very recent. The first example of dual Ni/heterogeneous CN photoredox catalysis has been reported in 2019 by König and co-workers, who investigated a mesoporous graphitic carbon nitride (mpg-CN) combined with a Ni catalyst for the under blue light irradiation to perform C–N couplings between aryl halides and amines under blue light irradiation (Figure 3.4).¹⁰⁷

a) Mesoporous graphitic carbon nitride (mpg-CN) preparation



b) Dual Ni/mpg-CN catalytic C–X functionalizations

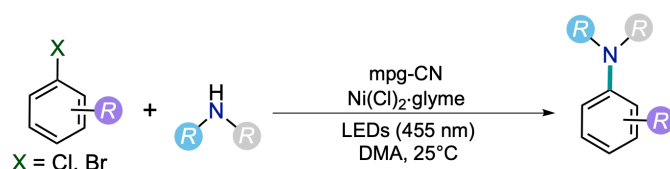


FIGURE 3.4: First reported study of dual Ni/CN photocatalysis employing mpg-CN. a) Synthetic procedure of mpg-CN. b) Dual Ni/mpg-CN catalytic C–X functionalizations' protocol.

Numerous studies followed in the next years, focusing not only on expanding the scope of C–N, C–O, and C–S cross-couplings across a broad range of reactions, exploring the catalytic effect of altering the structure of the CN. Moreover, important insights were acquired on the deactivation of the catalytic system due to the formation of nickel black, and on the possibility of catalyst recycling.^{108–110} More recently, these dual semi-heterogeneous catalytic systems have been explored as fully heterogeneous platform, where a CN–Ni catalyst is preassembled, forming a "all-in-one" CN–Ni photocatalyst.^{111–113} It must be emphasized that the integration of Ni on carbon nitride requires the availability of suitable coordination environment (typically N moieties on the CN), able to bind the Ni without quenching its catalytic activity. Another possibility is to anchor the metal in form of active nanoparticles.

The mechanism of dual nickel-carbon nitride catalysis has been widely discussed, and several hypotheses have been advanced. Currently, the most widely accepted mechanism, also supported by density functional theory (DFT) calculations, entails a single electron transfer (SET) from the photo-excited semiconductor to the Ni(II) precatalysts, forming a reactive Ni(I) intermediate, which is then capable of initiating a self-sustaining Ni(I)/Ni(III) dark catalytic cycle (Figure 3.5).^{106,114}

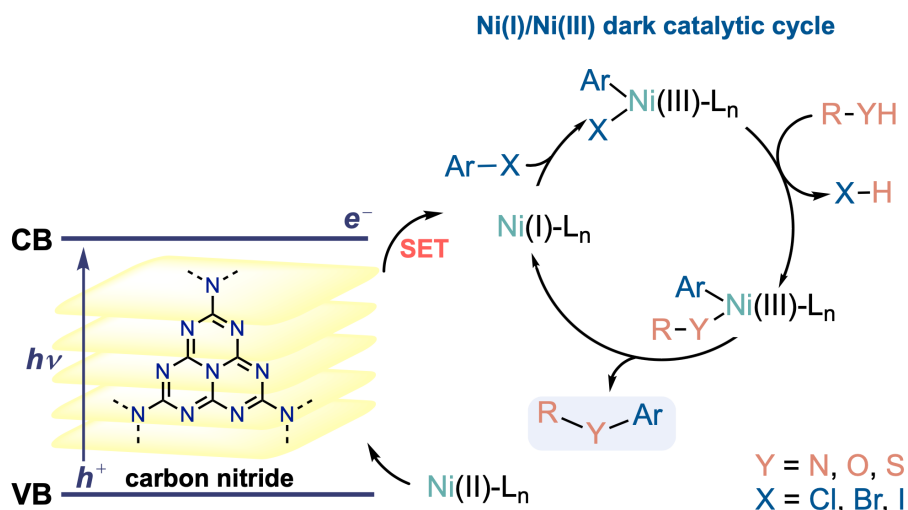


FIGURE 3.5: Proposed mechanism of dual Ni/CN photocatalysis.

In this mechanistic scenario, the photocatalyst ensures the reactivity by continuously reducing the eventually regenerated Ni(II) catalyst into active Ni(I) species, through SET, thereby maintaining the catalytic cycle. In both semi- and fully heterogeneous systems, the interaction between the heterogeneous catalyst and the homogeneous Ni complex represents a key element for efficient electron transfer. However, this interplay remains elusive and not fully understood. It remains still unclear whether the electron transfer occurs after nickel adsorbs onto the CN surface or if it is mediated by molecular radicals formed in the solution. This is an important point, because it implies considerations on the the diffusion of the Ni complex towards the SC's surface as a catalytic relevant factor. Moreover, the reaction may also take place directly on the semiconductor-bound nickel, making the CN design crucial to ensure suitable anchoring of the nickel for optimal performance.

3.1.2 Post-Synthetic Modifications of Carbon Nitride

Carbon nitride can be a versatile platform for numerous types of modifications, allowing a fine-tuning the physiochemical properties. Such a possibility leads to an optimum design of optimized photocatalysts that meet the specific requirements of targeted applications. In

fact, CN materials present structural a rich variety of defects, which can be exploited for various purposes in catalysis, provided that such a defect type distribution is controlled upon synthesis of the finale material. Common CN modifications include non-metal heteroatom doping, introduction of covalent functional groups, nanostructure and defect engineering (Figure 3.6), and provide a wheel to modulate electronic band edges and the bandgap, to extend the lifetime of photogenerated charges, to increase the typically small surface area, and to introduce additional catalytic sites.^{79,115,116}

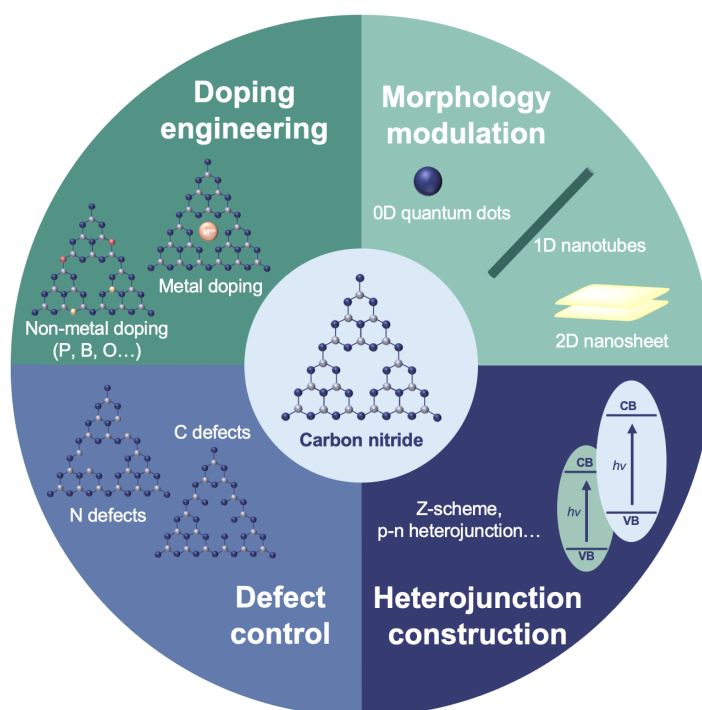


FIGURE 3.6: Overview of the most employed modification strategies for carbon nitride.

Structural alteration of CN can be achieved either through *in situ* modifications during the preparation process, or *via* post-synthetic treatment of the pre-formed carbon nitride. Post-synthetic routes, in particular, are effective means to *ad hoc* tailor the photocatalytic properties with easier control, and have been explored in various applications, including organic photocatalytic transformations. On the other hand, post-synthetic treatments remain relatively underutilized in organic photocatalysis, leaving considerable opportunities for further exploitation. Several examples demonstrate the power of post-synthetic modification of CN in altering the photocatalytic behavior. Dai *et al.* reported a comparison between g-CN nitride and amorphous carbon nitride (**am-CN**), the latter deriving from a process of annealing at 630°C under Ar atmosphere of the g-CN. The explored reaction was the selective photoreduction of nitrobenzene to azobenzene or azoxybenzene.¹¹⁷ Even though **am-CN** had a higher surface area, it showed a too strong adsorption towards hydrogen atoms (H_{ads}), that

prevented their ability to effectively reduce the substrate, with an overall poor performance. On the contrary, in 2020 our group investigated the use of amorphous CN (am-CN) for successful photocatalytic perfluoroalkylations of electron-rich organic substrates.¹¹⁸ In particular, various post-synthetic modifications of a melamine-derived g-CN were explored: amorphization, reduction and oxidation treatments of CN structure. The cross-comparison among these modified CNs highlighted the strong structure/activity relationship and, notably, the importance of reagent affinity with the catalyst surface through halogen bonding. From advanced NMR techniques, combined with DFT calculations, it turned out that am-CN had the highest affinity towards the fluorinated substrate, one of the main factors to ensure the highest activity. The highest energy of halogen bonding originated from the amorphization treatment itself, which leads to a partial disruption of the intraplanar hydrogen bonds of the NH/NH₂ groups within the melem strands, reducing long-range order and increasing the availability of N atoms to engage in halogen bonds. Moreover, longer annealing treatment for a higher grade of amorphization has been reported to improve the catalytic performance in the perfluoroalkylation.¹¹⁹

Another example is represented by oxidized CN, which are characterized by the introduction of carboxyl, hydroxyl and ketone groups over the CN surface. Krishnan and co-workers developed a rationally designed oxidized carbon nitride, prepared by chemical oxidation of pristine CN, for efficient catalytic hydrogen transfer reactions of carbonyl compounds to alcohols, where the introduced C=O functional groups on the CN surface act as catalytic active sites.¹²⁰ Gentile *et al.* studied the deprotonation treatment through an alkaline washing of oxidized CN material, which causes deprotonation of the carboxylic groups introduced after oxidation. The resulting material behaves as a heterogeneous base catalyst, as also confirmed by pH measurements. Thanks to the introduction of basic sites, Knoevenagel condensation reactions between benzaldehydes and malononitrile were successfully performed, with good to excellent yield.¹²¹

An interesting example of post-functionalization of CN has been reported by Nocera and co-workers in the context of Ni dual photoredox catalysis for the C–N and C–O couplings.¹²² In this case, they employed a cyanamide-functionalised carbon nitride ($^{\text{NCN}}\text{CN}_x$), which exhibited an extended absorption in the visible region, together with a reduced charge recombination rate as compared to the unmodified CN. As a consequence, the long-lived electrons could be more effectively used to reduce Ni(II) species and therefore driving a productive Ni(I/III) catalytic cycle.

The various examples mentioned above demonstrate the potential of post-synthetic functionalization, by which the catalytic properties of CN structures can be adapted to the specific reaction requirements. Despite the very rapid growth of interest, the field is still in its early development, not only in terms of extension of the applicative scope, but in particular in relation to the fundamental and general aspects of the structure/activity relationship of the photocatalytic system. In-depth knowledge of the mechanistic details, and hence of the

catalysts' limitations and potentiality will be crucial for future implementation at industrial level.

3.2 Aim of the Research Project

On account of the above described large interest in developing and understanding dual Ni-CN organic redox photocatalysis, the objective of the present project was to study in detail the effect of structural modification of CN for enhancing the activity in Ni-CN dual photocatalysis for various C-X (X = N, O, S) heterocoupling reactions. The strategy leverages on the optimization of the binding of Ni species to the CN surface, in order to control the photoinduced electron transfer process and thereby the activity and stability of the catalytic system. The designed post-synthetic modification of the melamine-derived **g-CN** involves the use of low-cost microwave irradiation under optimized conditions. Such a treatment generates suitable N moieties on the CN through a mechanism assisted by C-vacancies formation. The modified structure is able to coordinate the Ni center during the dual mechanism of the catalysis with opportune strength, which is dependent on the specific oxidation state of the Ni during the catalytic cycle. The resulting dual photoredox cycle can therefore works in a semi-heterogeneous fashion, driven by a bind/release equilibria of the Ni active site to/from the CN surface. Efforts were made on unraveling the key features of the mechanisms, for which a profound knowledge of the Ni-CN interaction was necessarily acquired using multiple characterization techniques and computational analysis.

3.3 Results and Discussion

3.3.1 Preparation and Characterization of Microwave-Treated Carbon Nitride (mw-CN)

Carbon nitride can be modified through post-synthetic treatments to introduce task-specific vacancies within its structure. Although less explored than N-vacancies, the generation of C-vacancies in the the CN network has typically been achieved through thermal treatments under various conditions, and applied in several energy- or environmental-related processes.^{123–126} In this project, we developed a simple yet effective approach post-synthetic approach using microwave (MW) irradiation to tune the pristine CN into a functional defective structure.¹²⁷ Microwave irradiation, being a low-energy and industrially appealing strategy, has generally been employed for the bottom-up synthesis of carbon nitride to drive precursor polymerization.^{128,129} In contrast, using MW treatment as a controlled method of modification on the ready CN scaffold is a novel approach, with the potential to subtly tailor the catalyst structure. As part of this work, we investigated the introduction of C-vacancies in the CN network, which consequently evolve into the formation of triazole and

imine/amine N moieties (Figure 3.7). In detail, graphitic carbon nitride (g-CN) was first synthesized through thermal polymerization of melamine at 550°C, and the pristine g-CN was subsequently treated in an aqueous medium at 190°C for 45 minutes under MW irradiation at a maximum of 300 W, yielding microwave-treated carbon nitride (**mw-CN**).

As terms of comparison, we synthesized different reference CN materials: oxidized CN (**ox-CN**), strongly oxidized CN (**CNO**), and amorphous CN (**am-CN**), following established procedures in the literature.^{118,121} Detailed information regarding the synthetic protocols and their characterization is provided in the Experimental Section.

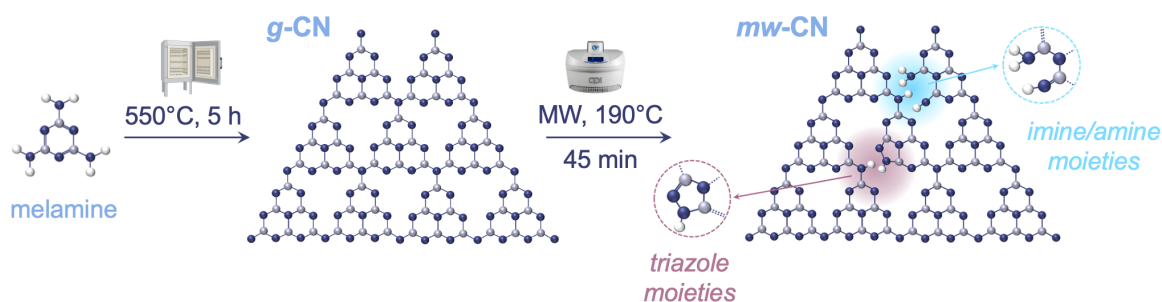


FIGURE 3.7: Schematic representation of the synthetic procedure for **mw-CN**.

It turns out that the MW treatment does not affect significantly the crystallinity of the CN, and the **mw-CN**'s lattice remains largely unchanged, as confirmed by X-ray diffraction analysis (XRD) and Raman spectroscopy. The reflection peaks in the diffractograms and the absorption peaks in Raman spectra of both exhibit similar width and intensity in **mw-CN** as those observed in the untreated **g-CN** (Figure 3.8a and 3.8b). Furthermore, UV-Vis diffuse reflectance spectroscopy (DRS) absorption spectra and subsequent Tauc plot analysis revealed that the optical properties of mw-CN are comparable to those of **g-CN**, with a bandgap values of 2.66 eV and 2.64 eV, respectively, indicating a minimal alteration in the optical features. Consistently with these observations, scanning transmission electron microscopy (STEM) analysis shows no visible change of morphology following MW treatment (Figure 3.9c and 3.9d).

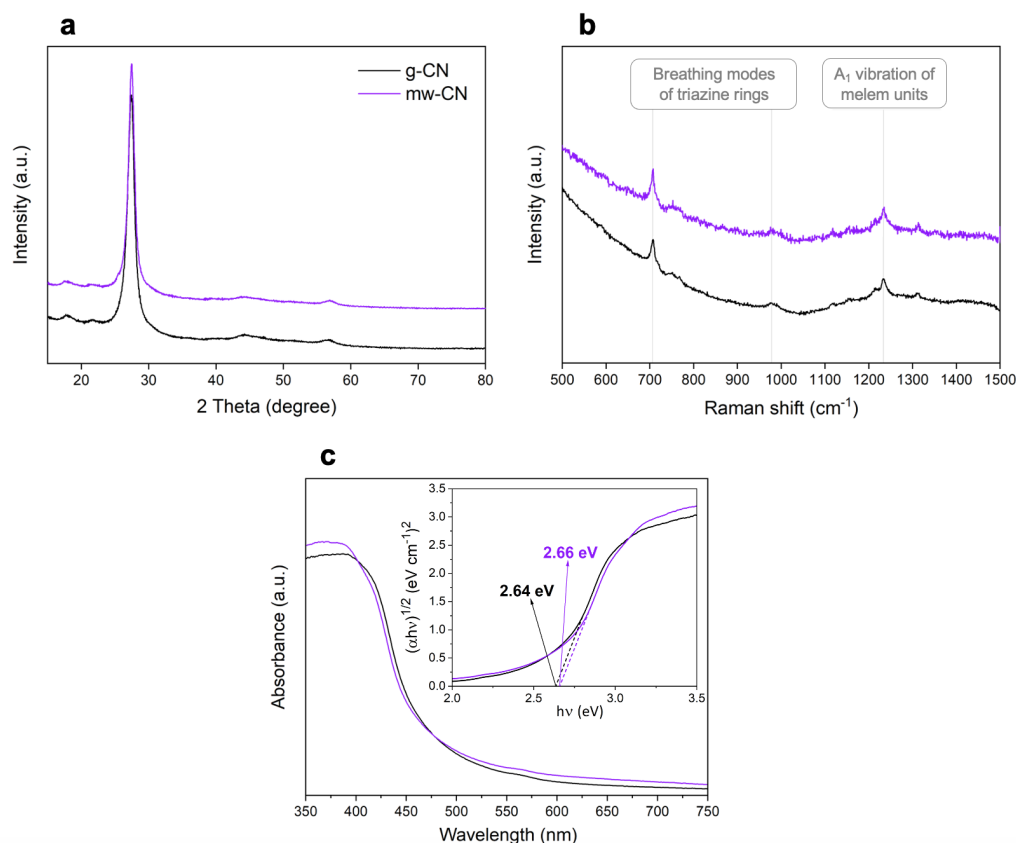


FIGURE 3.8: Material characterizations. (a) XRD diffractograms, (b) Raman spectra, (c) UV-Vis DRS spectra and the corresponding Tauc plot with band gaps (inset) of **g-CN** and **mw-CN**.

Despite the similarities of the crystalline and optical properties, a distinct enhancement in both surface area and cumulative pore volume is observed after MW irradiation (Figure 3.9). N₂ physisorption analysis shows that **mw-CN** exhibits a pronounced type IV isotherm, with a pronounced hysteresis loop, characteristic of mesoporous materials. The Brunauer-Emmett-Teller (BET) surface area of **mw-CN** is approximately six times larger than that of pristine **g-CN**, reaching 61.6 m² g⁻¹, with a corresponding increase in cumulative pore volume to 0.22 cm³ g⁻¹. Additionally, **mw-CN** displays a bimodal pore size distribution, with maxima at 40 nm and 7 nm as calculated from by the Barrett-Joyner-Halenda (BJH) analysis of the desorption branch of the isotherms. Compared to **g-CN** and other CN derivatives listed in Table 3.1, **mw-CN** distinguishes itself with a more porous structure and reduced pore diameters.

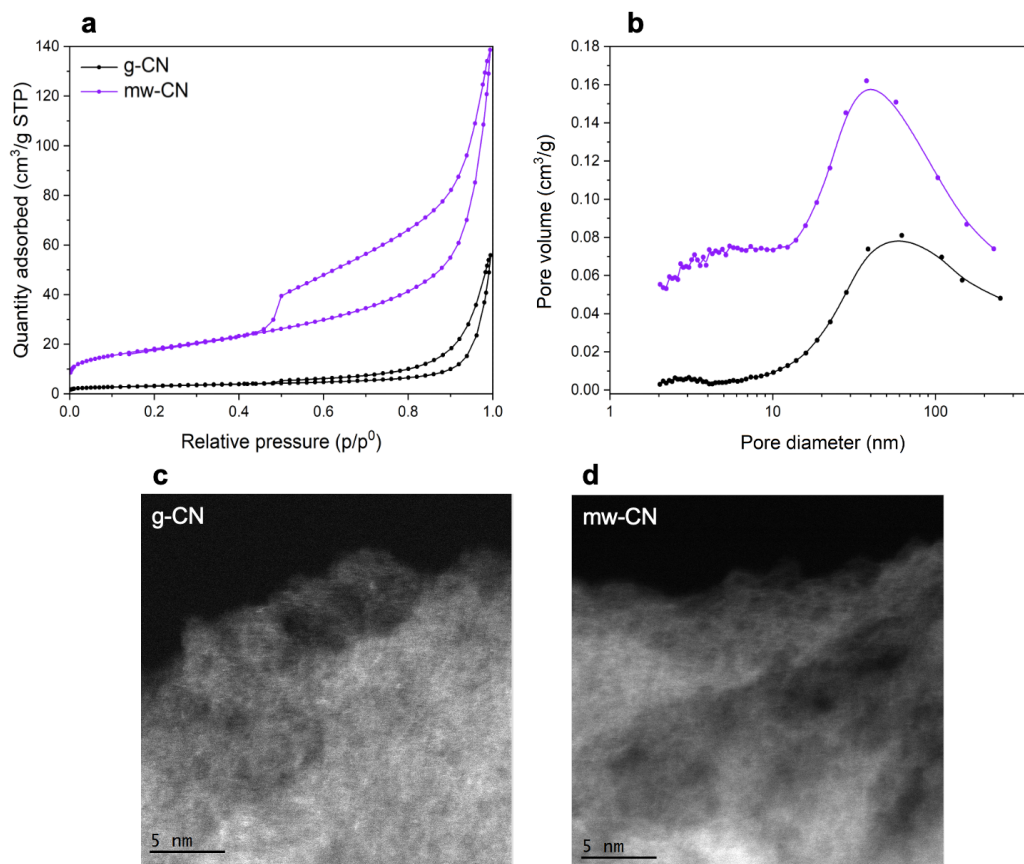


FIGURE 3.9: Materials characterizations. (a) N₂ physisorption isotherms at liquid nitrogen temperature of **g-CN** and **mw-CN**. (b) BJH pore size distributions of **g-CN** and **mw-CN**. STEM images of (c) **g-CN** and (d) **mw-CN**.

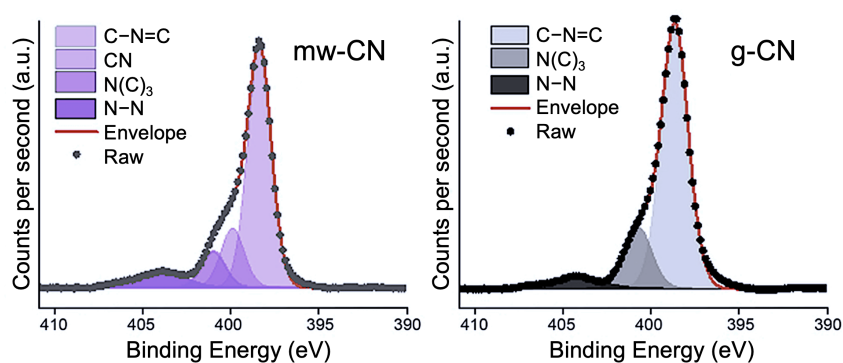


FIGURE 3.10: N1s high-resolution XPS spectra for **mw-CN** (left) and **g-CN** (right).

The comparison between **mw-CN** and **g-CN** through X-ray photoelectron spectroscopy

(XPS) provided crucial insights into the structural changes induced by microwave treatment. In particular, the deconvolution of N1s XPS spectrum of **mw-CN** reveals the presence of the typical CN components at 398.3 eV (C=N-C) and 401.0 eV (N(C)₃),¹¹⁸ along with an additional contribution at 399.9 eV, which is frequently assigned to N-H moieties. This component was identified in both **mw-CN** and **g-CN**, although its percentage was notably higher in **mw-CN** (9.6 at%) compared to **g-CN** (6.4 at%). These XPS spectral assignments, including peak positions and relative areas, are reported in detail for the various CN derivatives in the Experimental Section 3.5 (Table 3.3) Furthermore, **mw-CN** shows a significant lower C at%, resulting in a reduced C/N ratio of 0.70, in agreement with the formation of carbon vacancies within the heptazine network after the MW treatment, aligning with the observed increase in N-N and N-H components. In fact, the introduction of C-vacancies has been reported to occur through unpaired electrons on nitrogen sites,¹³⁰ which may either couple to form N-N bonds (as in triazole moieties) or generate imine/amine groups by abstracting a hydrogen atom from the solvent.

TABLE 3.1: Textural properties, bandgap and XPS data of **g-CN** and **mw-CN**.

Material	BET surface area (m ² g ⁻¹)	Cumulative pore volume (cm ³ g ⁻¹)	Cumulative pore maximum (nm)	Bandgap (eV)	C at%	N at%	O at%	C/N
g-CN	10.2	0.09	56	2.64	42.3	57.7	–	0.73
ox-CN	7.4	0.09	57	2.68	41.9	52.7	5.4	0.79
CNO	21.8	0.15	58	2.93	39.8	52.8	7.4	0.75
am-CN	14.8	0.14	108	2.49	43.1	56.9	–	0.76
mw-CN	61.6	0.22	40 and 7	2.66	40.2	57.1	2.6	0.70

Additional characterization techniques were carried out to corroborate the hypothesis of the mild introduction of C-vacancies and related nitrogen functionalities within the heptazine framework, additional advanced characterizations are required. In collaborations with the University of Manchester (group of Prof. C. D’Agostino), the University of Torino (group of Prof. M. Chiesa) and Elettra Sincrotrone Trieste (Dr. Federica Piccirilli), a comprehensive analysis of the **mw-CN** structure was performed by means of solid-state nuclear magnetic resonance (ssNMR), electron paramagnetic resonance (EPR) spectroscopy, and Fourier transform infrared (FTIR) spectroscopy with nanoscale resolution. Q-band EPR experiments were used to understand differences in defectivity between the two samples **g-CN** and **mw-CN**. The resulting spectra, shown in Figure 3.11a, are nearly

superimposable, demonstrating that the two samples contain comparable amounts of native $S = 1/2$ paramagnetic defects. This suggests that the paramagnetic defect structure remains largely similar between the materials even after MW treatment. Moreover, electron nuclear double resonance (ENDOR) experiments revealed no substantial differences in the local proton environment of the defects. The absence of clearly resolved components indicates that the paramagnetic species share a relatively heterogeneous local environment. The minimum electron spin-proton distance, estimated using a point-dipolar approximation, is approximately 4.3 Å, consistent with a heptazine-based structure. However, ^{15}N ssNMR spectra (Figure 3.11c) reveal distinct differences in the terminal region of heterogeneous $-\text{NH}_2$ environments (between -270 and -300 ppm relative to CH_3NO_2) for **mw-CN**. This region is partly related to the twisting of the heptazine chains, which facilitate a porous structure.¹³¹ Specifically, **mw-CN** exhibits an increased peak intensity, indicating a higher proportion of NH_2 environments compared to **g-CN**.

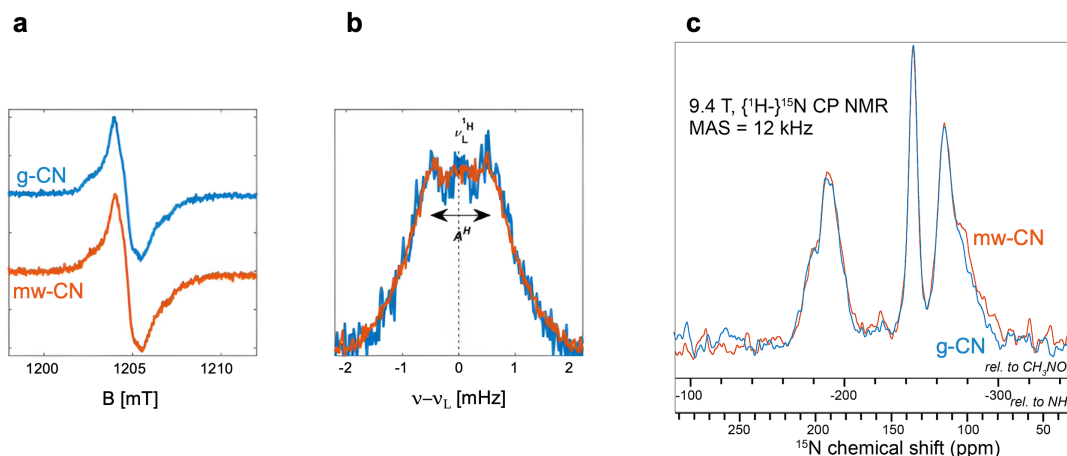


FIGURE 3.11: (a) Q-band EPR spectra recorded at room temperature of **g-CN** (blue) and **mw-CN** (orange); (b) ENDOR spectra recorded at the field position correspondent to the maximum echo intensity (1204.6 mT); (c) ^1H ^{15}N CPMAS NMR spectra of **g-CN** and **mw-CN** recorded at 9.4 T using a MAS frequency of 12 kHz at ambient temperature.

The FTIR absorption spectrum of **mw-CN** (Figure 3.12a) presents distinct differences primarily in the range of vibration modes associated with the heptazine skeleton ($1400\text{--}1700\text{ cm}^{-1}$). Nanoresolved IR measurements highlights an overall enhancement of the absolute absorption, particularly in the spectral regions $1400\text{--}1600\text{ cm}^{-1}$, which is mainly related to C–N stretching, and $2000\text{--}2300\text{ cm}^{-1}$, suggesting the formation of a denser population of $-\text{NH}_2$. In addition, a blueshift of heterocycle vibrational modes is detectable, which can be associated with C-vacancies formation.¹³² These structural modifications were further investigated using nanoresolved imaging analysis. Topography maps were generated for three selected signals: 1400 and 1575 cm^{-1} (both related to C–N modes), and 1640 cm^{-1} (due

to C=N vibrations). The corresponding absorption maps, as shown in Figure 3.12b, confirm the more intense absorption throughout the **mw-CN** sample, consistent with the IR spectra. Notably, **mw-CN** exhibits a higher standard deviation compared to **g-CN**, indicating that **mw-CN** functionalities are less homogeneous at the nanoscale.

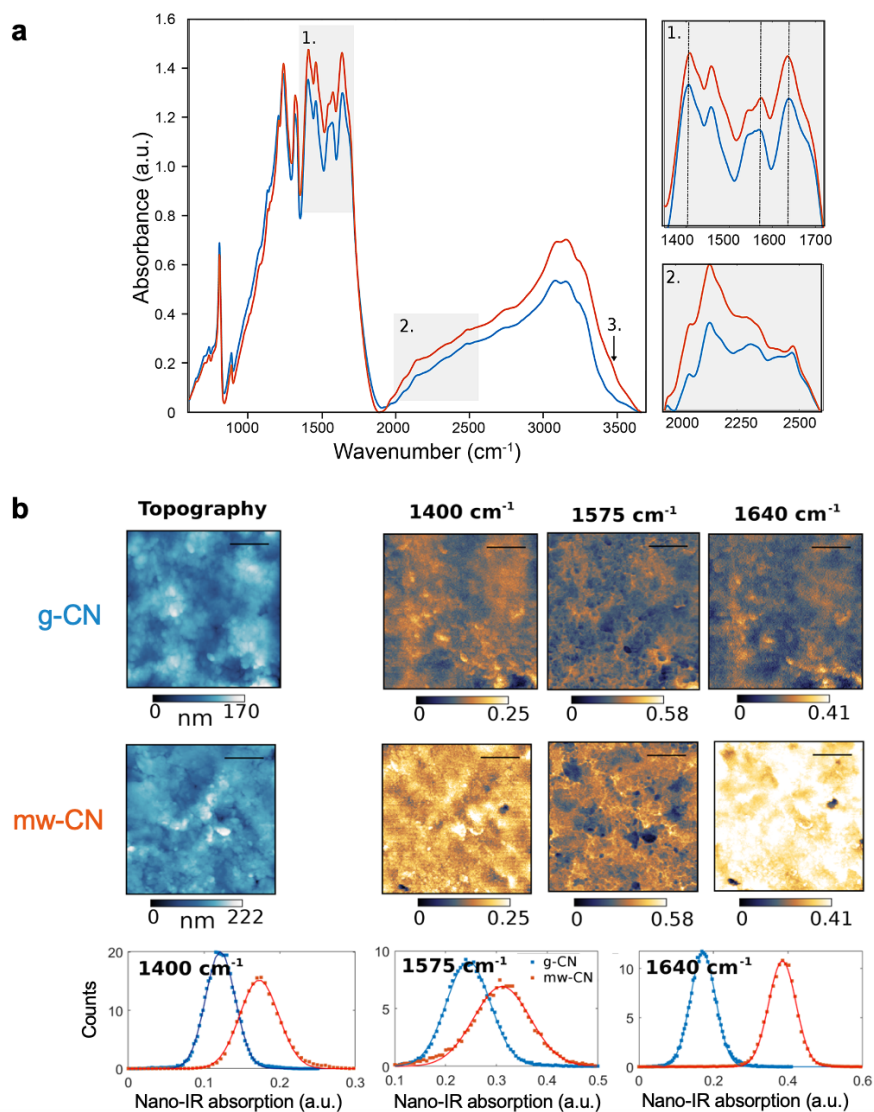


FIGURE 3.12: a) FTIR absorption spectra in KBr pellets 10% w/w of g-CN (blue) and mw-CN (orange). b) Topography maps (AFM), absorption maps and phase distribution plots of g-CN and mw-CN acquired at three wavenumbers, from left to right respectively at 1400, 1575 and 1640 cm⁻¹.

3.3.2 Initial Studies on Dual Ni/CN Photoredox Catalysis

The C–X coupling reactions were initially investigated through a model C–N coupling reaction between methyl 4-bromobenzoate (**1a**) and pyrrolidine (**2a**) under blue-light irradiation

to evaluate the photocatalytic activity of the CN materials (Figure 3.13). The experiments were conducted at room temperature in dimethylformamide (DMF) under blue-light irradiation by a light-emitting diode (LED, $\lambda = 450$ nm) strip over a period of 24 hours. A low photocatalyst loading (2.5 mg mL^{-1}) was set for g-CN and its various CN derivatives, ensuring a meaningful comparison of the activities. Control experiments were carried out to confirm the dual photocatalytic nature of the process. Reactions performed in the absence of light, without the Ni salt, or without the photocatalyst resulted in no observable product formation (Entries 8-10, Table 3.2). Preliminary optimization studies for this model reaction are detailed in the Experimental Section 3.5.

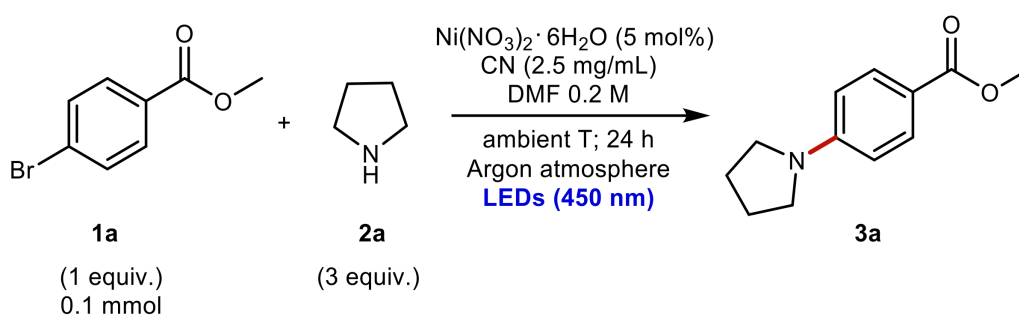


FIGURE 3.13: Scheme of the model C-N coupling reaction.

Pristine g-CN achieved a moderate chemical yield of the desired product **3a** at 48% (Entry 1, Table 3.2). In contrast, the oxidized carbon nitrides (**ox-CN** and **CNO**) and amorphous CN (**am-CN**) exhibited lower performances, with significantly reduced yields. The decrease in yield should originate from the structural, electronic and optical modifications of the properties of these materials. For example, the bandgap energy is different for **CNO** and **am-CN**, the former exhibiting a wider bandgap (2.93 eV) and the latter a narrower one (2.43 eV). Additionally, the introduction of oxygen-containing functional groups through oxidative treatment may alter the electronic structure, the catalytic active sites and the interaction between the semiconductor and the Ni catalyst. The loss of crystallinity in **am-CN** could also negatively affect this particular catalytic reaction, for instance undergoing faster charge recombination rates due to defect sites that can act as recombination centers. On the contrary, **mw-CN** demonstrated a substantial improvement in the performances, achieving a yield of 87% (Entry 5, Table 3.2). When employing a higher intensity Kessil lamp (456 nm, 200 W m^{-2}), the yield was further enhanced, reaching 97% (Entry 6, Table 3.2). The use of Kessil lamp not only increased the yield, but also reduced the standard deviation across repeated measurements, thereby improving reproducibility and consistency of the results. To compare our result with existing literature, we evaluated the rate of production of **mw-CN**, which reached $3.0 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$. To rule out a mere geometric effect due to the higher surface area of **mw-CN**, the rate of production was also calculated after normalization by

the surface area, achieving a $4.87 \times 10^{-2} \text{ mmol m}_{\text{cat}}^{-2} \text{ h}^{-1}$, which suggests that the new catalyst has a significant higher intrinsic activity than the benchmark material consisting of mesoporous carbon nitride (mpg-CN), that showed a production rate of $0.67 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ and a much lower surface area-normalized rate of 4.79×10^{-3}).

TABLE 3.2: Comparison of activity between the various CN photocatalysts of the model C–N coupling schematized in Figure 3.13 and control experiments performed on the best catalyst to confirm the nature of the synthetic approach. Reactions were performed on a 0.1 mmol scale, with three independent replicates. (a) Yield determined by ^1H NMR spectroscopy using 1-fluoro-2-nitrobenzene as internal standard.

Entry	CN photocatalyst	Deviation	Yield 3a % ^(a)
1	g-CN	None	48 ± 5
2	am-CN	None	7 ± 5
3	ox-CN	None	24 ± 2
4	CNO	None	5 ± 2
5	mw-CN	None	87 ± 8
6	mw-CN	Kessil lamp (456 nm)	97 ± 3
7	mw-CN	In the dark	0
8	mw-CN	No Ni catalyst	0
9	None	None	0
10	mw-CN	In air	0

3.3.3 Mechanistic Investigation

As discussed in the Section 3.1, the accepted mechanism for the dual Ni-CN photoredox catalysis is initiated by the photoinduced SET from the photo-excited semiconductor to the Ni(II) precatalysts, reducing the oxidation state of the Ni center to +1. The redox cycle can then start with a sequential Ni(I)/Ni(III) switch on the Ni oxidation state. On the developed Ni/**mw-CN** catalytic system, EPR experiments and density functional theory (DFT) analysis confirmed a predominant charge transfer from the CN photocatalyst to the nickel center, in particular to the $d(x^2-y^2)$ orbital.¹²⁷ Although the theoretical calculations performed in collaboration with Prof. R. Lazzaroni of University of Mons will not be discussed in great detail in this chapter, as they fall outside my project, they provide valuable insights regarding the dual mechanism and the binding of CN to the nickel species. Therefore, they are briefly outlined below to highlight the main points.

After initial calculations on the model Ni complex in the reaction conditions, the binding between mw-CN to nickel was computed. Heptazine-based molecular models have been selected to represent the various defects that were experimentally identified in the CN materials, and they were used as ligands for the nickel center. For the **g-CN**, tertiary nitrogen

atoms of heptazine and -NH_2 groups have been investigated, while tertiary and secondary nitrogen of the triazole and imine/amine nitrogen coordinating sites were added in the case of **mw-CN**. The computed complexation energy indicated that the imine N strongly coordinates the nickel ion, with the highest complexation energy of -101.0 kcal/mol. Additionally tertiary nitrogen-coordinating triazole and the nitrogen in the heptazine structure have been identified as favorable sites for the binding of Ni atoms, with complexation energies close to that of imine nitrogen (Experimental Section 3.5, Table 3.5) In contrast, the secondary nitrogen of triazole and the -NH_2 functionalities act as weaker ligand. Therefore, the **mw-CN** structure presents additional sites that favor the binding of Ni species on CN surface. Importantly, after the photoinduced electronic transfer from **mw-CN** to the metal complex, the resulting Ni(I) centers are no longer energetically stable and readily dissociate. From the mechanism point of view, the de-coordinated Ni(I) complex can sustain the subsequent catalytic step in the form a homogeneous catalyst. The overall catalytic process can therefore be considered as semi-heterogeneous, because of the different phases in which the Ni active site is found during catalysis.

A substantial contribution to the enhanced activity is also attributed to the larger specific area in **mw-CN**, with a consequent increases of density of active sites, including the suitable tertiary nitrogen atoms of heptazine units, available for the Ni bonding. Furthermore, the imine and triazole nitrogens, distinctive of **mw-CN**, further facilitate the nickel coordination during Ni/CN dual photoredox catalysis. Hence, Figure 3.14 illustrates the proposed mechanism with the introduction of the new nitrogen-based binding sites. Specifically, following the SET from the semiconductor to the Ni(II) pre-catalyst, the reactive Ni(I) species is converted into a Ni(III) complex *via* an oxidative addition step. This complex then undergoes ligand exchange, followed by reductive elimination, resulting in the formation of the desired product and closure of the catalytic cycle.

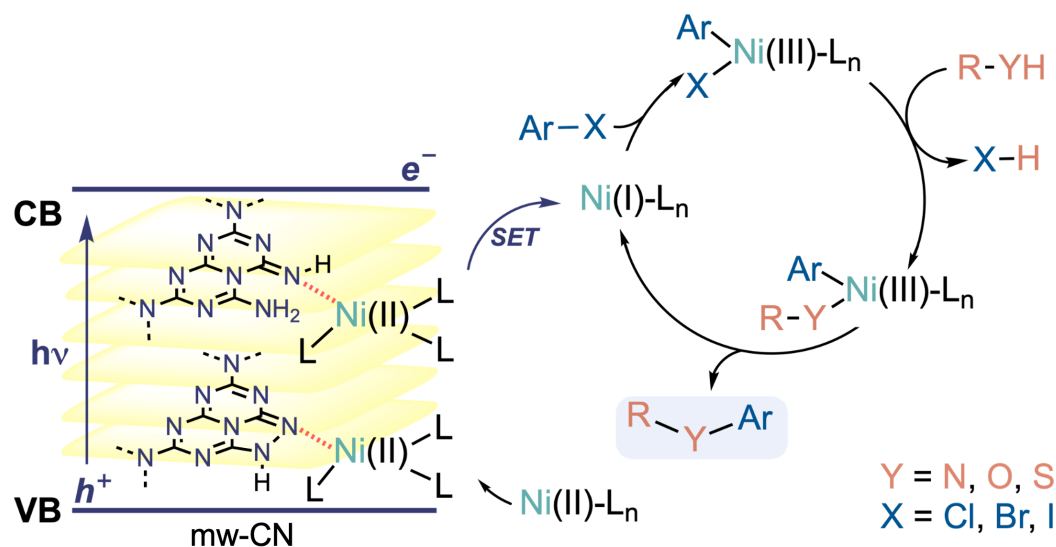


FIGURE 3.14: Proposed dual photoredox catalysis mechanism of Ni/mw-CN catalytic system.

The catalytic activity of mw-CN was also evaluated after recycling the photocatalyst. However, the yield of the C–N model reaction dropped from 97% to 50%, indicating a partial deactivation of the catalyst. A similar trend, though with a greater loss of activity, had been obtained for g-CN, with a drop from 48% to 12%. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) confirms that the CN photocatalyst retained the morphology after the catalysis. On the other hand, energy-dispersive X-ray (EDX) spectra show the aggregation of Ni, in particular in the form of NiO_x particles, and its deposition on the recovered photocatalyst, which can be the main reason for the deactivation of the catalytic system.

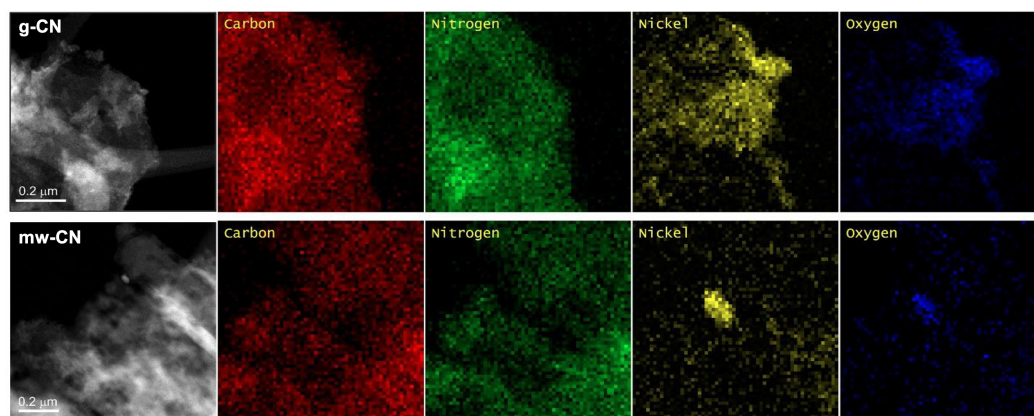


FIGURE 3.15: HAADF-STEM images and EDS maps of recovered g-CN (top) and recovered mw-CN (bottom).

3.3.4 Scope of C–N, C–O and C–S coupling reactions

The synthetic potential of the dual Ni/**mw-CN** photocatalytic approach was assessed by exploring C–N coupling reactions under optimized conditions (Figure 3.16). Various differently substituted aryl halides (generalized as **1** in the scheme below) were reacted with a range of secondary amines (**2** in the scheme below), providing the desired products **3a–e** in good isolated yields (as high as 90% for some entry). In contrast, couplings with primary aliphatic amines proved to be more challenging. However, we report an example of a coupling reaction between 4-iodobenzoate and butylamine, which produced the corresponding coupling adduct **3f** with a moderate yield of 48% at ambient temperature. The use of different electron-withdrawing groups on the aryl halides was also investigated, resulting in good isolated yields of products **3g–i**.

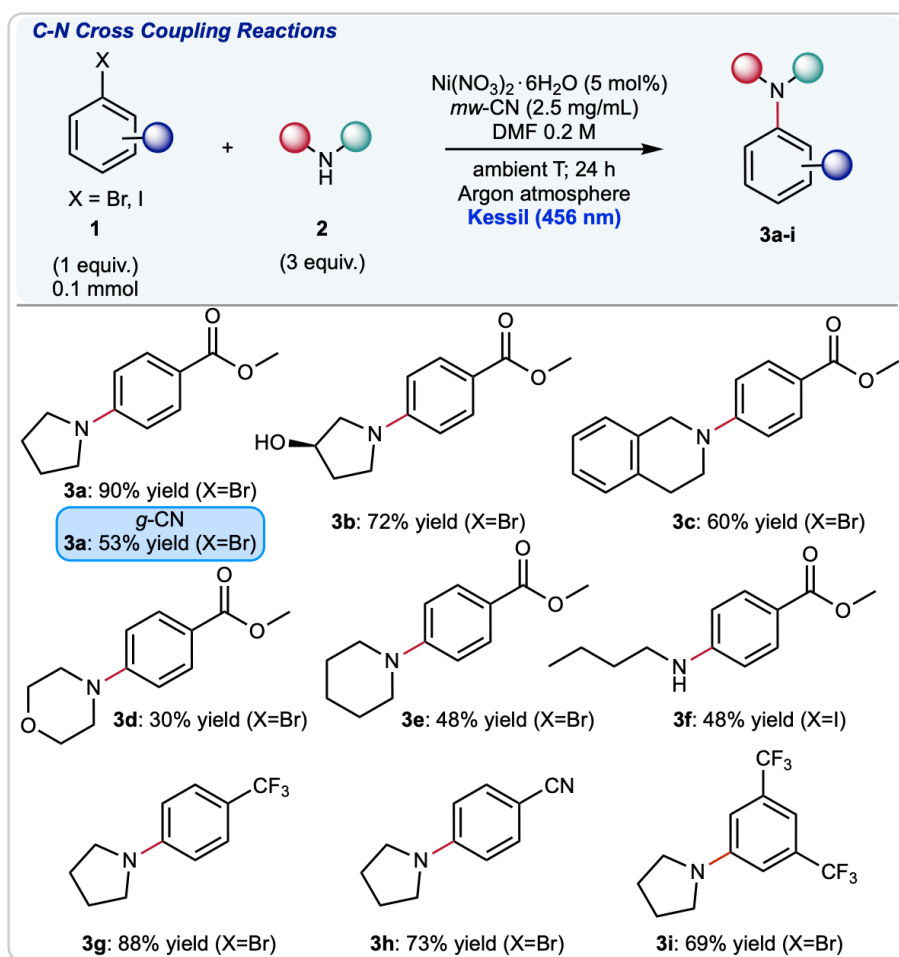


FIGURE 3.16: Evaluation of the scope of C–N coupling reactions.

To demonstrate the versatility of **mw-CN**, the scope of the reaction was extended to C–O and C–S couplings, and the activity with the new CN photocatalyst turned out to be

higher than those with **g-CN** (Figure 3.17). In particular, phenol derivatives (**6a,b**) were obtained through C–O coupling with water as a precursor, achieving isolated yield up to 80%. Additionally, methanol, benzyl alcohol and cyclohexanol were employed as substrates to form the corresponding ethers **6c–e** in good isolated yields (up to 66%). The formation of C–S bonds under reaction conditions was confirmed by four examples, affording the corresponding products with good to excellent yields (up to 83% product **7d**). In Figure 3.17 and 3.16, C–N, C–O and C–S coupling model reactions are highlighted, with a comparison of yields obtained with **g-CN** and **mw-CN**, showing the improved performance achieved by using the novel **mw-CN** as photocatalyst.

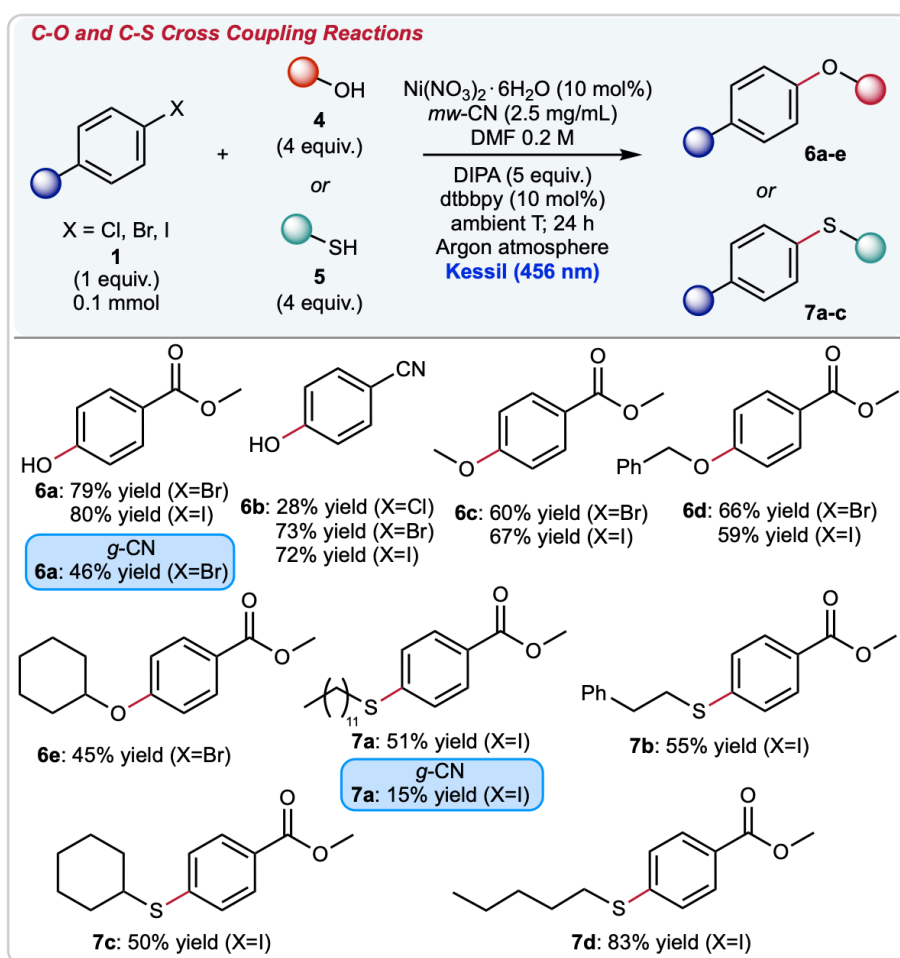


FIGURE 3.17: Evaluation of the scope of C–O and C–S coupling reactions.

3.4 Conclusions and Outlooks

This study demonstrates that cost-effective microwave treatment offers a practical and sustainable method for modifying carbon nitride materials to tune its structure and lead to improve their performances in Ni-dual organic photoredox catalysis, more specifically for C–X coupling reactions. The introduction of carbon vacancies and their evolution to additional coordinating N moieties during the MW treatment was key to enhancing the interaction between CN and nickel complexes in dual Ni/CN photocatalysis. The as-formed nitrogen moieties were in fact capable of efficiently binding Ni(II) centers, facilitating more efficient electron transfer processes. In addition to improving the photocatalytic activity, the study helped gained important fundamental insights to clarify some of the mechanistic aspects of Ni/CN dual catalysis. The improved interaction between the nickel species and the **mw-CN** surface, resulting from structural changes and increased surface area, highlights the potential of tailoring CN materials for specific catalytic functions.

The results presented here may pave the way for further development of dual photocatalytic systems, particularly in the context of single-atom catalysts (SACs).^{133,134} By fine-tuning the CN structure, it may be possible to develop more efficient and robust catalysts that are also recyclable, offering practical advantages for industrial applications.

In conclusion, MW-treated CN materials represent a promising direction for developing more versatile and efficient photocatalysts, with potential to address both performance and sustainability challenges in catalysis.

3.5 Experimental Section

3.5.1 Materials and Methods

Materials. Commercial reagents and solvents were purchased Sigma-Aldrich, Fluka, Alfa Aesar, Fluorochem, VWR and used as received, without further purification. Ultrapure fresh water obtained from a Millipore water purification system (>18 M Ω Milli-Q, Millipore) was used in all experiments.

Methods. The microwave treatment was performed on a CEM Discover-SP instrument. The NMR spectra were recorded on Varian 400 spectrometer (¹H: 400 MHz; ¹⁹F: 376.0 MHz; ¹³C: 101.0 MHz). The photochemical reactions were setup under an argon atmosphere in Schlenk tubes. Chromatographic purification of products was accomplished using flash chromatography on silica gel (SiO₂, 0.04–0.063 mm, 60 Å) purchased from Machery-Nagel, with the indicated solvent system according to the standard techniques or using a Biotage Isolera automated flash chromatography system with cartridges packed with SiO₂. Thin-layer chromatography (TLC) analysis was performed on precoated Merck TLC plates (silica

gel 60 GF254, 0.25 mm). Visualization of the developed chromatography was performed by checking UV absorbance (254 nm, with potassium permanganate or ninhydrin stain solution). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. The irradiation was performed using a) light emitting diode strips as light source at 450 nm, and b) Kessil lamp PR160L-456 (50 W) purchased from Kessil webpage: <https://www.kessil.com/science/PR160L.php> as light source at 456 nm.

Characterization. Raman spectroscopy was performed using an Invia Renishaw spectrometer equipped with a diode laser at 785 nm. Diffuse reflectance UV-vis spectra were acquired with a Thermo Scientific Evolution 600 spectrophotometer, equipped with a diffuse reflectance accessory Praying-Mantis sampling kit (Harrick Scientific Products, USA). High-resolution mass spectra were obtained using Bruker micrOTOF-Q (Electrospray Ionization Time-of-Flight). XPS measurements were carried out using a SPECS Sage HR 100 spectrometer with a non-monochromatic X-ray source of magnesium with a $K\alpha$ line of 1253.6 eV energy and 250 W. XPS data were fitted using CasaXPS software. N_2 physisorption measurements were performed with a Micrometrics ASAP 2020 analyzer at liquid nitrogen temperature. The materials were degassed at 150 °C for 12 h at 10 μ mHg. The surface areas were calculated applying the Brunauer-Emmett-Teller (BET) method equation. Pore size distributions were determined to the adsorption branch of the isotherms with Barrett-Joyner-Halenda (BJH) method equation.

IR absorbance spectra were acquired in transmission mode with a Vertex89v spectrometer equipped with a KBr beamsplitter, a deuterated triglycine sulfate detector, and a thermal source (Glow bar). Data were collected in the spectral range 600–4000 cm^{-1} with a resolution of 4 cm^{-1} . Scattering-type Scanning Near-field Optical Microscopy (s-SNOM) analyses were carried out using Neaspec instrument (Attocube systems AG) equipped with spectroscopy and imaging (PsHet detection module) modules, allowing to decouple intensity and phase of the signal at a specific illumination frequency. Measurements were performed by using a Naespec tip (arrow type, PtIr coated, 20 nm wide), in tapping mode with driving frequency of 277 kHz. Free amplitude was set to 108 nm with approaching point at 80%. These settings ensured a penetration of the radiation up to 100 nm below the sample surface. A tunable Quantum cascade laser, operating in the 600–1800 cm^{-1} range, was used for measurements at a power of 1 mW. Point spectra on areas 20 nm wide were acquired between 1300 and 1700 cm^{-1} and averaged, 2nd-harmonic of the imaginary part of the signal was used to reconstruct nanoIR absorption. Gwyddion software was employed for image processing and statistical analysis.

Solid-state NMR spectra were recorded employing a Bruker 9.4 T (400 MHz ^1H Larmor frequency) AVANCE III spectrometer equipped with a 4 mm HFX magic angle spinning (MAS) probe. Experiments were acquired at ambient temperature using a MAS frequency of 12 kHz. ^1H -pulses of 100 kHz were used, and ^{15}N spin-locking at ≈ 31 kHz was applied

for 3 ms, with the corresponding ramped (70–100%). ^1H spin-locking matched for optimum cross-polarization (CP) experiments with 100 kHz of SPINAL-64 heteronuclear ^1H decoupling used throughout signal acquisition. Samples were packed into 4 mm o.d. zirconia rotors and sealed with a Kel-F rotor cap. ^{15}N NMR chemical shifts were referenced to both liquid NH_3 and CH_3NO_2 (90% in CDCl_3) externally.

Q-band (microwave frequency 33.8 GHz) continuous wave (CW) and pulse EPR experiments were performed on a Bruker ELEXYS 580 EPR spectrometer equipped with a Bruker EN 5107D2 resonator, an Oxford Instruments CF935 liquid helium cryostat, and an ITC503 temperature control unit. The magnetic field was measured by a Bruker ER035 M NMR gaussmeter. CW EPR spectra were recorded at room temperature with a modulation frequency of 50 kHz and a modulation amplitude of 0.1 mT. Mims ENDOR spectra were recorded at -223°C at the field position correspondent to the maximum of the echo intensity (1204.6 mT). The pulse sequence was $\pi/2-\tau-\pi/2-\pi_{\text{Radio frequency (RF)}}-\pi/2-\tau$ -echo with $t_{\pi/2} = 16\text{ ns}$, $\tau = 216\text{ ns}$, $t_{\pi_{\text{RF}}} = 14\text{ }\mu\text{s}$ and additional waiting times of $1\text{ }\mu\text{s}$ were used before and after the π_{RF} pulse. The spectra were recorded in a 5 MHz window centered at the ^1H Larmor frequency, with a 0.02 MHz spectral resolution.

HAADF-STEM and EDX spectroscopy were performed with a JEOL NEORM operating at 200 kV with a convergence angle of 27 mrad. The sample was prepared by dropping the powder sample on a lacey carbon-coated Cu grid. For STEM imaging and EDS, the probe current was 150 pA and the camera length was 4 cm. EDX signals were collected with two JEOL EDS detectors located above the sample.

Preparation of the CN Materials.

g-CN: melamine (10 g) was transferred in a covered alumina crucible and heated in a muffle furnace up to 550°C for 300 min with a ramping time of 5°C min^{-1} . The final product was milled in a mortar to have a uniform powder.

ox-CN: 0.75 g of pristine g-CN was dispersed in 300 mL of a 4 M solution of nitric acid and sonicated for 5 h. The solid was filtered and washed with 500 mL of MilliQ water for 2 times and 250 mL of methanol.

am-CN: 0.75 g of g-CN was heated in a boat-shaped alumina crucible at 620°C for 120 min with a ramping time of 2°C min^{-1} under argon flow.

CNO: g-CN (1 g) was added to a mixture of concentrated sulfuric acid and nitric acid with a volume ratio of 1:2 (200 mL). After being stirred overnight, the mixture was poured into 500 mL of MilliQ water and collected by filtration. The product was washed with water for several times and dried at room temperature.

mw-CN: g-CN (200 mg) was heated at 190°C for 45 min by microwave irradiation under stirring. The sample was collected by filtration and dried at 80°C overnight.

3.5.2 Photochemical Reaction Set-up.

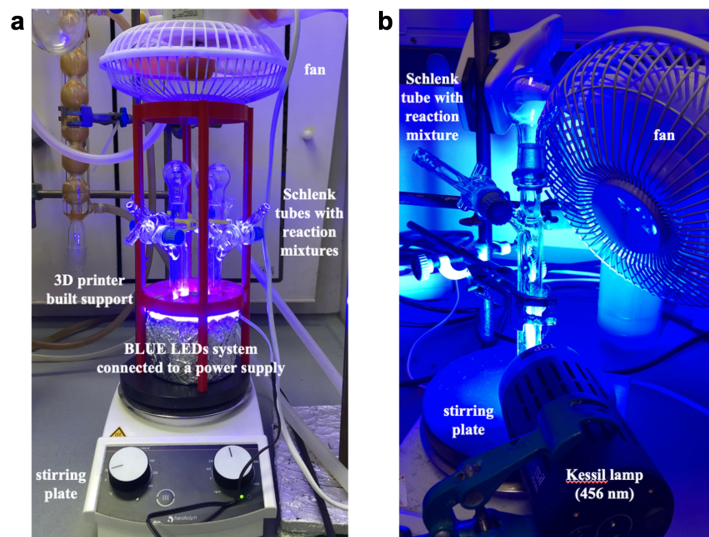


FIGURE 3.18: Batch photochemical set-up: a) blue LED strips (450 nm); b) Kessil lamp (456 nm).

3.5.3 Additional Characterization of the CN Materials

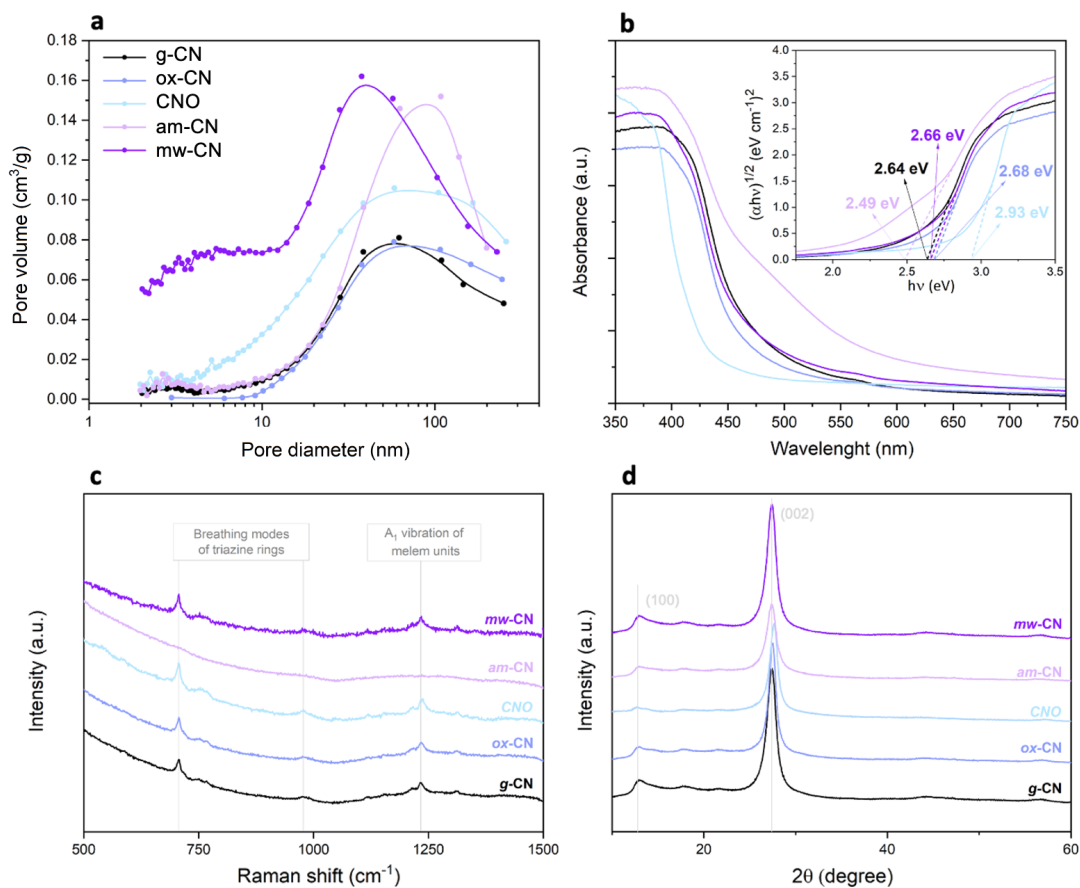


FIGURE 3.19: (a) BJH pore size distribution; (b) UV-Vis DRS spectra and the corresponding band gap (inset) for all samples; (c) Raman spectra; (d) XRD diffractogram of the materials.

TABLE 3.3: XPS peak assignments, positions and relative areas of the CN materials.

Material	Component	BE (eV)	Area (%)
g-CN	N–N	404.4	6.4
	N(C) ₃	400.8	17.6
	C=N–C	398.7	76.0
mw-CN	N–N	404.0	9.6
	N(C) ₃	401.0	9.6
	CN	399.9	16.1
	C=N–C	398.4	64.7
ox-CN	N–N	404.9	6.3
	N(C) ₃	400.6	19.1
	C=N–C	398.6	74.6
am-CN	N–N	404.4	5.4
	N(C) ₃	400.9	18.1
	C=N–C	398.8	74.5

3.5.4 Optimization Studies of Model C–N Coupling Reaction

TABLE 3.4: Optimization studies and control experiments of the model C–N coupling reaction reported in Figure 3.13.

Entry	CN (mg/mL)	Deviation	Yield3a (%) ^[a]
1	g-CN (5)	None	> 99
2	g-CN (5)	Dark	0
3	g-CN (5)	Air	0
4	None	No g-CN	0
5	g-CN (5)	No Ni catalyst	0
6	g-CN (5)	0.5 mmol	> 99
7	g-CN (5)	525 nm	0
8	g-CN (5)	Ni catalyst (2.5 mol%)	58 ± 3
9	g-CN (5)	Pyrrolidine (2 equiv.)	64 ± 3
10	g-CN (2.5)	None	48 ± 5
11	am-CN (2.5)	None	7 ± 5
12	CNO (2.5)	None	5 ± 2
13	ox-CN (2.5)	None	24 ± 2
14	mw-CN (2.5)	None	87 ± 8
15	mw-CN (2.5)	Kessil (456 nm)	97 ± 3

3.5.5 General Procedure for the C–N Coupling Reactions

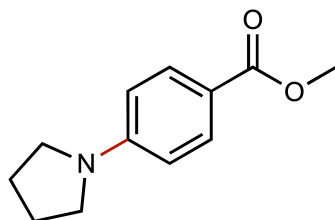
A 10 mL Schlenk tube was charged with the appropriate aryl halide **1** (0.1 mmol, 1 equiv.), the corresponding amine **2** (0.3 mmol, 3 equiv.), the mw-CN photocatalyst (2.5 mg/mL), nickel(II) nitrate hexahydrate (5% mol), and N,N-dimethylformamide (DMF, $[1]_0 = 0.2$ M). The reaction mixture was thoroughly degassed by freeze-pump-thaw (four times), and the Schlenk tube was filled with argon and irradiated with blue light (456 nm, Kessil lamp). The temperature was kept at around 30°C by using a fan. Stirring (400 rpm) was maintained for 24 hours, then the irradiation was stopped. The reaction crude was diluted with aqueous LiCl (5% wt/v) and extracted with ethyl acetate (5 x 10 mL). The organic phase was filtered through sodium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography to give the corresponding aniline products **3** in the stated yield.

3.5.6 General Procedure for the C–O and C–S Coupling Reactions

A 10 mL Schlenk tube was charged with the appropriate aryl halide **1** (0.1 mmol, 1 equiv.), the corresponding alcohol **4** or thiol **5** (0.4 mmol, 4 equiv.), the mw-CN photocatalyst (2.5 mg/mL), nickel(II) nitrate hexahydrate (10% mol), diisopropyl amine (0.5 mmol, 5 equiv.), 4,4'-di-tert-butyl-2,2'-dipyridyl (dtbbpy, 0.01 mmol, 10 mol%) and N,N-dimethylformamide (DMF, $[1]_0 = 0.2$ M). The reaction mixture was thoroughly degassed by freeze-pump-thaw (four times), and the Schlenk tube was filled with argon and irradiated with blue light (456 nm, Kessil lamp). The temperature was kept at around 30°C by using a fan. Stirring (400 rpm) was maintained for 24 hours, then the irradiation was stopped. The reaction crude was diluted with aqueous LiCl (5% wt/v) and extracted with ethyl acetate (5 x 10 mL). The organic phase was filtered through sodium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography to give the corresponding products **6** or **7** in the stated yield.

3.5.7 Product Characterization Data

Methyl 4-(pyrrolidin-1-yl)benzoate (**3a**)

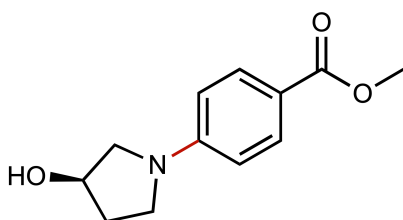


3a was synthesized according to the general procedure from methyl 4-bromobenzoate (21.5 mg, 0.1 mmol, 1 equiv.) and pyrrolidine (25.0 μ L, 0.3 mmol, 3 equiv.). Reaction time: 24 hours. The final product **3a** was obtained with 90% yield.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.90 (d, $J = 9.0$ Hz, 2H), 6.53 (d, $J = 9.0$ Hz, 2H), 3.85 (s, 3H), 3.43 – 3.32 (m, 4H), 2.06 – 1.97 (m, 4H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 167.73 (s), 150.85 (s), 131.53 (s), 116.76 (s), 111.03 (s), 51.59 (s), 47.89 (s), 25.58 (s); HRMS (ESI, positive mode)

calculated for $C_{12}H_{15}NO_2$ $[M+Na]^+$: 228.0994, found: 228.0995.

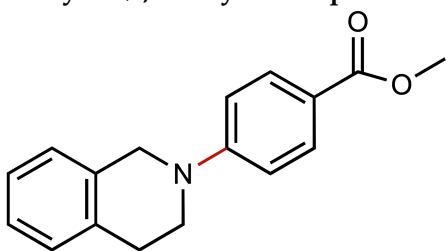
Methyl (R)-4-(3-hydroxypyrrolidin-1-yl)benzoate (3b)



3b was synthesized according to the general procedure from methyl 4-bromobenzoate (21.5 mg, 0.1 mmol, 1 equiv.), (R)-3-pyrrolidinol (37.07 mg, 0.3 mmol, 3 equiv.) and DABCO (44.87 mg, 0.4 mmol, 4 equiv.). Reaction time: 24 hours. The final product **3b** was obtained with 72% yield.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.89 (d, J = 7.4 Hz, 2H), 6.49 (d, J = 7.0 Hz, 2H), 4.63 (s, 1H), 3.85 (s, 3H), 3.55 (m, J = 8.1, 7.6 Hz, 2H), 3.48 – 3.39 (m, 1H), 3.37 – 3.30 (m, 1H), 2.29 – 1.85 (m, 3H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 167.81 (s), 150.91 (s), 131.53 (s), 116.96 (s), 110.93 (s), 71.14 (s), 56.15 (s), 51.64 (s), 45.57 (s), 34.20 (s); HRMS (ESI, positive mode) calculated for $C_{12}H_{15}NO_3$ $[M+Na]^+$: 244.0944, found: 244.0945.

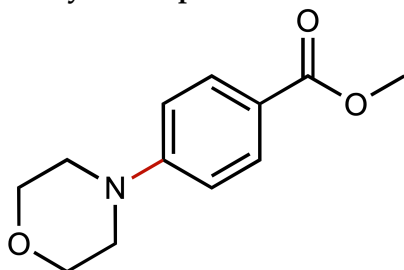
Methyl 4-(3,4-dihydroisoquinolin-2(1H)-yl)benzoate (3c)



3c was synthesized according to the general procedure from methyl 4-bromobenzoate (21.5 mg, 0.1 mmol, 1 equiv.), 1,2,3,4-tetrahydroisoquinoline (37.5 μl , 0.3 mmol, 3 equiv.). Reaction time: 24 hours. The final product **3c** was obtained with 60% yield. .

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.95 (d, J = 9.1 Hz, 1H), 7.25 – 7.14 (m, 4H), 6.88 (d, J = 9.1 Hz, 1H), 4.52 (s, 2H), 3.87 (s, 3H), 3.66 (t, J = 5.9 Hz, 2H), 3.00 (t, J = 5.9 Hz, 2H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 167.45 (s), 153.14 (s), 135.16 (s), 133.94 (s), 131.48 (s), 128.35 (s), 126.85 (s), 126.63 (s), 126.50 (s), 118.42 (s), 112.21 (s), 51.71 (s), 49.18 (s), 44.93 (s), 29.18 (s); HRMS (ESI, positive mode) calculated for $C_{17}H_{17}NO_2$ $[M+Na]^+$: 268.1332, found: 268.1330.

Methyl 4-morpholinobenzoate (3d)

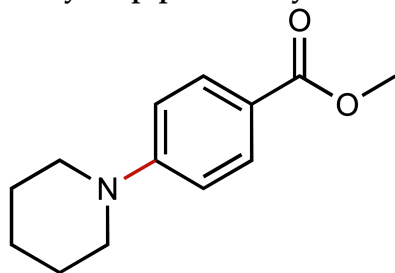


3d was synthesized according to the general procedure from methyl 4-bromobenzoate (21.5 mg, 0.1 mmol, 1 equiv.) and morpholine (26.1 μl , 0.3 mmol, 3 equiv.). Reaction time: 24 hours. The final product **3d** was obtained with 30% yield.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.94 (d, J = 9.1 Hz, 2H), 6.86 (d, J = 9.1 Hz, 2H), 3.89 – 3.82 (m,

7H), 3.28 (t, 4H); ^{13}C -NMR (101 MHz, CDCl_3) δ 167.05 (s), 154.19 (s), 131.21 (s), 120.32 (s), 113.47 (s), 66.60 (s), 51.69 (s), 47.71 (s); HRMS (ESI, positive mode) calculated for $\text{C}_{12}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: 244.0944, found: 244.0944.

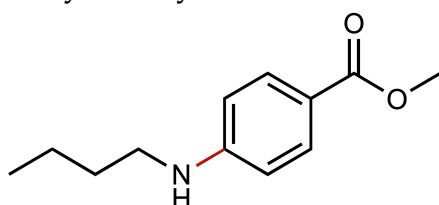
Methyl 4-(piperidin-1-yl)benzoate (3e)



3e was synthesized according to the general procedure from methyl 4-bromobenzoate (21.5 mg, 0.1 mmol, 1 equiv.) and morpholine (29.6 μl , 0.3 mmol, 3 equiv.). Reaction time: 24 hours. The final product **3e** was obtained with 48% yield.

^1H -NMR (400 MHz, CDCl_3) δ 7.89 (d, J = 9.2 Hz, 2H), 6.85 (d, J = 9.1 Hz, 2H), 3.85 (s, 3H), 3.36 – 3.28 (m, 4H), 1.66 (m, 6H); ^{13}C -NMR (101 MHz, CDCl_3) δ 167.39 (s), 154.65 (s), 131.36 (s), 118.79 (s), 113.70 (s), 51.69 (s), 48.92 (s), 25.52 (s), 24.49 (s); HRMS (ESI, positive mode) calculated for $\text{C}_{13}\text{H}_{17}\text{NO}_2$ $[\text{M}+\text{Na}]^+$: 242.1151, found: 242.1151.

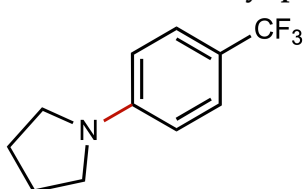
Methyl 4-(butylamino)benzoate (3f)



3f was synthesized according to the general procedure from methyl 4-iodobenzoate (26.2 mg, 0.1 mmol, 1 equiv.) and morpholine (26.1 μl , 0.3 mmol, 3 equiv.). Reaction time: 24 hours. The final product **3f** was obtained with 48% yield.

^1H -NMR (400 MHz, CDCl_3) δ 7.85 (d, J = 8.9 Hz, 2H), 6.53 (d, J = 8.9 Hz, 2H), 4.09 (s, 1H), 3.84 (s, 2H), 3.16 (t, J = 7.0 Hz, 2H), 1.61 (m, J = 14.6, 7.3 Hz, 2H), 1.43 (m, J = 14.4, 7.3 Hz, 2H), 0.96 (t, J = 7.3 Hz, 3H); ^{13}C -NMR (101 MHz, CDCl_3) δ 167.39 (s), 154.65 (s), 131.36 (s), 118.79 (s), 113.70 (s), 51.69 (s), 48.92 (s), 25.52 (s), 24.49 (s); HRMS (ESI, positive mode) calculated for $\text{C}_{12}\text{H}_{17}\text{NO}_2$ $[\text{M}+\text{Na}]^+$: 230.1151, found: 230.1152.

1-(4-(Trifluoromethyl)phenyl)pyrrolidine (3g)

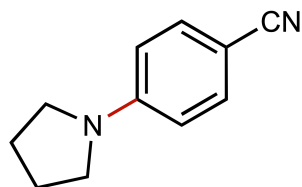


3g was synthesized according to the general procedure from 4-bromobenzotrifluoride (14.0 μl , 0.1 mmol, 1 equiv.) and pyrrolidine (25.0 μl , 0.3 mmol, 3 equiv.). Reaction time: 24 hours. The final product **3g** was obtained with 88% yield.

^1H -NMR (400 MHz, CDCl_3) δ 7.44 (d, J = 8.5 Hz, 2H), 6.55 (d, J = 8.7 Hz, 2H), 3.36 – 3.29 (m, 4H), 2.07 – 2.00 (m, 4H); ^{19}F NMR (376 MHz, CDCl_3) δ -60.62 (s, 3F); ^{13}C -NMR (101 MHz, CDCl_3) δ 150.14 (s), 133.57 (s), 121.14 (s), 111.57 (s), 96.66 (s), 47.60 (s), 25.53 (s); HRMS (ESI,

positive mode) calculated for $C_{11}H_{12}F_3N$ $[M+H]^+$: 216.0995, found: 216.0997.

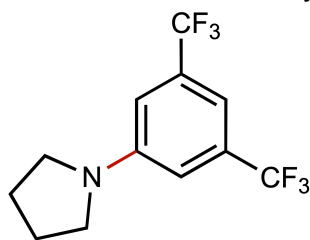
4-Pyrrolidin-1-yl-benzonitrile (**3h**)



3h was synthesized according to the general procedure C.1 from 4-bromobenzonitrile (18.2 mg, 0.1 mmol, 1 equiv.) and pyrrolidine (25.0 μ l, 0.3 mmol, 3 equiv.). Reaction time: 24 hours. The final product **3h** was obtained with 73% yield.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.44 (d, J = 9.0 Hz, 2H), 6.49 (d, J = 9.0 Hz, 2H), 3.36 – 3.29 (m, 4H), 2.08 – 2.01 (m, 4H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 150.14 (s), 133.57 (s), 121.14 (s), 111.57 (s), 96.66 (s), 47.60 (s), 25.53; HRMS (ESI, positive mode) calculated for $C_{11}H_{12}N_2$ $[M+Na]^+$: 195.0893, found: 195.0890.

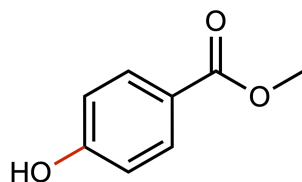
1-(3,5-Bis(trifluoromethyl)phenyl)pyrrolidine (**3i**)



3i was synthesized according to the general procedure from 1-bromo-3,5-bis(trifluoromethyl)benzene (17.3 μ l, 0.1 mmol, 1 equiv.) and pyrrolidine (25.0 μ l, 0.3 mmol, 3 equiv.). Reaction time: 24 hours. The final product **3i** was obtained with 69% yield.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.08 (s, 1H), 6.85 (s, 2H), 3.38 – 3.29 (m, 4H), 2.10 – 2.03 (m, 4H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.09 (s, 6F); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 148.03 (s), 132.26 (d, J = 32.4 Hz), 123.99 (d, J = 272.6 Hz), 110.89 (s), 108.08 (s), 47.90 (s), 25.60 (s); HRMS (ESI, positive mode) calculated for $C_{12}H_{11}F_6N$ $[M+H]^+$: 284.0868, found: 284.0866.

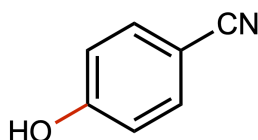
Methyl 4-hydroxybenzoate (**6a**)



6a was synthesized according to the general procedure from methyl 4-bromobenzoate (21.5 ml, 0.1 mmol, 1 equiv.) / methyl 4-iodobenzoate (26.2 mg, 0.1 mmol, 1 equiv.) and water (7.2 μ l, 0.4 mmol, 4 equiv.). Reaction time: 24 hours. The final product **6a** was obtained with 79% and 80% yield respectively.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.96 (s, 1H), 6.90 (s, 1H), 3.90 (s, 3H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 167.66 (s), 160.47 (s), 132.12 (s), 122.37 (s), 115.45 (s), 52.28 (s); HRMS (ESI, positive mode) calculated for $C_8H_8O_3$ $[M+Na]^+$: 175.0367, found: 175.0366.

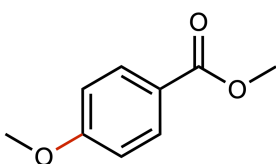
Methyl 4-hydroxybenzoate (**6b**)



6b was synthesized according to the general procedure from methyl 4-chlorobenzonitrile (13.8 mg, 0.1 mmol, 1 equiv.) / methyl 4-bromobenzonitrile (18.2 mg, 0.1 mmol, 1 equiv.) / methyl 4-iodobenzonitrile (22.9 mg, 0.1 mmol, 1 equiv.) and water (7.2 μ l, 0.4 mmol, 4 equiv.). Reaction time: 24 hours. The final product **6b** was obtained with 28%, 73% and 72% yield respectively.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.55 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 160.11 (s), 134.31 (s), 119.24 (s), 116.44 (s), 103.22 (s); HRMS (ESI, positive mode) calculated for $\text{C}_7\text{H}_5\text{NO}$ $[\text{M}+\text{Na}]^+$: 142.0263, found: 142.0261.

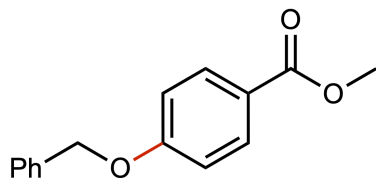
4-Methoxymethylbenzoate (**6c**)



6c was synthesized according to the general procedure from 4-bromobenzoate (21.5 mg, 0.1 mmol, 1 equiv.) / methyl 4-iodobenzonitrile (22.9 mg, 0.1 mmol, 1 equiv.) and methanol (16 μ l, 0.4 mmol, 4 equiv.). Reaction time: 24 hours. The final product **6c** was obtained with 60% and 67% yield respectively.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.00 (d, 2H), 6.92 (d, 2H), 3.88 (s, 3H), 3.86 (s, 3H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 167.01 (s), 163.47 (s), 131.74 (s), 122.76 (s), 113.74 (s), 55.58 (s), 52.02 (s); HRMS (ESI, positive mode) calculated for $\text{C}_9\text{H}_{10}\text{O}_3$ $[\text{M}+\text{Na}]^+$: 189.0522, found: 189.0497.

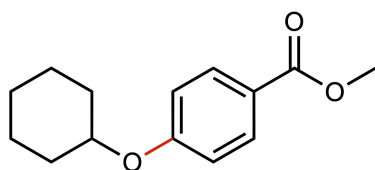
4-Benzyloxy-benzoic acid methyl ester (**6d**)



6d was synthesized according to the general procedure from 4-bromobenzoate (21.5 mg, 0.1 mmol, 1 equiv.) / methyl 4-iodobenzoate (22.9 mg, 0.1 mmol, 1 equiv.) and cyclohexanemethanol (42 μ l, 0.4 mmol, 4 equiv.). Reaction time: 24 hours. The final product **6d** was obtained with 66% and 59% yield respectively.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 8.00 (d, J = 8.8 Hz, 2H), 7.45 – 7.32 (m, 5H), 7.00 (d, J = 8.8 Hz, 2H), 5.12 (s, 2H), 3.89 (s, 3H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 166.95 (s), 162.62 (s), 136.39 (s), 131.74 (s), 128.81 (s), 128.34 (s), 127.62 (s), 122.98 (s), 114.59 (s), 70.23 (s), 52.00 (s); HRMS (ESI, positive mode) calculated for $\text{C}_{13}\text{H}_{14}\text{O}_3$ $[\text{M}+\text{Na}]^+$: 265.0835, found: 265.0837.

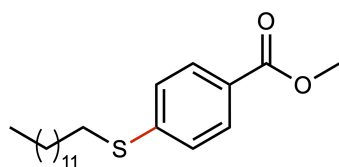
Methyl 4-cyclohexyloxybenzoate (**6e**)



6e was synthesized according to the general procedure from 4-bromobenzoate (21.5 mg, 0.1 mmol, 1 equiv.) and cyclohexanol (42 μ l, 0.4 mmol, 4 equiv.). Reaction time: 24 hours. The final product **6e** was obtained with 45% yield.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 4.36 – 4.30 (m, J = 8.9, 4.4 Hz, 1H), 3.87 (s, 3H), 2.03 – 1.94 (m, 2H), 1.86 – 1.77 (m, 2H), 1.63 – 1.48 (m, 3H), 1.46 – 1.23 (m, 3H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 167.07 (s), 161.90 (s), 131.71 (s), 122.21 (s), 115.26 (s), 75.53 (s), 51.94 (s), 31.75 (s), 25.66 (s), 23.79 (s); HRMS (ESI, positive mode) calculated for $\text{C}_{14}\text{H}_{18}\text{O}_3$ $[\text{M}+\text{Na}]^+$: 257.1148, found: 257.1149.

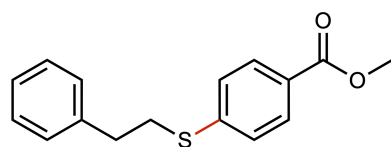
Methyl 4-dodecylthiobenzoate (**7a**)



7a was synthesized according to the general procedure from methyl 4-iodobenzoate (22.9 mg, 0.1 mmol, 1 equiv.) and 1-dodecanthiol (96 μ l, 0.4 mmol, 4 equiv.). Reaction time: 24 hours. The final product **7a** was obtained with 51% yield.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.92 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 3.89 (s, 3H), 2.99 – 2.96 (m, 2H), 1.72 – 1.66 (m, 2H), 1.47 99 – 1.41 (m, 2H), 1.31 – 1.26 (m, 18H), 0.88 (t, 3H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 166.83 (s), 144.53 (s), 129.87 (s), 126.51 (s), 126.26 (s), 51.99 (s), 32.07 (s), 31.90 (s), 29.62 (s), 29.61 (s), 29.55 (s), 29.46 (s), 29.33 (s), 29.13 (s), 28.88 (s), 28.74 (s), 22.68 (s), 14.10 (s), 1.01 (s); HRMS (ESI, positive mode) calculated for $\text{C}_{20}\text{H}_{32}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 359.2015, found: 359.2015.

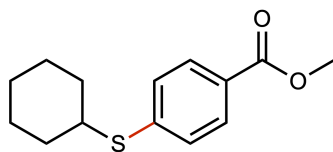
Methyl 4-(phenethylthio)benzoate (**7b**)



7b was synthesized according to the general procedure from 4-iodobenzoate (22.9 mg, 0.1 mmol, 1 equiv.) and benzeneethanethiol (54 μ l, 0.4 mmol, 4 equiv.). Reaction time: 24 hours. The final product **7b** was obtained with 50%.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.94 (d, J = 8.4 Hz, 2H), 7.27 (m, J = 35.7, 8.4 Hz, 7H), 3.91 (s, 3H), 3.29 – 3.20 (t, 2H), 3.04 – 2.94 (t, 2H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 166.91, 143.89, 139.88, 130.11, 128.75, 128.63, 126.99, 126.81, 126.72, 52.18, 35.32, 33.74; HRMS (ESI, positive mode) calculated for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 295.0763, found: 295.0762.

Methyl 4-(cyclohexylthio)benzoate (**7c**)



7c was synthesized according to the general procedure from 4-iodobenzoate (22.9 mg, 0.1 mmol, 1 equiv.) and benzenethiol (54 μ l, 0.4 mmol, 4 equiv.). Reaction time: 24 hours. The final product **7b** was obtained with 50%.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.92 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 3.89 (s, 3H), 3.32 – 3.18 (m, 1H), 2.12 – 1.99 (m, 2H), 1.81 – 1.79 (m, 2H), 1.71 – 1.62 (m, 1H), 1.46 – 1.30 (m, 5H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 166.95 (s), 143.16 (s), 130.01 (s), 128.65 (s), 127.26 (s), 52.17 (s), 45.23 (s), 33.24 (s), 26.08 (s), 25.83 (s); HRMS (ESI, positive mode) calculated for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{S} [\text{M}+\text{Na}]^+$: 273.0919, found: 273.0920.

3.5.8 Computational Data

All structures were optimized at the B3LYP level of theory in the ground state, using the Def2SVP basis set for non-metal atoms and the LanL2DZ ECP basis set for nickel. A Polarizable Continuum Model (PCM) with N,N-dimethylformamide (DMF) was included. Excited-state calculations were performed using TD-DFT at the HSE06 level of theory. TD-DFT calculations used molecular models for carbon nitride binding sites to nickel to explore electronic properties.

TABLE 3.5: Complexation energies of the Ni(II) complexes containing the CN models as ligands.

Complexes	Complexation energies (kcal/mol)
–NH ₂ -coordinating	–86.6
N-coordinating Pristine	–96.6
N-coordinating Triazole	–94.6
NH-coordinating Triazole	–79.5
Defective Imine	–101.0
Defective Amine	–90.5

Chapter 4

CO₂ Electroreduction into Value-Added Chemicals Using Bismuth-Based Catalysts

4.1 Introduction

The increase in atmospheric carbon dioxide (CO₂) levels is one of the main contributors to anthropogenic global warming.^{135–137} Since the onset of Industrial Revolution, CO₂ concentrations have risen dramatically, now reaching around 422 parts per million (ppm) according to recent data from the Mauna Loa Observatory. The concentration of CO₂ in the atmosphere, monitored by the National Oceanic and Atmospheric Administration (NOAA), can be checked in real-time through NOAA's public platform [here](#). The rapid rise in CO₂ emissions is primarily driven by the combustion of fossil fuels, deforestation, and industrial activities.¹³⁸ Before industrialization, natural processes maintained a balance in the atmosphere, keeping CO₂ levels between 260 and 280 ppm for over 10000 years. If left unchecked, the continuous rise in CO₂ emissions will intensify climate change, with significant impacts on ecosystems and human societies.¹³⁵ To mitigate the current environmental crisis, innovative technologies aimed at reducing atmospheric CO₂ are crucial. One well-established method is Carbon Capture and Storage (CCS), where CO₂ emissions from industrial sources, such as power plants, are captured, compressed, and stored.^{139,140} While CCS has shown effectiveness in reducing emissions, it primarily serves to merely isolate CO₂, without converting it into usable products. As a result, the focus has increasingly shifted towards more useful approaches to improve the carbon management, that offer both environmental and economic benefits. A promising alternative is Carbon Capture and Utilization (CCU), where the captured CO₂ is transformed into valuable chemicals and fuels. Industrial processes like dry reforming, Fischer-Tropsch process, and reverse water-gas shift

reaction have been explored to convert CO₂ into essential products such as carbon monoxide (CO), hydrogen (H₂), methanol (CH₃OH), and hydrocarbons. While these methods typically operate at high temperatures, advances in technology have the potential to reduce energy inputs, making them more compatible with the transition to renewable energy. In this context, a particularly attractive opportunity is the electrocatalytic reduction of CO₂ (eCO₂RR), which operates under milder conditions by using renewable electricity to convert CO₂ into value-added products like methane (CH₄), ethylene (C₂H₄), carbon monoxide (CO), and formic acid/formate (HCOOH/HCOO⁻). The key advantage of eCO₂RR lies in its compatibility with clean energy sources, such as wind and solar power, which can serve as a supply of the required electricity, creating a pathway to integrate CO₂ reduction with sustainable energy production. Despite the great interest in developing such a strategy on large scale, significant challenges remain. The electrochemical reduction of CO₂ is fundamentally challenging due to the molecule's high thermodynamic stability. In fact, CO₂ is a linear, centrosymmetric molecule characterized by strong C=O bonds (approximately 750 kJ/mol).^{141,142} To achieve a viable reduction, the system requires sufficient energy input to overcome this barrier. This large activation energy takes expression into the large overpotential (that is the additional voltage needed to drive an electrochemical reaction beyond its thermodynamic potential) requirements to drive the overall reaction. Furthermore, the conversion may proceed via several different reaction pathways and it varies depending on the number of electrons transferred in the process. For example, the electrochemical production of carbon monoxide (CO) or formate typically involves a two-electron transfer process, while more demanding products, such as hydrocarbons or alcohols, may require multiple electron transfers, so that they are more difficult to achieve efficiently under standard conditions. Moreover, associated with the higher number of electron transfer steps is a higher complexity of the mechanism, which strongly affects both the rates and selectivity of the transformation. The main half reactions of eCO₂RR are summarized in Table 4.1, with their corresponding standard electrode potentials (E^0) calculated at pH = 7.^{143,144} It is important to highlight that in general the sluggish kinetics of the CO₂ reduction requires the application of a considerably more negative potential than the E^0 value to drive the conversion with an appreciable reaction rate.¹⁴⁵ In fact, the reduction potential for the initial formation of the intermediate CO₂^{•-} radical anion, which is in most cases the first elementary electron transfer step, is thermodynamically very demanding, requiring a standard potential as negative as -1.90 V vs SHE. This radical anion is highly unstable and, as a result, is quickly protonated or stabilized through adsorption onto catalytic active sites, facilitating further reduction to desired products. The concurrent hydrogen evolution reaction (HER) is also reported in the following table, as it occurs at a potential close to that of CO₂ reduction, making it difficult to selectively reduce CO₂ without substantial hydrogen production.¹⁴⁶

TABLE 4.1: Selected half-electrochemical thermodynamic reactions of CO₂ reduction and hydrogen evolution reaction (*gray*) with their corresponding electrode potential versus standard hydrogen electrode (SHE) (pH = 7, 1 atmospheric gas pressure).^{143,144}

Half-electrochemical thermodynamic reaction	Electrode potential vs SHE (V)
$\text{CO}_2(\text{g}) + \text{e}^- \rightarrow \text{CO}_2^{\bullet-}(\text{aq})$	-1.90
$\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}(\text{l})$	-0.61
$\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$	-0.53
$\text{CO}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO}(\text{g}) + \text{H}_2\text{O}(\text{l})$	-0.48
$\text{CO}_2(\text{g}) + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH}(\text{l}) + \text{H}_2\text{O}(\text{l})$	-0.38
$\text{CO}_2(\text{g}) + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	-0.24
$2\text{CO}_2(\text{g}) + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4(\text{g}) + 4\text{H}_2\text{O}(\text{l})$	-0.34
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	-0.41

Efficient catalysts are key for lowering the activation energy, thus improving the kinetic of the reduction (reduced overpotential). It is important that together with faster kinetics, the catalyst is also able to favor specific reaction pathways, so that the desired product is obtained. Hence, selecting the right catalyst plays a key role to promote high activity and selectivity for a specific compound, thereby decreasing the energy inputs and avoiding costly separation processes that would arise from a mixture of complex products. To add up sustainability appeal, the majority of studies focused on the use of aqueous electrolytes, to reduce environmental impact of the process. While very appealing, this poses additional challenges, because of the low solubility of CO₂ in water and the readily available and competing HER process that causes reduced CO₂ electroreduction selectivity. Catalytic materials for eCO₂RR the subject of extensive research, with a wide variety of metals and alloys have been proposed as effective eCO₂RR catalysts.¹⁴³ In general, the most common metals eCO₂RR catalysts for eCO₂RR can be categorized into four main groups, based on their ability to bind reaction intermediates and steer the reaction towards specific products, as described in Figure 4.1. Group 1 metals, including Ni, Fe, Pt, and Ti, are generally poorly active for CO₂ reduction, and instead tend to favor hydrogen evolution in aqueous electrolytes, limiting their efficiency for CO₂-related processes. In contrast, Group 2 metals, such as Au, Ag, Zn, and Pd, excel at reducing the *COOH intermediate to carbon monoxide, although they do not further carry out the reduction due to relatively weak CO binding to the metal surface. Group 3 metals, which include Pb, Bi, Sn, and In, are more selective for formic acid/formate production, with HCOOH production proceeding through the *OCHO pathway (or the less favorable *COOH route). Finally, Group 4, represented by Cu, is unique

in its ability to further reduce CO₂ into multi-carbon products (often indicated generally as C₂₊), leading to more complex hydrocarbons and alcohols through subsequent reductions of *CO intermediates and C–C bond formation.^{147–150}

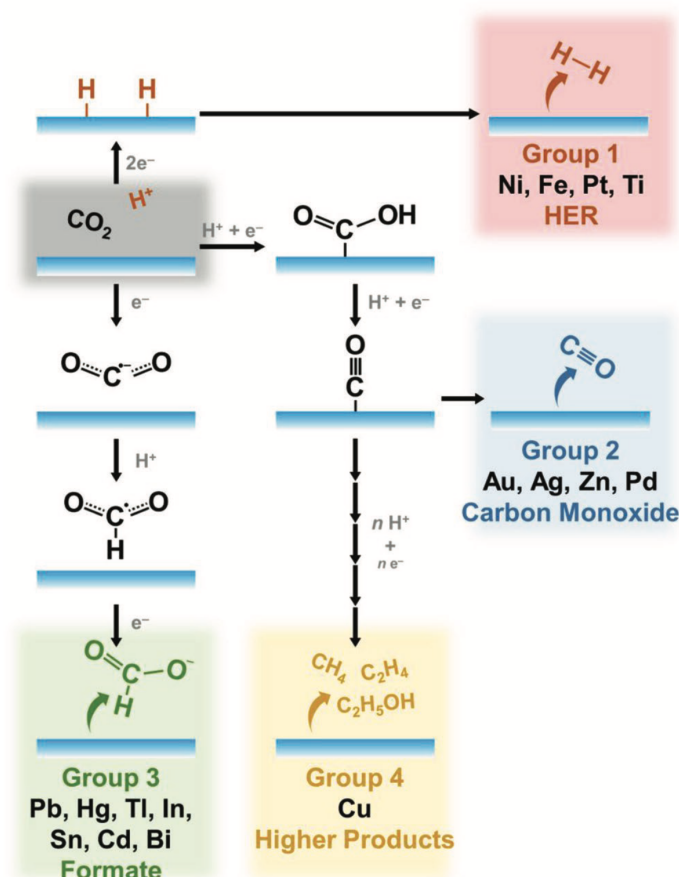


FIGURE 4.1: Electrochemical CO₂RR reaction mechanism on metal electrodes. Reproduced with permission.¹⁴⁷

4.1.1 CO₂ Reduction into Formic Acid by Bi-based Materials

Formic acid (FA) has garnered significant attention as one of the most valuable products derived from electrochemical CO₂ reduction. This compound is a widely used commodity chemical, functioning as a key building block in reactions such as esterification, formylation, and addition to olefins.¹⁵¹ Moreover, its non-toxic and non-corrosive nature enhances its industrial relevance.^{151,152} Notably, FA is recognized as a promising liquid hydrogen carrier, offering an efficient and practical solution to hydrogen storage in renewable energy systems.^{153,154} Currently, formic acid is predominantly produced via the carbonylation of methanol, followed by the hydrolysis of methyl formate.¹⁵⁵ Given its increasing industrial

demand, electrochemical CO₂ reduction has emerged as a sustainable and attractive alternative for FA synthesis, offering a carbon-neutral route by converting CO₂ directly into formic acid under mild conditions using renewable electricity.¹⁵⁶

In the framework of HCOOH electrosynthesis, bismuth-based electrocatalysts represent a particularly attractive class of catalysts within the p-block post-transition metal materials.^{148,157,158}

In fact, bismuth is non-toxic, environmentally friendly, relatively affordable and abundant, and also more stable than Sn- or In-based materials. Additionally, bismuth is frequently obtained as a byproduct of lead and copper refining, further contributing to its lower cost. However, it was classified as a critical raw material from the European Union in 2017 due to supply risks (as China is the top producer of mined and refined bismuth) and such a classification has persisted up to the most recent "European Commission, Study on the Critical Raw Materials" for the EU 2023 final report.^{159,160}

The use of Bi-based electrocatalysts for CO₂ conversion was first reported in 1995,¹⁶¹ but research on these catalysts slowed down in the following years. Recently, however, there has been a renaissance on these catalysts due to their promising properties, with studies exploring a variety of Bi-based catalyst structures and compositions.¹⁶² Several bismuth-based materials, such as bismuth oxide (Bi₂O₃), bismuth sulfides (Bi₂S₃) and bismuth oxyhalides (BiOX, with X = Cl, Br or I), exhibited notable CO₂ reduction performance in terms of selectivity, reaching Faradaic efficiencies (FEs) for formic acid of up to nearly 100%.^{157,162–164}

A problem with this material is the typically low electric conductivity, which results in small catalytic current densities, and a recurrent theme of exploration has been therefore the incorporation of conductive carbon matrixes, such as graphene, carbon nanotubes, or activated carbon.^{165–171} This approach may not only boost the efficiency but also allows for better utilization of the bismuth, reducing the amount of metal required while maintaining or even improving catalytic performance. In 2018, Chen *et al.* developed a composite catalyst made of bismuth oxide nanosheets (Bi₂O₃) and nitrogen-doped graphene quantum dots (NGQDs), which displayed a nearly 100% Faradaic efficiency for HCOOH at moderate overpotentials. The improved activity and stability over a wide potential range were attributed to the enhanced adsorption of CO₂ and OCHO* intermediate due to the combination of Bi₂O₃ and NGQDs, as also confirmed by DFT calculations.¹⁷² Melchionna and colleagues investigated nanocomposite materials of graphene oxide (GO) or reduced graphene oxide (rGO) with Bi@Bi₂O₃ core-shell nanoparticles, demonstrating that carbon/bismuth (oxide) interface leads to higher efficiency of the CO₂ conversion into formic acid, especially for the hybrid rGO/Bi@Bi₂O₃ material.¹⁶⁶ In 2024, a novel study of two-dimensional fullerene nanosheets (a novel carbon material) anchored with ultrafine Bi nanoparticles was published for selective formic acid production, presenting a material with superior carrier transport capacity, particularly high cathodic current densities (-88.29 mA cm⁻²) and FEs up to 94.3%.¹⁷¹

These recent examples suggest a possible general avenue for improving the Bi-based catalysts for eCO₂RR. The subject of the present chapter deals with the additional knowledge acquired on the possible integration of carbon nanostructures into Bi-based catalyst formulation.

4.2 Aim of the Research Project

The objective of this research project was to investigate the synthesis of nanohybrid materials consisting of carbon nanohorns (CNH) supporting different Bi (or Bi oxide) phases to enhance the eCO₂RR performance for the CO₂ to HCOOH conversion. This chapter will be divided into two main sections, where:

1. The first section focuses on developing a stable and efficient bismuth oxide catalyst, and understand in details its structural changes during CO₂RR *operando* conditions. In particular, the catalyst's structural reconstruction under catalytic conditions was elucidated by *in situ* Raman spectroscopy and *in situ* X-ray diffraction.
2. The second section examines the integration of single-walled carbon nanohorns (CNHs) as an active scaffold able to support and boost the activity of bismuth-based nanoparticles. CNHs are a fascinating carbon nanomaterial that, despite their unique properties, have yet to be thoroughly investigated for these applications.

4.3 Insights into structural modifications during CO₂RR of Bi₂O₃ rods

The investigation of the dynamic transformations of Bi-based materials during eCO₂RR is an important tool to guide new synthetic designs to improve the effectiveness of the catalysis. Thus, *in situ* techniques can provide a comprehensive view of both bulk and surface features of a material, allowing to understand the real-time behavior of catalysts. In particular, we investigated a monoclinic bismuth oxide (α -Bi₂O₃) as representative catalytic material through Raman spectroscopy and X-ray diffraction under operative conditions of CO₂ reduction.

4.3.1 Results and Discussion

α -phase Bi₂O₃ is the most stable form of bismuth oxide at room temperature. Through a precipitation method, we synthesized a pure α -phase Bi₂O₃ (rBi₂O₃) with rod-like shape and high crystallinity was synthesized. As shown in Figure 4.2, rBi₂O₃ presents the characteristic XRD pattern of the α -phase of Bi oxide, in good agreement with the Powder Diffraction

Standards data (JCPDS Card no. 76-1730). The Raman spectrum is characterized by several peaks, with the most intense appearing at around 155, 180, 210, 280, 315, 410 and 460 cm⁻¹ related to the A_g and B_g active modes of bismuth oxide.¹⁷³

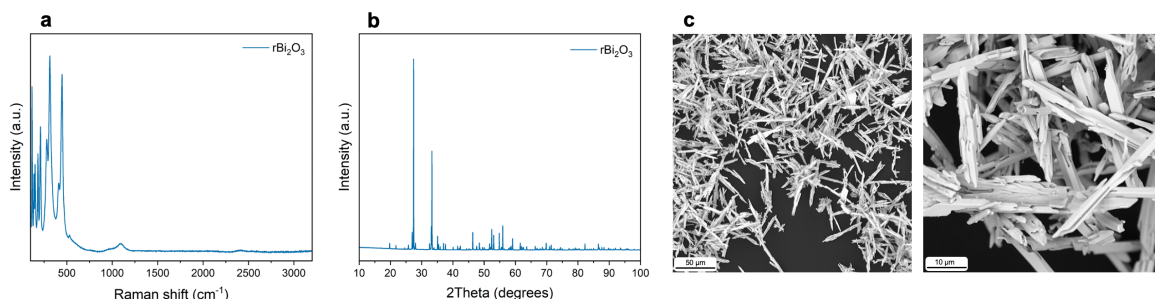


FIGURE 4.2: (a) Raman spectrum with 532 nm laser, (b) X-ray diffractogram, and (c) SEM images of **rBi₂O₃**.

The electrocatalytic performance of **rBi₂O₃** was evaluated through six-hour chronoamperometric (CA) experiments, utilizing an H-type electrochemical cell with a typical three-electrode configuration in 0.1 M KHCO₃ aqueous electrolyte. This setup was chosen due to its widespread use, facilitating direct comparison with literature data. CA measurements were performed at four different potentials (-0.68 V, -0.78 V, -0.88 V, and -0.98 V vs RHE) to assess the product distribution and formic acid production activity. The resulting products and the corresponding FE are displayed in Figure 4.3. A high selectivity for formic acid was observed, with the selectivity peaking at FE of 96% at -0.98 V vs RHE, while only minor traces (< 1.5% FE) of CO were obtained. Competitive H₂ formation occurred during CA, yet it remained below 20% FE, with relatively stable values over the entire six-hour period.

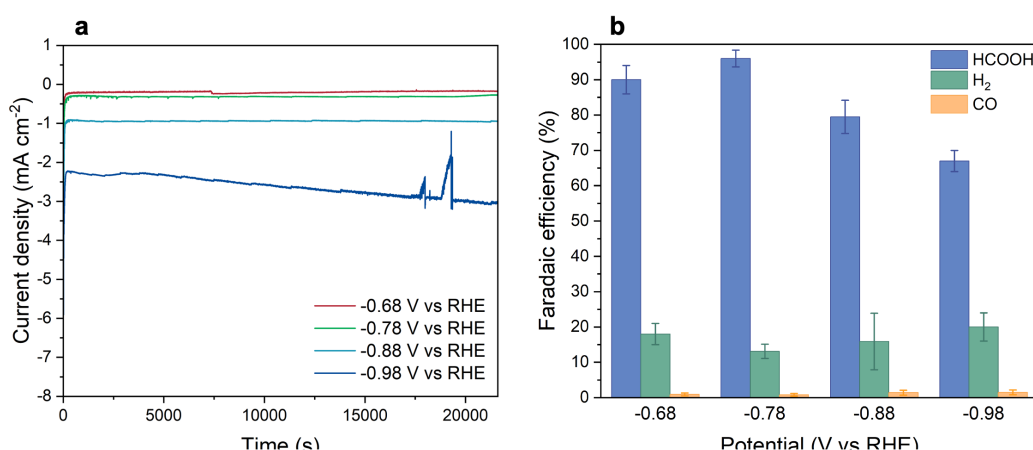


FIGURE 4.3: (a) CA curves of **rBi₂O₃** on Toray carbon paper under CO₂-saturated conditions KHCO₃ 0.1 M for 6 hours. (b) Faradaic efficiencies and current densities obtained using **rBi₂O₃** at different applied potential.

The morphological restructuring of the catalyst was first investigated through *ex situ* SEM images of the recovered electrode after 6-hours long CA experiment at fixed potential of -1.18 V vs RHE for 6 h. The spent catalyst showed good preservation of the morphology compared to the fresh sample (Figure 4.4).

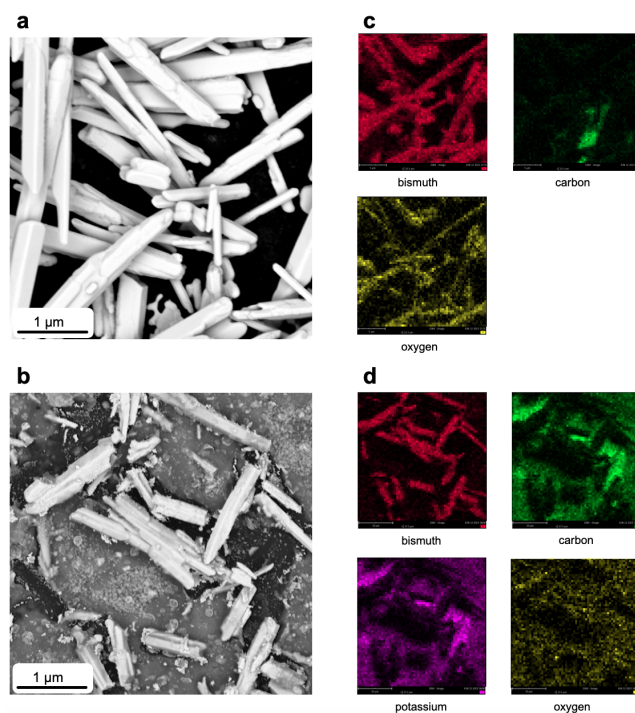


FIGURE 4.4: SEM images of fresh (a) and spent (b) rBi_2O_3 electrode and corresponding EDX maps (c, d).

The dynamics of the structural changes and the active phases of rBi_2O_3 during the catalysis were then evaluated by *in situ* time-resolved Raman spectroscopy measurements were performed, with a rate of 4 s for each spectrum. At open circuit potential (OCP), the catalyst showed the characteristic peaks of $\alpha\text{-Bi}_2\text{O}_3$ previously described, confirming that no structure modification occurs in absence of flowing current. Subsequently, cyclic voltammetry (CV) scans in the range of 0.62 V/-0.98 V vs RHE were performed at 5 mV/s, while Raman spectra were acquired. Figure 4.5 correlates CV features to the Raman spectroscopy signals, showing a heatmap where the y axis represents the Raman wavenumbers and the double x -axes were used to present the data as a function of number of spectrum (bottom axis) and potential (top axis). The Raman scattering intensity was plotted in the z direction and illustrated using the heatmap. During the cathodic sweep, after the broad cathodic peak at -0.46 V vs RHE in the first cycle, the combination of $\alpha\text{-Bi}_2\text{O}_3$ features and a new signal pattern related to the reduction $\text{Bi}^{3+}/\text{Bi}^0$ of the metal oxide to metallic bismuth are visible. From -0.73 V vs RHE, no Bi_2O_3 domains are any longer detectable, showing that the catalyst surface

primarily reconstructed into metallic bismuth. The remaining features of metallic Bi(0) consist of three peaks, specifically a signal of high intensity at 98 cm⁻¹ related to A_{1g} first-order Raman mode of bismuth, a broad low-intensity peak at 130 cm⁻¹, usually associated with phonon confinement effects, and at 184 cm⁻¹ a second-order Raman scattering mode.^{174,175} The dynamic restructuring of the Bi₂O₃ electrode surface observed by Raman spectroscopy shows no forms of bismuth oxides or oxycarbonate traces after the first complete reduction of the material.

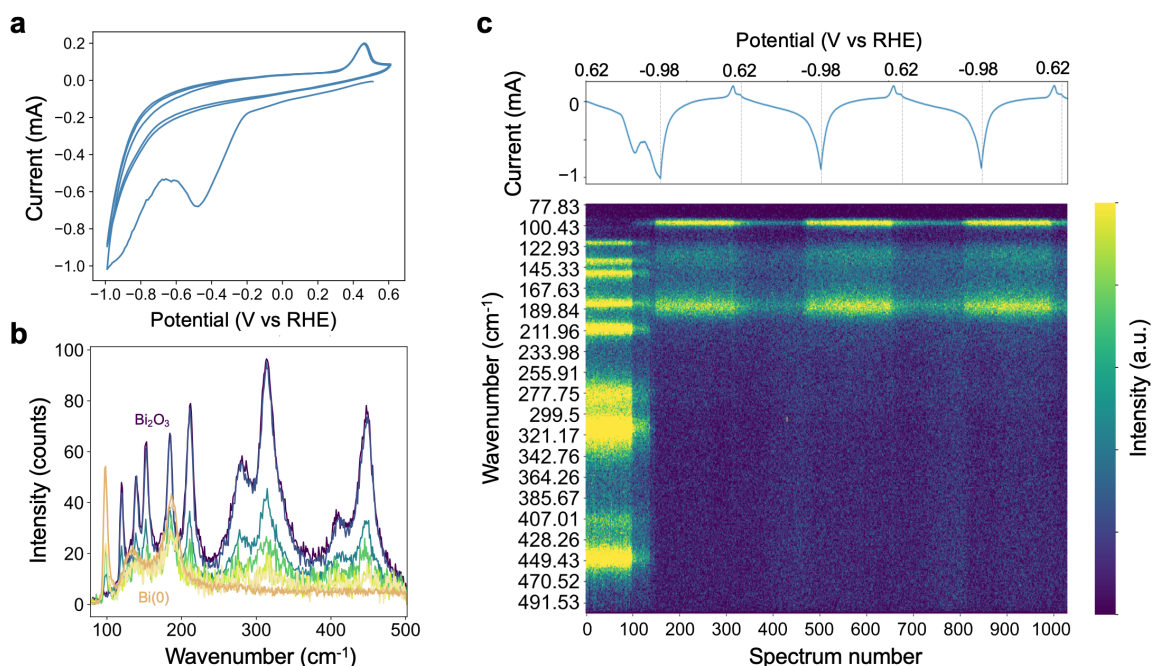


FIGURE 4.5: *In situ* Raman spectra during cyclic voltammetry under CO₂-saturated conditions. (a) CV profile of rBi₂O₃; (b) selected Raman spectra during the CV measurement; (c) heatmap of Raman spectra related to CV features.

CA experiments in a home-made H-type cell in flow coupled with *in situ* XRD could provide additional insights into the structural evolution of the catalyst deposited on glassy carbon supporting electrode under catalytic conditions. Figure 4.6a presents time-resolved XRD diffractograms acquired every 6 minutes, starting from OCP (purple diffractogram), where the characteristic reflections of monoclinic Bi₂O₃ are clearly observed, to those measured over time at an applied potential of -0.98 V vs RHE. The complete reduction of the bulk catalyst to metallic Bi (Bi(0)) is confirmed by the appearance of reflections at 27.2°, 37.9°, and 39.5°, corresponding to the (012), (104), and (110) planes of rhombohedral Bi(0). Tests at varying potentials confirmed that the activated Bi catalyst consistently adopts the same conformation, independent of potential during electrocatalytic activation (Figure 4.6a). To improve resolution, a smaller 2 θ range was examined, enabling XRD acquisition every 1.5

minutes. From the time-resolved diffractograms can be seen that during the electrocatalytic process, the diffraction peak intensities of Bi₂O₃ gradually disappear, while the metallic Bi phase reflections gradually emerge. Such a transformation occurs rapidly in the potentials range between -0.88 V and -1.18 V (Figure 4.6b), while at potentials less negative than -0.78 V, the two phases coexist (Figure 4.6c). It is therefore expected that under this conditions the catalytic behavior is also affected. The XRD findings are in very good agreement with the Raman data, both confirming the dynamic restructuring of the material. Further experimental results at varying potentials are provided in the Experimental Section.

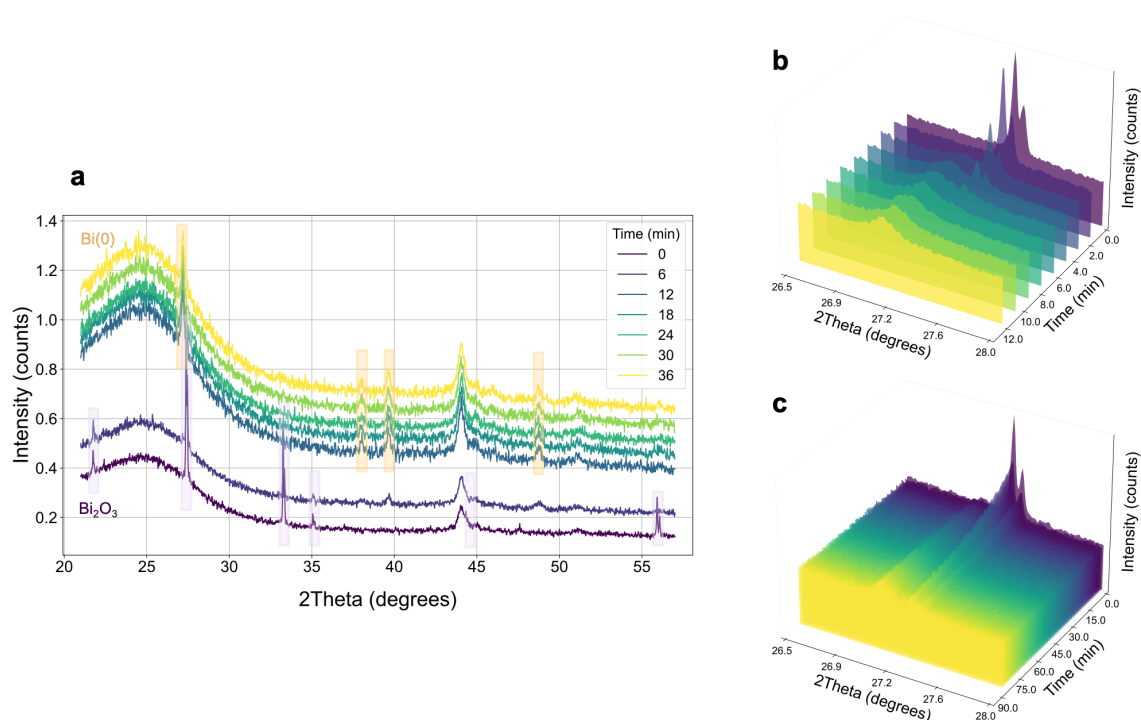


FIGURE 4.6: *In situ* XRD experiments. (a) XRD diffractogram acquired every 6 minutes during CA measurement at -0.98 V vs RHE; XRD diffractogram acquired every 1.5 minutes at (b) -0.98 and (c) -0.78 V vs RHE.

The behavior of rBi₂O₃ under catalytic conditions mirrors that of other bismuth oxide-based electrocatalysts recently reported in the literature, where a complete transformation into the active metallic Bi(0) phase was observed during operation.^{163,176–178} This dynamic evolution emphasizes the key role of bismuth restructuring in achieving high catalytic activity and selectivity.

4.3.2 Conclusions and Outlooks

In conclusion, a monoclinic rod-shaped Bi₂O₃ material exhibiting high selectivity for CO₂ electroreduction into HCOOH was effectively monitored using *in situ* Raman and XRD analyses. These measurements revealed the intrinsic restructuring of bismuth oxide into an active metallic bismuth phase, both at the surface and in the bulk, under negative applied potential and operative conditions. The ability to dynamically track this phase transition provides crucial insights into the behavior of the catalyst under working conditions. Understanding such transformations is essential for evaluating the active phases not only in simple systems like Bi₂O₃ but also in more complex Bi-based materials, where similar structural changes may occur. These findings highlight the significance of real-time characterization techniques for optimizing catalyst performance. Future investigations with nanostructured monoclinic Bi₂O₃ catalysts could reveal more active facets, morphologies, and surface properties, further enhancing the activity and efficiency of eCO₂RR. The techniques will allow better design of Bi-based eCO₂RR catalytic materials enhancing their activity, stability and selectivity.

4.3.3 Experimental Section

Materials. Potassium bicarbonate (KHCO₃ purity >99.7%) was purchased from Fluka. Bismuth(III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O, purity 98%), nitric acid (HNO₃, 70%), potassium hydroxide (KOH, puriss. p.a. >85%) were purchased from Sigma Aldrich. Carbon dioxide gas (CO₂, purity: 99.995%) was purchased from Linde Gas. All experiments were conducted using milliQ water obtained by Direct-Q (Millipore) water purification system.

rBi₂O₃ preparation. Bi(NO₃)₃·5H₂O was dissolved in 65% HNO₃ by slow addition under stirring. A KOH solution (50% w/v) was then added dropwise under vigorous stirring until the pH reached 13. The resulting yellow suspension was heated at 80°C for two hours. The precipitate obtained was filtered and washed with water till the neutral pH. The solid was dried at 120°C overnight. After grinding, it was calcined at 500°C for 6 hours with a heating rate of 3.5°C/min.

Characterization. SEM images were acquired using a Phenom ProX electron microscope. XRD measurements were conducted on a Bruker D8 Phaser diffractometer equipped with a Cu K α source ($\lambda = 1.54056 \text{ \AA}$). Raman measurement were performed on a Renishaw inVia Raman microscope with a 785 nm laser at 1% power

Electrochemical measurements. The chronoamperometric experiments were performed using an Ivium CompactStat.h10800 potentiostat. A custom quartz gas-tight three-electrode H-cell was employed, with a proton exchange membrane (Nafion 117, Dupont) to separate the two chambers. A leakless Ag/AgCl reference electrode and a Pt mesh counter electrode

were used. CO₂-saturated 0.1 M KHCO₃ solution at pH 7.2 was employed. CO₂ was continuously bubbled into the cathodic compartment at a flow rate of 10 mL/min, while Argon was delivered into the anodic chamber.

The ink formulation consisted of 5 mg of catalyst in 0.5 mL of methanol with the addition of 20 μ L Nafion 117 binder solution 5% (v/v). The ink was sonicated for 2 hours in iced water. To fabricate the working electrodes, 50 μ L of catalyst ink were deposited by drop-casting onto 1 cm² Toray carbon paper. The electrode was dried for 30 minutes.

Product analysis. Gaseous products were analysed using online gas chromatography with both a thermal conductivity detector and a flame ionization detector. The gaseous products were detected every four minutes during the CA experiments. The liquid products were determined at the end of the CAs by ¹H NMR spectroscopy recorded on Varian 400 spectrometer (400 MHz) with water suppression mode, using 0.5 mL of electrolyte and 0.1 mL of deuterated water. Dimethylsulfoxide was used as internal standard for a quantitative analysis. Faradaic efficiency (FE) for both gaseous and liquid products were calculated using the Equation 2.21 in Chapter 2.

In situ measurements. *In situ* XRD measurements were conducted on a Bruker D8 Phaser diffractometer equipped with a Cu K α source ($\lambda = 1.54056$ Å). A back illumination configuration was used for the XRD measurements in Bragg mode. A custom-made flow cell was employed, consisting of a glassy carbon wafer (SIGRADUR K film, thickness 1800 μ m, diameter 22 mm) drop-cast with the catalyst, a Pt wafer as counter electrode and a leakless miniature Ag/AgCl as reference electrode. The electrolyte (CO₂-saturated 0.1 M KHCO₃ aqueous solution) was introduced into the electrochemical cell at a flow rate of 10 mL/min. An InVium CompactStat.h10800 potentiostat was used for the electrochemical tests.

In situ Raman analyses were carried out using a Renishaw inVia Raman microscope with a 785 nm laser at 1% power and a Nikon N40X-NIR water-dipping objective. An Autolab PG-STAT 101 potentiostat was employed for the electrocatalytic measurements. A custom-made cell was used, with a Pt wire as counter electrode and a leakless Ag/AgCl as reference electrode.

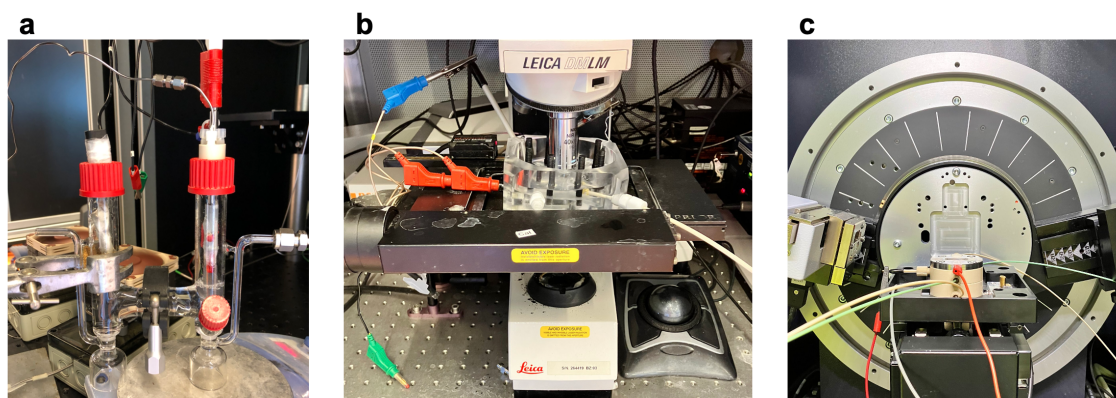


FIGURE 4.7: (a) H-type cell for CA experiment set-up; (b) *In situ* Raman experiment set-up; (c) *In situ* XRD experiments set-up.

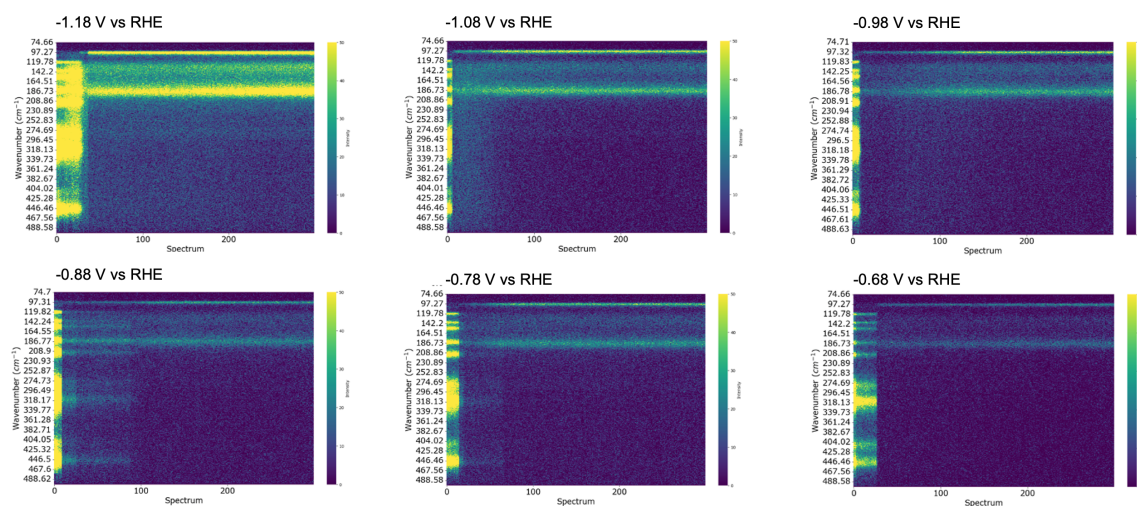


FIGURE 4.8: *In situ* Raman experiments coupled with chronoamperometric experiments at different applied potentials.

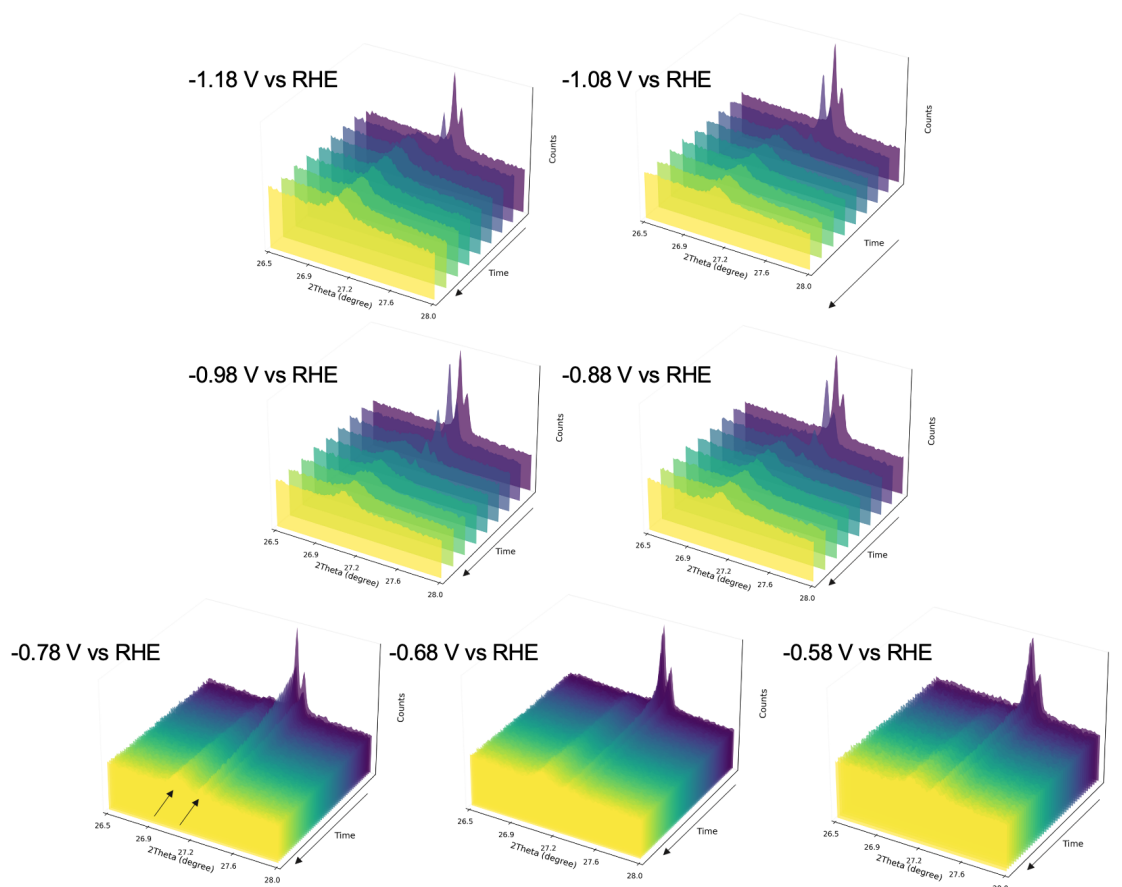


FIGURE 4.9: *In situ* XRD experiments coupled with chronoamperometric experiments at different applied potentials. CAs of 12 minutes were carried out in the range -1.18 V / -0.88 V vs RHE, while CAs of 2 hours were performed in the range -0.78 V / -0.58 V vs RHE.

4.4 Bi-based Nanoparticles Decorating Carbon Nanohorns for Efficient CO₂ Conversion into Formic Acid

As previously introduced in Chapter 1, carbon nanostructures (CNSs) are a support widely employed components in materials for electrocatalysis. Combining an inorganic phase with a CNS component is an effective approach that can improve: (a) charge transfer at the (active) inorganic phase during electrocatalysis, (b) catalytic stability, (c) the system's surface area. In recent years, among the various CNS, carbon nanohorns (CNHs) have attracted considerable attention in electrocatalytic applications in view of their unique structural and surface features. CNHs exhibit a highly porous architecture and often offer a larger surface area compared to other carbon-based nanomaterials, such as carbon nanotubes (CNTs) and graphene (G). Structurally, CNHs are composed of closed cages of sp²-bonded carbon atoms. These nanostructures typically have diameters ranging from 2 to 5 nm and lengths

of approximately 40 to 50 nm, giving them an elongated, cone-like shape with significant aspect ratio.¹⁷⁹ Their distinctive form can be considered a bridge between fullerenes and carbon nanotubes (CNTs). CNHs are usually found in spherical "dahlia-like" aggregates, roughly 100 nm in diameter, where the carbon nanohorns radiate outward from a central core, creating a distinctive morphology reminiscent of a dahlia flower. Another possible configuration includes "bud-like" CNHs, where the horns remain embedded within the aggregate, rather than protruding outward.¹⁸⁰ As for other CNS, the surface of CNHs can be modified by means of oxidation, which cause partial opening their structure by removing the tips of the horns, which are more reactive because of higher curvature, allowing an increased surface area.¹⁸¹ The most common method for the commercial production of CNHs involves pulsed laser ablation of graphite under Ar atmosphere, which has high production rate and leads to high yield.¹⁷⁹ This approach is advantageous because it allows for the large scale, cost-effective synthesis of CNHs without the need for metal catalysts and therefore additional purification steps to remove metallic impurities. In fact, the absence of metal catalyst eliminates the risk of metallic impurities in the final product, offering a significant advantage over CNTs, which are often synthesized through chemical vapor deposition (CVD) processes that require metals.¹⁸² It is worth noting that because of the truly metal-free nature, CNHs afford better reproducibility of catalytic results in comparison with CNT and G.

The use of CNHs as carbon support for hybrid inorganic-carbon materials have been explored in different applications, and interesting cases have been highlighted by our group and others by interfacing CNH with metal oxides or by assembling ternary CNH/metal/metal oxide systems.^(183,184) In these studies, the formation of a inorganic-organic interface and the presence of the carbon matrix allowed to achieve not only a better dispersal of the electrocatalyst, but also a handle to tune the electronic properties of the catalytically active inorganic phase, leading to high current densities and enhanced performances. In this project, we aimed to prepare a Bi oxide (or oxycarbonate) composite with CNHs as electrocatalyst for CO₂ reduction. The rationale is to exploit the unique morphology of this carbon support to allow nanostructuring of the Bi phase, and to take advantage of the electronic CNH-BiO_x interplay to boost the performance towards CO₂RR.

4.4.1 Results and Discussion

The incorporation of Bi-based nanoparticles (NPs) onto CNHs relied on the development of a robust synthetic procedure using an *in situ* growth approach of the Bi component, yielding a Bi₂O₂CO₃/Bi₂O₃-oxCNH nanohybrid material. The first step of the synthesis consists in a controlled oxidation of the CNHs *via* a mild acid treatment using relatively diluted HNO₃ solution. The purpose of this first step is to enhance the surface area with minimal disruption of the CNH polyaromatic framework, and introduce oxygenated functional groups

that serve as anchoring sites for promoting interaction with the Bi precursor. Following this surface modification, the Bi salt is thermally decomposed directly onto the carbon scaffold at 320°C, ensuring strong adhesion, uniform nanoparticle distribution, and intimate contact between the Bi₂O₂CO₃/Bi₂O₃ NPs and the oxidized carbon substrate.

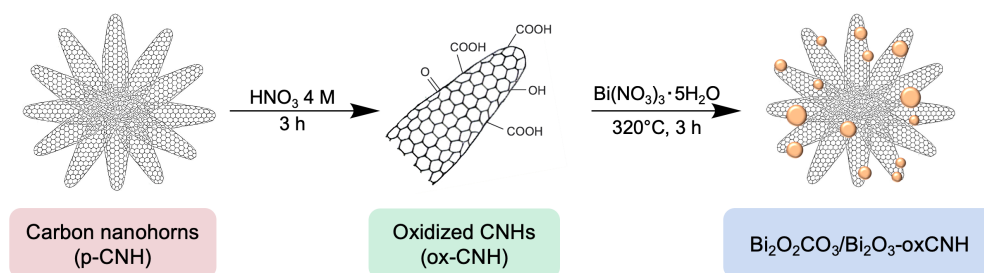


FIGURE 4.10: Schematic representation of the synthetic protocol of Bi₂O₂CO₃/Bi₂O₃-oxCNH.

Figure 4.11 presents the TEM images of (a) pristine CNHs (**p-CNH**), (b) oxidized CNHs (**ox-CNH**) and (c) thermally-treated ox-CNH (**ox-CNH-T**), so to assess the structural evolution of the CNH under the different synthetic conditions. Both oxidative treatment and thermal treatment employed do not significantly alter the overall morphology of the pristine carbon nanomaterial, mostly preserving the structural integrity of the nanohorns. Notably, both dahlia-like and bud-like CNH morphologies are clearly visible in the samples, as highlighted Figure 4.11c. The formation of the nanohybrid is validated by TEM investigation, revealing that almost spherical Bi₂O₂CO₃/Bi₂O₃ NPs are uniformly integrated and well-dispersed on the CNH surface (Figure 4.11d, e). The TEM images show a relatively narrow particle size distribution, with an average size of approximately 8.4 nm (Figure 4.11f). No isolated aggregates of Bi-based nanoparticles were found upon thorough inspection of the sample.

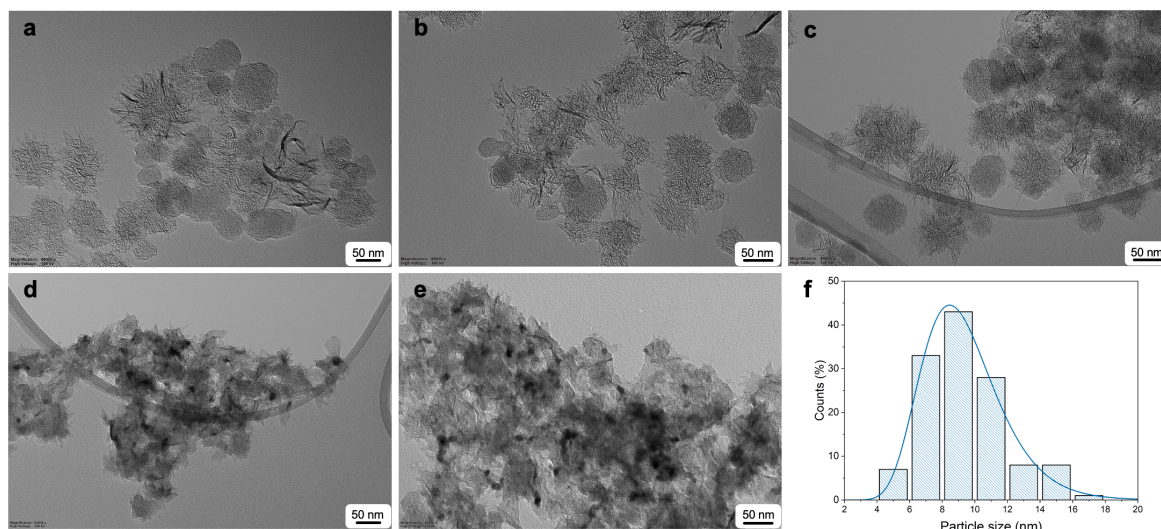


FIGURE 4.11: TEM images of: (a) **p-CNH**; (b) **ox-CNH**; (c) **ox-CNH-T**; (d,e) **Bi₂O₂CO₃/Bi₂O₃-oxCNH** and; (f) particle size distribution histogram calculated from measurements of 100 NPs in the TEM images of the nanohybrid material.

Graphene oxide (**GO**) and oxidized multi-walled carbon nanotubes (**ox-MWCNTs**) were also tested as carbon supports for comparative purposes, adopting the same methodology. However, such CNS failed to exert the proper templating effect for the controlled growth of the bismuth nanoparticles. Rather than obtaining well-dispersed Bi nanoparticles, the bismuth species grown on **GO** and **ox-MWCNTs** formed significantly larger and heterogeneous Bi-based plate-like aggregates (Figure 4.12). In contrast, CNHs proved more effective at promoting controlled Bi nanoparticle growth and preventing excessive aggregation. It is important to note, however, that the effectiveness of CNHs as a support depends on the type, purity, and supplier of the carbon material. For instance, when the synthetic procedure was performed using a lower grade of CNHs (grade 2, as opposed to grade 4 used in the primary synthesis), the resulting Bi-based nanoparticles exhibit a mixture of almost spherical and rod-like morphologies. This result highlights the notorious problem of reproducibility and batch-dependence when working with carbon nanostructures.

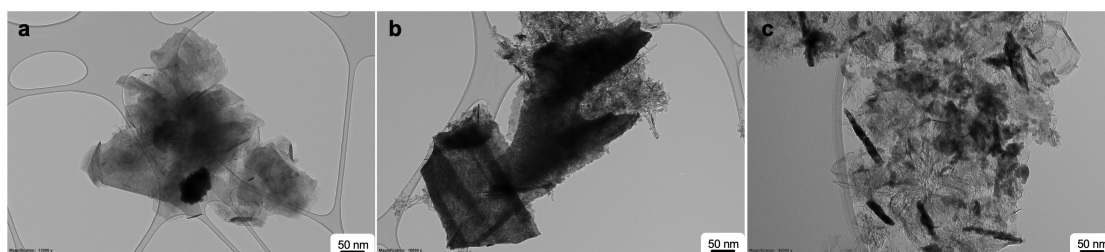


FIGURE 4.12: TEM images of: (a) **Bi₂O₂CO₃/Bi₂O₃-GO**; (b) **Bi₂O₂CO₃/Bi₂O₃-oxMWCNTs**; (c) **Bi₂O₂CO₃/Bi₂O₃-oxCNH** using grade 2 CNHs.

Figure 4.13 shows the Raman spectra of **p-CNH**, **ox-CNH**, **ox-CNH-T**, and **Bi₂O₂CO₃/Bi₂O₃-oxCNH**. The G and D bands, characteristic of carbon materials, are located in all the materials at approximately 1580 and 1360 cm⁻¹, respectively. These bands correspond to the stretching vibrations of sp² carbon atoms (G band) and the breathing modes of carbon atoms related to structural defects (D band). As expected, the oxidation treatment increases the structural disorder, as demonstrated by the higher I_D/I_G ratio for **ox-CNH** (1.67) compared to the pristine carbon nanostructure (1.52). However, after the thermal treatment partially restores the structural order and degree of graphitic character. In contrast, the nanohybrid material does not follow this trend. Despite undergoing thermal treatment, the I_D/I_G ratio remains high (1.71), indicating significant structural disorder. Additionally, the D' band at 1614 cm⁻¹ is more pronounced in the nanohybrid compared to the other CNH samples, where it only appears as a shoulder of the G band. This further suggests a higher degree of irregularities in the structure. Therefore, the impregnation of the Bi precursor and its subsequent thermal decomposition significantly alter the carbon structure, introducing more defects. The Raman peaks in the range of 110-630 cm⁻¹ (highlighted with a blue frame in Figure 4.13) are associated with Bi–O stretching vibrations, with an intense band at 315 cm⁻¹, characteristic of the β-phase of Bi₂O₃. Moreover, two small signals at approximately 1040 and 1065 cm⁻¹ are attributed to carbonate groups (highlighted in the graph using two arrows), due to the creation of new C–O–C bonding within the inorganic component, likely in the form of bismuth oxycarbonate (Bi₂O₂CO₃). Hence, Raman spectra are in agreement with TEM analysis to claim a tight contact between the carbon support and the inorganic phase through an interface of Bi₂O₂CO₃.

X-ray diffraction (XRD) measurements reported in Figure 4.13 confirmed the presence of β-Bi₂O₃ and Bi₂O₂CO₃ phases in the nanohybrid catalyst. The reflections of cubic β-Bi₂O₃ are consistent with JCPDS Card No. 27-0050 and can be indexed at 2θ values of 27.5°, 46.9°, 67.4° corresponding to the crystal planes (201), (400), (521), respectively.¹⁸⁵ In contrast, the reflections at 12.8°, 23.9°, 25.9°, 30.2°, 39.4°, 42.3°, 52.3°, and 54.4° can be indexed to the (002), (101), (004), (103), (006), (114), (211), and (204) lattice planes of tetragonal Bi₂O₂CO₃ (JCPDS card no. 41-1488).¹⁸⁶ The XRD diffractogram of the CNH materials reveals that the oxidation process successfully removes impurities of amorphous carbon, which were previously present in **p-CNH** and manifested as a broad shoulder at around 22.1°. Both **ox-CNH** and **ox-CNH-T** exhibit nearly identical diffraction patterns, characterized by a well visible reflection at 26°, indicative of more disordered graphitic regions. Additionally, a sharp peak at 27° corresponds to the (002) plane of well-ordered graphitic carbon. An asymmetric, broad signal at approximately 42.9° is also observed, associated with the (100) plane, which is distinctive of short-range ordered graphitic carbon structures.

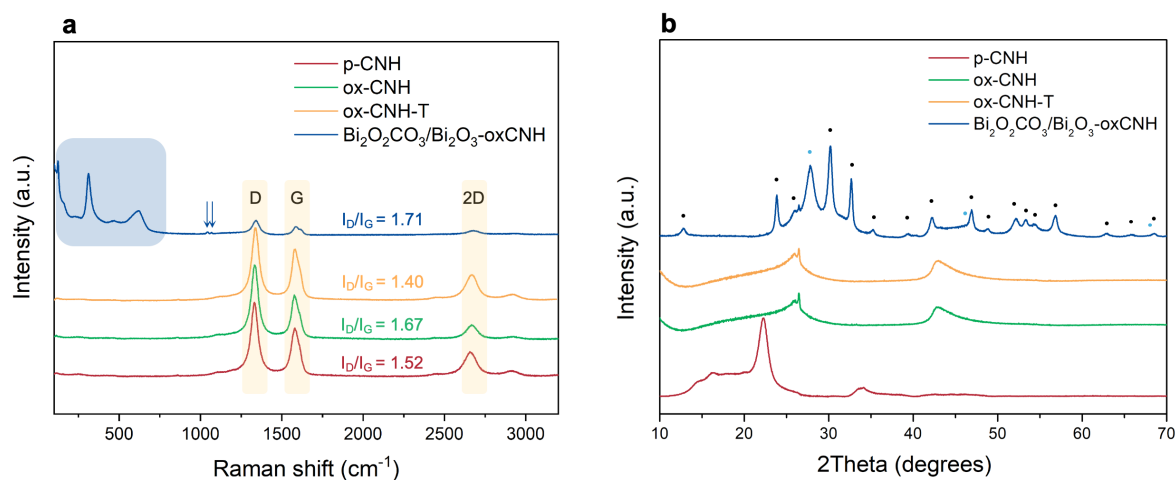
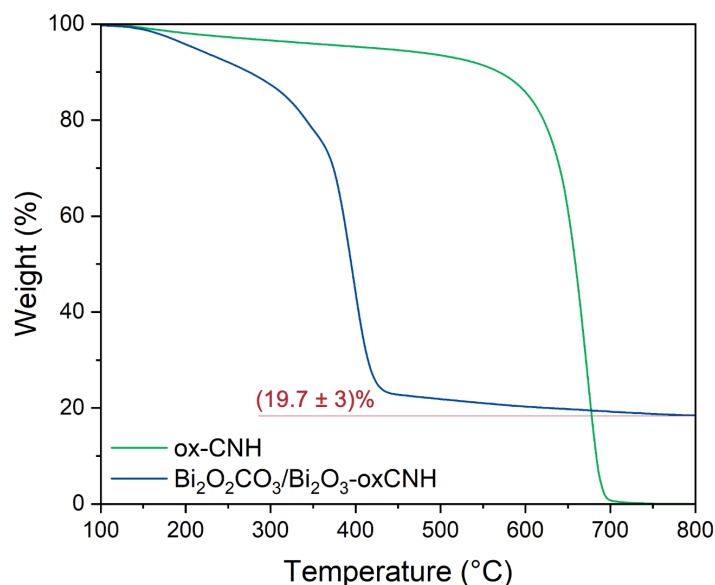
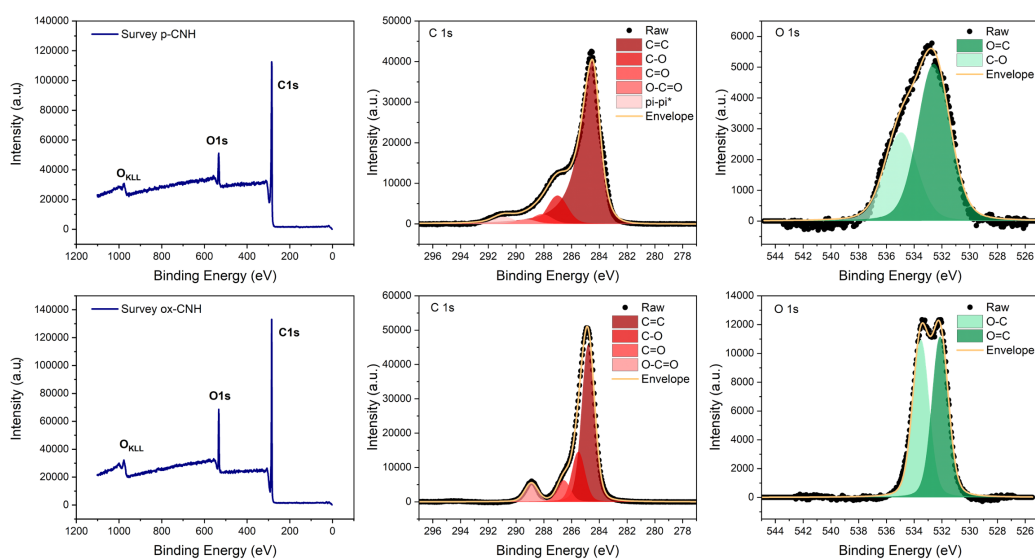


FIGURE 4.13: (a) Raman spectra and (b) XRD diffractograms of **p-CNH**, **ox-CNH**, **ox-CNH-T**, **Bi₂O₂CO₃/Bi₂O₃-oxCNH**. In the XRD diffractogram, black dots have been used to identify the reflection of Bi₂O₂CO₃, while light blue dots for β-Bi₂O₃.

Thermogravimetric analysis (TGA) conducted in air reveals an initial weight loss at lower temperatures (100-200°C), attributed to the evaporation of water and the release of weakly bound organic groups present on the CNH surface (Figure 4.14). This is followed by the decomposition of Bi₂O₂CO₃ to bismuth oxide releasing CO₂ in the process, which typically occurs between 300°C and 380°C. A more substantial weight loss around 400°C is associated with the combustion of the carbon structure. Significantly, this combustion temperature is notably lower for the nanohybrid compared to **ox-CNH** alone, suggesting a strong interaction between the Bi phase and the carbon surface, that could activate the combustion process. The analysis determined a Bi species (presumably oxide) of 19.7 wt% in the hybrid material.

FIGURE 4.14: TGA analysis of **ox-CNH** and **Bi₂O₂CO₃/Bi₂O₃-oxCNH**.

Further insights into the structural changes of the materials were obtained through X-ray photoelectron spectroscopy (XPS). As expected, the oxidation of the CNHs is accompanied by a notable increase in oxygen content, which rises from 5.27 at% in **p-CNH** to 11.46 at% in **ox-CNH**. This increase reflects the covalent attachment of oxygenated functional groups, particularly carboxylic acids, which contribute to the partial disruption of the graphitic carbon structure. The most prominent evidence of this structural change is the complete disappearance of the π - π^* peak, typically associated with shake-up processes occurring in graphitic domains, in the XPS spectra of **ox-CNH** (Figure 4.15).

FIGURE 4.15: XPS survey, C 1s and O 1s spectra of **p-CNH** and **ox-CNH**.

The XPS analysis of **Bi₂O₂CO₃/Bi₂O₃-oxCNH** confirmed the introduction of the metal with 1.91 at%. The Bi 4f spectrum exhibits two deconvoluted signals at 159.9 eV and 165.0 eV of 4f_{5/2} and 4f_{7/2} related to a (+3) oxidation state, characteristic of both Bi₂O₂CO₃ and Bi₂O₃. An additional smaller contribution for the 4f_{5/2} and 4f_{7/2} can also be observed, that could tentatively assigned to Bi⁵⁺, which however it's a rare state for bismuth oxide. Consistent with the literature, however, this second contribution is frequently not related to this oxidation state but to a minor surface charging effect caused by the change in polarization.¹⁸⁷ The O 1s XPS spectra confirms the presence of Bi in the composite sample, with the presence of an additional contribution at 531.0 eV related to Bi–O species.

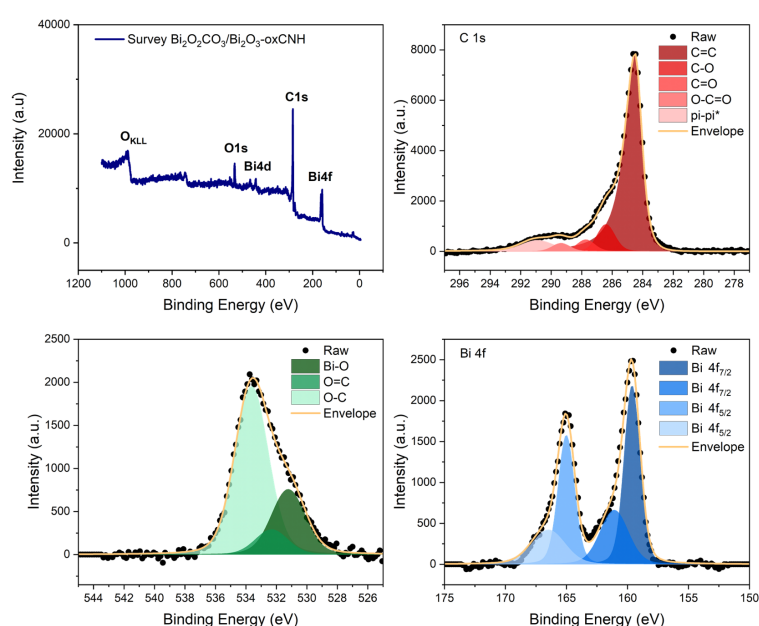


FIGURE 4.16: XPS survey, C 1s, O 1s and Bi 4f spectra of **Bi₂O₂CO₃/Bi₂O₃-oxCNH**.

N₂ physisorption isotherms and pore size distributions calculated from the analysis of the desorption branch of the isotherms are presented for **p-CNH**, **ox-CNH**, **ox-CNH-T**, and **Bi₂O₂CO₃/Bi₂O₃-oxCNH**. All the samples present type IV isotherms typically found in mesoporous materials. The pristine CNHs exhibit a high BET surface area of 438 m² g⁻¹, along with a broad range of micropores and mesopores, and a cumulative pore volume of 1.32 cm³ g⁻¹ (Table 4.2). Following oxidation treatment, the specific surface area increases significantly to 612 m² g⁻¹ for **ox-CNH**, possibly as a consequence of the opening generated at the tips of the horns, and further thermal treatment boosts this value to 1301 m² g⁻¹ for **ox-CNH-T**. Both **ox-CNH** and **ox-CNH-T** display a bimodal pore size distribution, with peaks around 3.5 nm and 29.0 nm. However, **ox-CNH-T** shows a larger proportion of microporosity. This structural transformation is also associated with an increase in pore volume, reaching up to 2.28 cm³ g⁻¹. **Bi₂O₂CO₃/Bi₂O₃-oxCNH** exhibits a BET surface area of 1025

m² g⁻¹, with a pore structure similar to that of **ox-CN**H and **ox-CN**H-T. However, there is a reduced contribution from the pore diameter at 36.0 nm and a higher presence of pores around 3.7 nm.

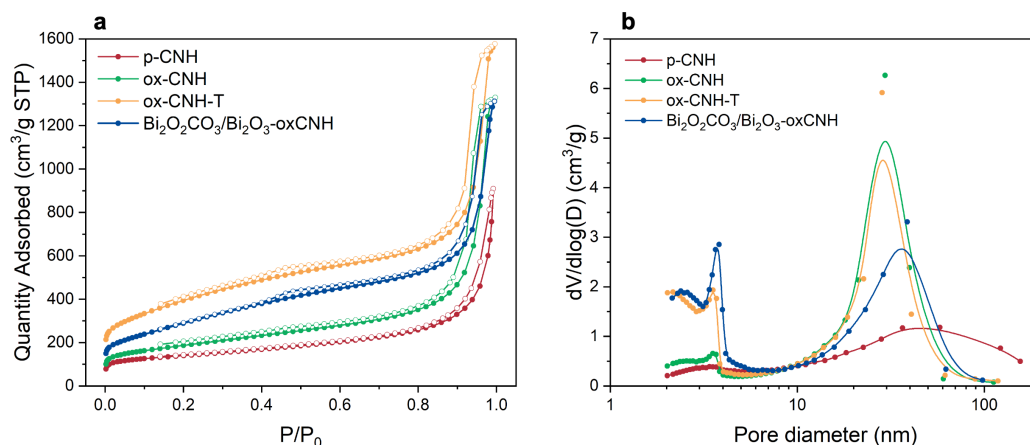


FIGURE 4.17: (a) Isotherms and (b) BJH pore size distribution from desorption branch data of N₂ physisorption for **p-CN**, **ox-CN**H, **ox-CN**H-T and **Bi₂O₂CO₃/Bi₂O₃-oxCNH**.

TABLE 4.2: BET surface areas and desorption cumulative pore volumes obtained from N₂ physisorption data.

Sample	BET surface area (m ² g ⁻¹)	Cumulative pore volume (cm ³ g ⁻¹)
p-CN	438	1.32
ox-CN	612	1.98
ox-CN-T	1301	2.28
Bi ₂ O ₂ CO ₃ /Bi ₂ O ₃ -oxCNH	1025	2.11

To evaluate the electrochemical activity of an electrode, measurements of the roughness factor (RF) and electrochemical surface area (ECSA) are essential. The ECSA provides an estimate of the active surface area available for electrochemical reactions, while the roughness factor (R_f) reflects surface irregularities by comparing the double-layer capacitance (C_{dl}) of the catalyst-coated electrode to that of a smooth reference electrode, thereby highlighting the increased availability of active sites. ECSA measurements were performed in KHCO₃ under argon atmosphere using a glassy carbon electrode with a geometric area of 0.196 cm². In the top panels of Figure 5.10, the cyclic voltammetry curves in a non-faradaic range of potential are shown, while the bottom panels display the corresponding ECSA calculations, derived from the interpolation of double-layer charging/discharging currents to

determine the double-layer capacitance. Compared to **ox-CNH** (ECSA 5.90 cm²) and **ox-CNH-T** (ECSA 19.50 cm²), the material with Bi-based nanoparticles shows a significantly higher ECSA value of 74.5 cm² (Table 5.3). This increase in electrochemical activity can be attributed both to the presence of Bi₂O₂CO₃/Bi₂O₃ NPs, which adds a large number of active sites, but also to a higher presence of defects in the carbon nanostructure resulting from the formation of an interface between the inorganic and organic phases.

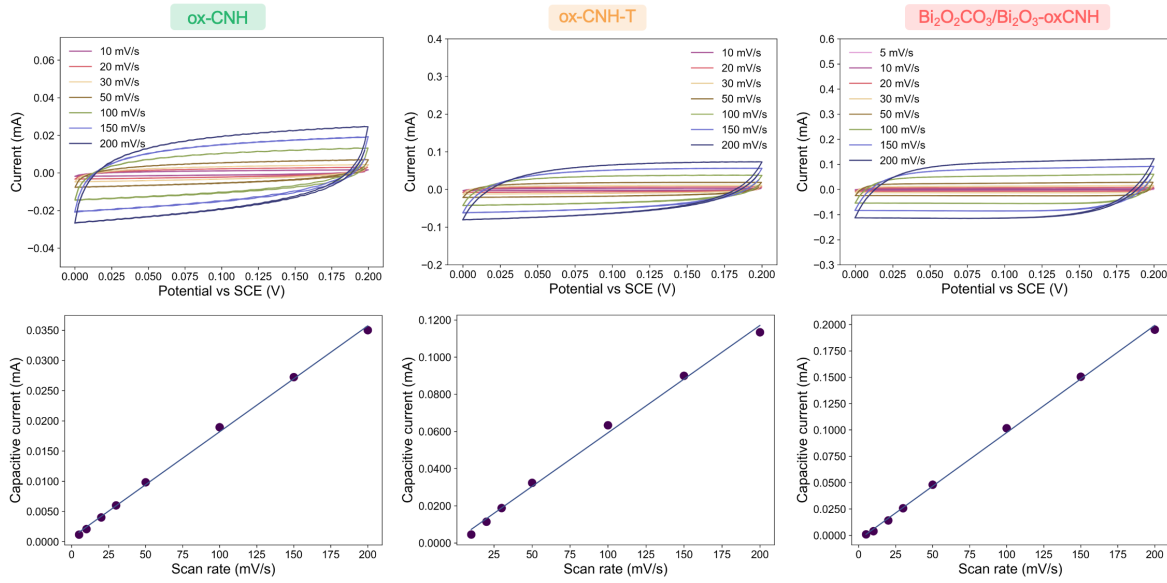


FIGURE 4.18: ECSA calculations in KHCO₃ 0.1 M electrolyte under Ar-saturated conditions. CV scans in non-faradaic regions of **ox-CNH**, **ox-CNH-T**, **Bi₂O₂CO₃/Bi₂O₃-oxCNH** (*top panels*) and capacitive current density plots at different CV scan rates; the current densities were obtained from double-layer charge/discharge curves at 0.1 V vs SCE (*bottom panels*).

TABLE 4.3: Double-layer capacitance (C_{dl}), roughness factor (RF) and electrochemical surface area (ECSA) obtained from ECSA calculations reported in Figure 5.10.

Sample	C_{dl} (mF)	RF	ECSA (cm ²)
ox-CNH	$1.75 \cdot 10^{-7}$	30.17	5.90
ox-CNH-T	$5.78 \cdot 10^{-7}$	99.50	19.50
Bi ₂ O ₂ CO ₃ /Bi ₂ O ₃ -oxCNH	$1.02 \cdot 10^{-6}$	380.09	74.50

The electrocatalytic response of **Bi₂O₂CO₃/Bi₂O₃-oxCNH** was initially assessed through

linear sweep voltammetry (LSV) under both Ar- and CO₂-saturated conditions in a three-electrode cell using a 0.1 M KHCO₃ electrolyte. Figure 4.23a displays the LSV curves for **ox-CN**H, **ox-CN**H-T, and **Bi₂O₂CO₃/Bi₂O₃-oxCN**H in both atmospheres. For the two carbon-based materials, no activation occurs in the presence of CO₂, as their current responses in an Ar atmosphere either coincide or exceed those in a CO₂ atmosphere, indicating minimal or no activity for eCO₂RR. The minor current contribution observed, however, could originate from the competing HER process. In contrast, the Bi-based catalyst exhibits significantly higher current responses in the presence of dissolved CO₂, providing clear evidence that a CO₂ reduction process is taking place. For the composite sample, prior to the catalytic wave, the LSV presents a well-defined reduction peak at -0.98 V vs. SCE is observed, corresponding to the Bi³⁺/Bi⁰ reduction, likely indicating the reduction of Bi₂O₃ to metallic bismuth. Additionally, a smaller peak at -1.36 V vs. SCE is present, which could be attributed to the reduction of Bi₂O₂CO₃.¹⁸⁸ CA tests were conducted for 1 hour to preliminarily assess the current response of the material at -1.5 V, -1.7 V, and -1.9 V vs. SCE in both Ar and CO₂ atmospheres. While no significant increase in current is observed in the CO₂ atmosphere at -1.5 V, the current at -1.7 V and -1.9 V shows a substantial increase compared to the Ar atmosphere, further suggesting enhanced activity for CO₂ reduction at more negative potentials.

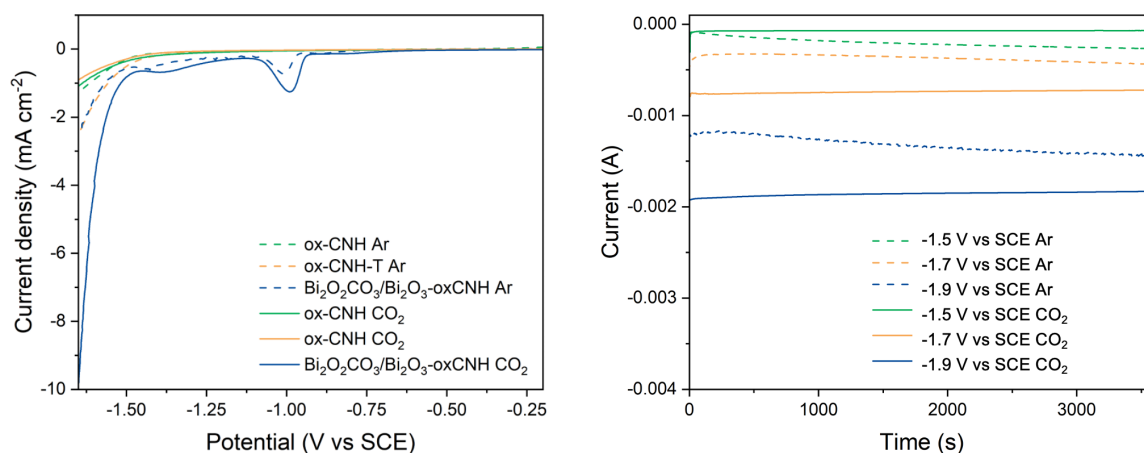


FIGURE 4.19: (a) LSV curves of **ox-CN**H, **ox-CN**H-T, and **Bi₂O₂CO₃/Bi₂O₃-oxCN**H in Ar and CO₂ atmosphere at 5 mV s⁻¹; (b) CA experiments at -1.5 V, -1.7 V, -1.9 V vs SCE of **Bi₂O₂CO₃/Bi₂O₃-oxCN**H under Ar and CO₂ atmosphere using a glassy carbon electrode with 0.196 cm² geometric area.

Subsequently, extended CA measurements were performed for 6 hours at four different potentials (-0.78 V, -0.88 V, -0.98 V, and -1.08 V vs. RHE) in an H-type cell to evaluate product formation and determine the corresponding FEs. Gas chromatography was employed to analyze the gaseous products, while NMR was used to quantify the liquid products. Initially, **ox-CN**H was tested to confirm that only H₂ is produced across the range of applied potentials with this catalyst. In contrast, **Bi₂O₂CO₃/Bi₂O₃-oxCN**H produced a mixture of

H₂, formic acid, and a minimal amount of CO. The CA curves and corresponding FEs are shown in Figure 4.20. At the lowest potential of -0.78 V, HER dominated, with an H₂ FE of 91.8%, and only minor amounts of formic acid and CO are detected. However, shifting the potential to more negative values, the FE for formic acid increases significantly, reaching a maximum of 85.1% at -1.08 V, indicating a definite switch of selectivity towards the CO₂ to HCOOH reduction.

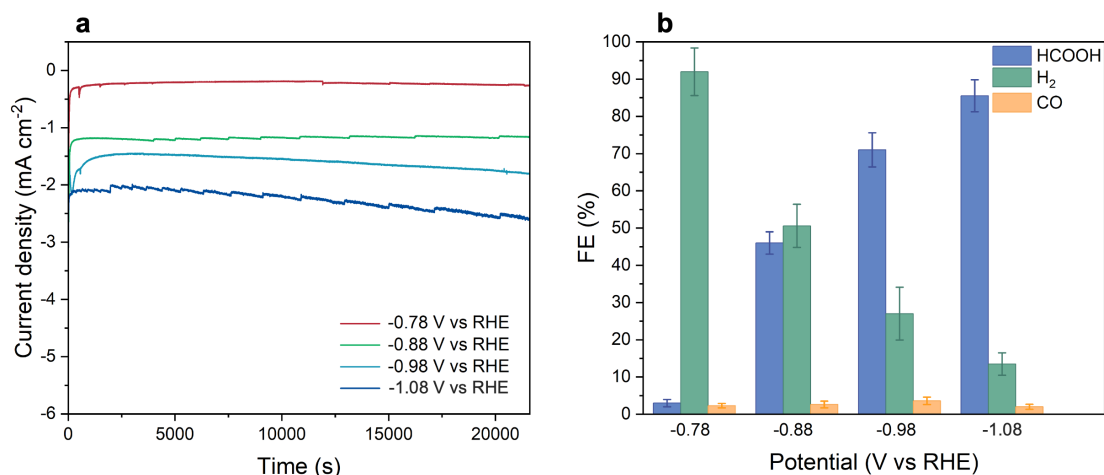


FIGURE 4.20: (a) CA experiments of **Bi₂O₂CO₃/Bi₂O₃-oxCNH** in CO₂-saturated conditions (CO₂ flow 10 mL min⁻¹) for 6 h at different applied potentials; (b) corresponding FEs of the CA tests at different applied potentials.

In situ Raman experiments were conducted to investigate the active phase of the Bi-based nanohybrid material and its structural changes during catalysis. However, the Raman signals from **Bi₂O₂CO₃/Bi₂O₃-oxCNH** in the *in situ* electrochemical cell were noisy, and, given also the use of a KHCO₃-based electrolyte, it is challenging to distinguish between the two phases of Bi₂O₂CO₃ and Bi₂O₃ during their reduction under catalytic conditions. Despite these technical challenges, the restructuring of the initial catalyst into metallic Bi is clearly evident in Figure 4.21, which displays selected spectra at 12-second intervals. In the observed wavenumber region of the reported Raman spectra, bands related to Bi–O bond stretching are visible. Upon applying a potential of -0.78 V vs RHE, these peaks disappear, revealing the characteristic Raman features of metallic bismuth, as discussed in the previous section of this chapter (with signals at 98 cm⁻¹, 130 cm⁻¹, and 184 cm⁻¹), suggesting that both Bi₂O₂CO₃ and Bi₂O₃ are converted into a metallic Bi phase, which is most likely the truly active species.

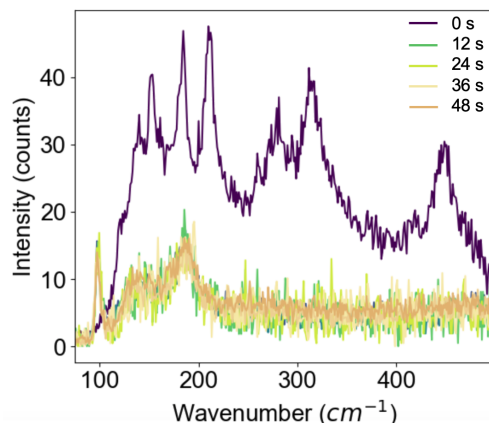


FIGURE 4.21: *In situ* Raman spectroscopy using a 785 nm laser, under -0.78 V vs RHE applied potential in CO₂-saturated conditions. Selected spectra at different time during the experiment are shown.

Finally, to compare the activity of **Bi₂O₂CO₃/Bi₂O₃-oxCNH** over **rBi₂O₃**, the amounts of produced HCOOH are shown in Figure 4.22. The amounts of HCOOH are reported in moles and normalized for the amount in grams of Bi, considering the loading of metal utilized in each catalyst. The nanohybrid material exhibits significantly improved production of HCOOH in the reported potential range. Hence, the bismuth component on the carbon support in **Bi₂O₂CO₃/Bi₂O₃-oxCNH** results more active for CO₂RR, allowing however for greater Bi atom economy.

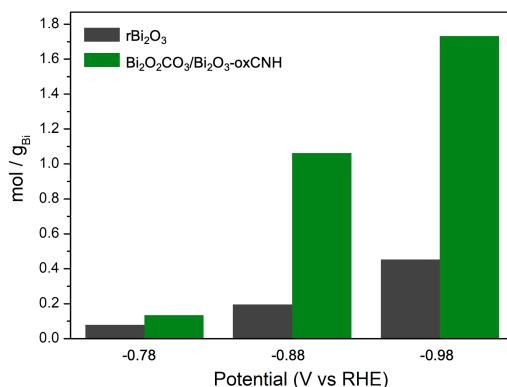


FIGURE 4.22: Comparison mol/g_{Bi} between **rBi₂O₃** and **Bi₂O₂CO₃/Bi₂O₃-oxCNH**

4.4.2 Conclusions and Outlooks

In summary, this study demonstrates the effective integration of Bi-based nanoparticles onto oxidized carbon nanohorns (**ox-CNH**) to form the **Bi₂O₂CO₃/Bi₂O₃-oxCNH** hybrid through

a facile and direct thermal decomposition of Bi precursor in presence of the carbon nanostructure, without the use of any additional templating agent. Exploiting the unique morphological and structural characteristics of CNHs, Bi-based particles growth and dispersion is facilitated to form Bi₂O₂CO₃/Bi₂O₃ NPs with an intimate interface with the carbon support. The developed nanohybrid material presents an elevated BET surface area (1025 m² g⁻¹), pore volume (2.11 cm³ g⁻¹) and ECSA (74.50 cm²), suggesting high accessibility of active sites. This nanohybrid demonstrates promising electrocatalytic performance, achieving Faradaic efficiencies of up to 85% at -1.08 V vs RHE. However, formic acid production diminishes at less negative applied potentials. Through *in situ* Raman spectroscopy, we observed the transformation of the Bi phases under applied potentials, confirming a transition to metallic Bi as active phase during CO₂RR. These findings underscore the potential of CNHs as a versatile support for designing hybrid materials, providing a robust platform for advancing CO₂ reduction catalysts with and promoting reaction kinetics by exploiting the conductive carbon platform.

4.4.3 Experimental Section

Materials. Potassium bicarbonate (KHCO₃ purity >99.7%) was purchased from Fluka. Bismuth(III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O, purity 98%) were purchased from Sigma Aldrich. Carbon dioxide gas (CO₂, purity: 99.995%) was purchased from Linde Gas. Single-walled carbon nanohorns (grade 4 and grade 2), multi-walled carbon nanotubes and graphene were purchased from Carbonium. All experiments were conducted using milliQ water obtained by Direct-Q (Millipore) water purification system.

Synthetic procedures.

ox-CNH: 100 mg of pristine CNH were dissolved in 20 mL of 4 M HNO₃ (69%) solution. The mixture was sonicated for 15 minutes and then stirred for 3 hours. The dispersion was filtered through Millipore membrane (0.1 μm) and extensively washed with water, dimethylformamide and ethanol.

ox-CNH-T: ox-CNH was treated at 320°C for 3 hours (3°C/min) in an alumina crucible.

Bi₂O₂CO₃/Bi₂O₃-oxCNH: 50 mg of ox-CNH were dispersed in 15 mL of ethanol and sonicated for 2 hours. 23.2 mg of Bi(NO₃)₃·5H₂O were sonicated at 50°C for 20 minutes in 1 mL of milliQ water. The solution was added dropwise to the ox-CNH dispersion. The mixture was vigorously stirred for 18 hours. The dispersion was evaporated under vacuum, and the obtained powder was treated at 320°C for 3 hours (3°C min⁻¹).

GO: 200 mg of pristine graphene was added to a 100 mL round-bottom flask containing K₂S₂O₈ (200 mg, 0.37 mmol), P₂O₅ (100 mg, 0.35 mmol), and H₂SO₄ (10 mL). The reaction mixture was sonicated for 30 minutes and then stirred at 80 °C for 4 hours. Upon cooling, the mixture was diluted with deionized water (50 mL), filtered through a Millipore membrane (JHWP, 0.45 μm), and washed with deionized water until the filtrate reached neutrality. The

black powder collected on the membrane was transferred to a round-bottom flask and dispersed in 20 mL of H₂SO₄ at 0 °C. KMnO₄ (100 mg, 0.63 mmol) was then added under stirring, and the reaction was stirred at 35 °C for 2 hours. Subsequently, deionized water (20 mL) and 30% H₂O₂ (2.4 mL) were added, and the mixture was stirred for an additional 15 minutes. The crude product was filtered through a Millipore membrane (0.45 μm) and washed with 1 M HCl (100 mL) followed by deionized water until neutral. Finally, the black powder was rinsed and dried with methanol and ethanol.

ox-MWCNTs: HNO₃ (69%, 4 mL) and H₂SO₄ (95%, 12 mL) were mixed in a round-bottom flask. Then, 100 mg of pristine MWCNTs was added on top. The resulting mixture was sonicated for 5 h at room temperature. The reaction was then quenched with cold water (200 mL). The crude mixture was filtered through a Millipore membrane (0.45 μm) and washed with deionized water until the washings reached neutral pH. The black powder was then washed and dried with methanol and ethanol.

Characterization. Raman spectra were recorded on a inVia Renishaw spectrometer equipped with a Nd:YAG laser using an excitation wavelength of 532 nm.

Thermogravimetric analysis (TGA) was carried out on a TA Discovery TGA 550 instrument with a heating rate of 10 °C min⁻¹ under N₂ flow. IR spectra were recorded in attenuated total reflectance (ATR) mode on a Shimadzu IRAffinity-1S spectrophotometer equipped with a QATR 10 accessory. TEM analyses were performed using a Philips EM 208 microscope operating at 100 kV and equipped with an 11 MP bottom-mounted CCD Olympus Quemesa camera. Textural properties were analyzed by N₂ physisorption at the liquid nitrogen temperature using a Micrometrics ASAP 2020 automatic analyzer. All the NPs were degassed at 120 °C for 12 h at 10 μmHg.

The specific surface area was obtained by applying the Brunauer–Emmett–Teller (BET) method equation and Langmuir equation. Pore size distribution was determined applying the Barrett, Joyner, and Halenda (BJH) method equation to the adsorption and desorption branch of the isotherms.

Powder X-ray diffraction analysis was performed on a Malvern PANalytical Empyrean Series 3 with Cu Long Fine Focus spot High Resolution tube comprehensice of Ni β filter, detector 1Der, over a 2θ range of 10–100° with a step size of 0.17°. The phase determination was performed through ICDD database.

Electrochemical measurements. LSV and CA measurements, Extended CA experiments in H-cell and corresponding electrochemical set-up, FE calculations and *in situ* Raman analyses were performed as previously described in Section 4.3.3.

The electrochemical surface area (ECSA) was determined using a glassy carbon (GC) electrode with a fixed geometric area (0.196 cm²). The setup consisted of a Pt counter electrode and a Saturated Calomel Electrode (SCE) as the reference electrode. Cyclic Voltammetry (CV) measurements were performed in an Ar-saturated 0.1 M KHCO₃ electrolyte. The scan

rates for obtaining the CV response were 10 mV/s, 20 mV/s, 30 mV/s, 50 mV/s, 100 mV/s, 150 mV/s and 200 mV/s over a potential range of 0 V to 0.2 V vs SCE, chosen to avoid any faradaic processes. The ECSA was calculated using the following equation:

$$\text{ECSA} = RF \cdot S$$

$$RF = \frac{C_{dl}(\text{catalyst})}{C_{dl}(\text{smooth glassy carbon})}$$

In the equations, RF represents the roughness factor, defined as the ratio of double layer capacitance (C_{dl}) of the working electrode to that of the smooth GC electrode. S denotes the geometric surface area of the GC electrode. The C_{dl} values were determined for both the catalyst-deposited working electrode (WE) and the smooth glassy carbon electrode. The C_{dl} values can be obtained by establishing a linear relationship between $\Delta j = (j_a - j_c)$, where j_a and j_c denote the anodic and cathodic current densities, respectively, measured at the scan rate at a potential value of 0.1 vs RHE. Additional theoretical details are reported in Chapter 2.

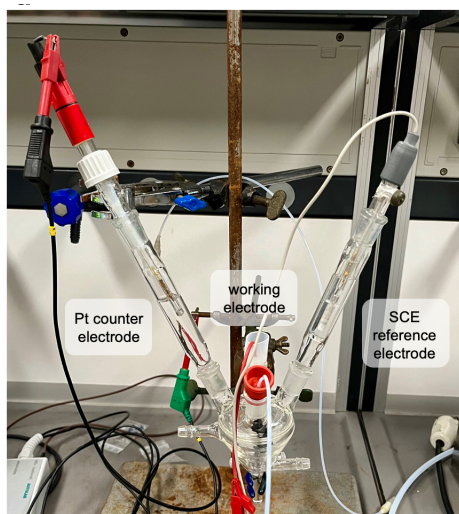


FIGURE 4.23: Single cell set-up with SCE reference electrode, Pt wire counter electrode and glassy carbon working electrode with 0.196 cm² geometric area, employed for screening LSV and CA measurements and ECSA calculations.

Chapter 5

Thermally Tunable Hyper-Crosslinked Polymer for Metal-Free Oxygen Reduction Reaction

5.1 Introduction

Hydrogen peroxide (H_2O_2) is a crucial chemical with a rapidly growing demand due to its versatility and environmental advantages. Typical applications feature H_2O_2 as an oxidizing agent in chemical synthesis,¹⁸⁹ pulp and paper bleaching,¹⁹⁰ wastewater treatment,¹⁹¹ and disinfection,¹⁹² where H_2O_2 is valued for its ability to perform the oxidation of the substrates under mild conditions, while producing only water as a byproduct.^{189,190} This makes it an attractive alternative to traditional oxidizers, which often generate hazardous wastes. As industries increasingly focus on sustainability and green chemistry, the relevance of H_2O_2 continues to grow, positioning it as a key reagent in chemical processes. Currently, the primary industrial method for producing H_2O_2 is the anthraquinone process, developed in 1939 by BASF.¹⁸⁹ The reaction consists of a very energy-intensive multistep synthesis, in which the anthraquinone compound is first hydrogenated using a palladium catalyst, followed by oxidation with atmospheric oxygen (Figure 5.1).¹⁹³ While effective, this process has significant drawbacks, including the use of expensive noble metal catalysts, massive waste production of organic solvents and undesired organic by-products formation, making it less sustainable in the long term. Additionally, concentrated H_2O_2 poses significant risks during storage and transportation, leading to increased costs and safety concerns.

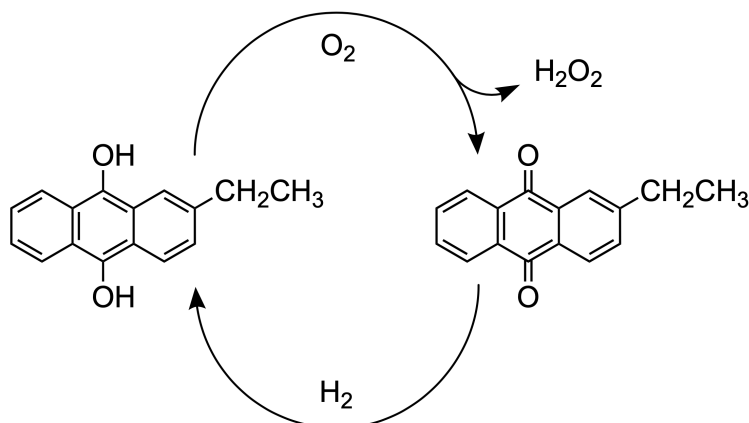


FIGURE 5.1: Catalytic cycle of the anthraquinone process for the synthesis of H₂O₂.

These issues have spurred research into alternative resource-efficient routes, aiming at reducing the environmental impact and cost of H₂O₂ production. The *in situ* generation of diluted H₂O₂ on demand offers a solution to mitigate both safety hazards and environmental impact, particularly when powered by renewable energy sources. Electrochemical synthesis, together with photosynthetic and other greener chemical approaches, has emerged as a promising route for the H₂O₂ production. This method allows for the direct generation of H₂O₂ either from molecular oxygen (O₂) at a cathode or through water oxidation (WOR) at an anode. The high availability on the Earth of both these potential starting compounds, oxygen and water, and the mild working conditions make this process highly attractive. Especially, it circumvents the need for hazardous materials and complex infrastructure usually required in the conventional method. Among these two approaches, this chapter will be focused on the electrochemical reduction of oxygen (oxygen reduction reaction, ORR) for the synthesis of H₂O₂. Despite the advantages mentioned above, the development of H₂O₂ production via ORR presents significant hurdles. Oxygen reduction can be effected *via* two competing pathways, one producing H₂O₂ (called the 2-electron pathway), the other producing H₂O (4-electron pathway). As the names suggest, the selectivity towards one of these two outcomes depends on the number of electrons involved in the reaction. The two pathways are based on two general types of mechanisms: the dissociative and the associative mechanism (Figure 5.2).¹⁹⁴ In the dissociative mechanism, the O₂ molecule undergoes O–O bond cleavage during the adsorption onto the catalyst surface, resulting in individual oxygen atoms adsorbed on the catalyst (*O). These atoms undergo a proton-coupled electron transfer from the catalyst, being reduced to hydroxyl intermediates (*OH) and eventually being fully reduced to water (H₂O). Therefore, this mechanism leads to the 4-electron reduction pathway (4e[−]), where oxygen is fully reduced to water. On the other hand, the associative mechanism involves the reduction of O₂ without initially breaking the O–O bond. Oxygen is first reduced in a proton-coupled electron transfer step leading to a hydroperoxyl

species (*OOH) adsorbed on the catalyst surface. From this point, *OOH can be decomposed to *O and *OH , continuing along to the further reduction into H_2O through a 4e^- pathway. Alternatively, *OOH can also follow the 2e^- pathway, where the *OOH intermediate desorbs from the electrodic surface, after another proton-coupled transfer step, leading to the formation of H_2O_2 through an electron-proton transfer. Therefore, the formation of H_2O_2 strongly depends on the interaction between the catalyst and the *OOH intermediate. If the binding is too strong, the dissociation of the O–O bond in the *OOH intermediate will be favored, resulting in water formation. If the interaction is weak enough, *OOH will be able to detach, resulting in the formation of H_2O_2 . However, another important factor influencing ORR selectivity is the strength of O_2 adsorption, which must be sufficient for ORR to occur. Moreover, the mode of adsorption can vary: O_2 may adsorb in an end-on geometry, favoring the associative mechanism, or in a side-on mode, which favors the dissociative mechanism.¹⁹⁵ Finally, once formed, H_2O_2 may also re-adsorb on the catalyst (especially if the H_2O_2 diffusion towards the bulk electrolyte is too slow) and undergo further reduction to H_2O *via* an additional 2-electron process (overall this process is often indicated as 2+2-electron pathway), reducing the overall peroxide productivity. Alternatively, the productivity of H_2O_2 may be caused by disproportionation in solution, a relatively facile process in absence of H_2O_2 stabilizing agents in solution, in particular at alkaline pH.

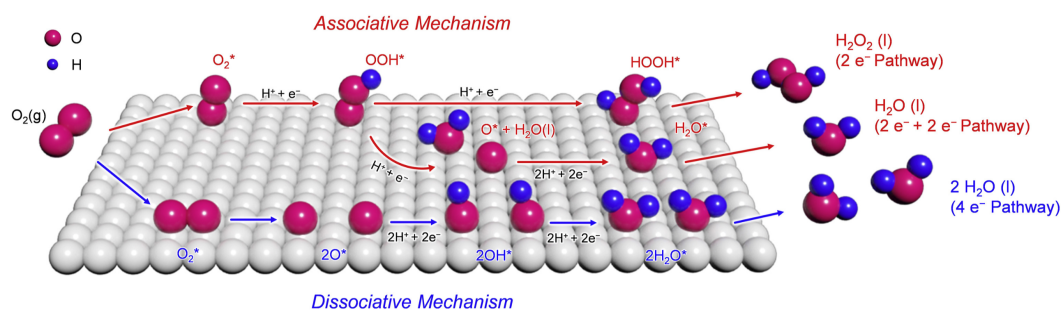


FIGURE 5.2: Reaction mechanisms of oxygen electroreduction. Reproduced with permission.¹⁹⁵

All of the above ORR pathways are considered attractive and important in different electrochemical application contexts. The importance of 4e^- ORR lies primarily in its fundamental role in energy applications, most significantly in fuel cells and metal-air batteries.¹⁹⁶ In these applications, hydrogen peroxide, even in low concentration, is an undesired and detrimental product, on account of its corrosive nature that may compromise the cell, and because less electronic charge (per O_2 molecule) is flown with a 2-electron reduction in comparison to a 4-electron reduction, thus diminished the current density. On the contrary, the selectivity production of H_2O_2 in significant amounts makes the 2e^- ORR a sustainable replacement of the anthraquinone process, particularly for decentralized H_2O_2 uses.¹⁹⁷

Moreover, the $2e^-$ ORR can be carried out effectively across a wide pH range, from acidic to alkaline conditions, offering versatility in relation to the specific application's requirements. It should be stressed that the choice of the electrolyte is a crucial variable of the electrocatalytic system, and the optimum pH is usually restricted by compatibility with the particular type of catalyst, whose performance may be strongly pH-sensitive. As a general trend, acidic and alkaline electrolytes are associated with higher catalytic activity, although stability issues may arise: for low pH, the electrode could undergo catalyst leaching, while high pH promote disproportionation, decreasing progressively the H_2O_2 concentration. Meanwhile, neutral pH environments, though kinetically less favorable, are ideal for producing medical-grade hydrogen peroxide for disinfection and biological purposes, given the compatibility with most of biological environments.

The effectiveness of ORR for selective hydrogen peroxide electrosynthesis is closely linked to the catalytic material employed. Catalysts play a fundamental role in dictating whether the reaction will proceed *via* the $2e^-$ or $4e^-$ pathway, significantly influencing both product selectivity, reaction efficiency and applied potential range. To date, a variety of catalysts, including molecular complexes, noble metals and their alloys,^{198,199} non-noble transition metals,^{200,201} single-atom catalysts,^{202,203} and carbon-based materials,^{204,205} have been explored to optimize this process.²⁰⁶ During the last years, carbon catalysts have received great attention from the scientific community as more sustainable, metal-free alternatives for H_2O_2 electrosynthesis, thanks to their high earth-abundance, low-cost, good chemical stability and high tunability. Several studies highlighted the potential of this class of electrocatalysts, with performances related in particular to their heteroatom doping, defects, functional groups, structural features and porosity.^{207–216} Carbon-based materials for ORR generally consists of doped carbon obtained through pyrolysis of organic precursor containing heteroatoms, functionalized/doped carbon nanostructures or carbon black.²¹⁷ In fact, introducing heteroatoms into carbon materials cause covalent bond polarization, with formation of dipoles which can favor the oxygen adsorption and acting as active sites.²¹⁸ N doping has been one of the most investigated and effective approach for selective H_2O_2 production, thanks to its electronegativity that can effect a redistribution of electrons and consequently of the active sites in the carbon catalyst. If appropriately integrated, N atoms in the carbon framework can be used to fine-tune basicity and hydrophilicity of the neighboring carbon atoms.^{26,211} Several studies have been conducted to investigate the optimal nitrogen configurations for ORR activity. Pyridinic, pyrrolic, and graphitic nitrogen species in carbon-based structures have been extensively studied due to their significant influence on the ORR mechanism. In particular, some reports suggest that while pyridinic nitrogen favors the highly efficient 4-electron pathway, a higher concentration of pyrrolic nitrogen tends to promote the 2-electron pathway.^{27,218,219} Such a statement, however, should be regarded as an extreme generalization, as multiple factors are in play making the mechanism highly complex and dependent on the specific type of N-doped carbon structure.

In this landscape, porous organic polymers (POPs) are emerging as promising electrocatalysts in several applications, including hydrogen evolution reaction, oxygen evolution reaction and oxygen reduction reaction.²²⁰ Although this class of materials is not new, their application in the electrocatalytic field is still in its early stages of development. POPs refer to different classes of porous carbon-based materials designed at molecular level, typically characterized by high surface areas, low densities and well-defined pore topologies.²²¹ The well-defined pore structure makes these materials very interesting for applications where the type of porosity of the catalyst (or support) has notable influence on the selectivity of the process. In fact, the diffusion rates of reagents and products to/from the pores of the catalyst can be a discriminating factor for the specific catalytic pathway. POPs can be assembled from a variety of organic building units, exploiting the covalent bonding of light elements (such as C, B, N and O) through chemical polymerization reactions. Based on their synthetic methods and structural properties, POPs can be classified into several categories, such as covalent organic framework (COFs), polymers of intrinsic microporosity (PIMs), hyper-crosslinked polymers (HCPs), conjugated microporous polymers (CMPs), covalent triazine frameworks (CTFs) and porous aromatic frameworks (PAFs).^{220,222,223} Despite their versatile features, the application of POP materials and their derivatives for metal-free ORR is still in its early stages, with only a limited number of studies currently available in the literature, mainly due to challenges related to low conductivity and structural instability under electrochemical conditions.^{224–227}

5.2 Aim of the Research Project

HCPs consists of a well-distributed crosslinking within a multidimensional porous network, which can be prepared by several methodologies starting from cost-effective precursors and reaction conditions.²²¹ This chapter focuses on the use of a hyper-crosslinked polymer synthesized from melamine and terephthalaldehyde as platform for constructing novel metal-free electrocatalysts for the oxygen reduction reaction (ORR). In particular, we investigate thermally treated HCP-based electrocatalysts for the production of H₂O₂. The structural rearrangement of the pristine HCP material at different pyrolysis temperature modifies multiple features, including key properties for ORR activity such as nitrogen configuration, porosity and graphitization grade. The treatment is expected to improve both the conductivity and the stability of the catalyst. One main objective is to highlight the structure/catalytic properties relationship of these thermalized HCPs in relation to the graphitization temperature, providing new insights into the use of porous organic polymers for the ORR.²²²

5.3 Results and Discussion

A hyper-crosslinked polymer was synthesized using melamine and terephthalaldehyde as building blocks to form an amorphous and highly cross-linked amina network (**mt-HCP**). The material was synthesized through a facile solvothermal method via a one-pot assembly through Schiff base chemistry, without the aid of additional catalysts or templates (Figure 5.3).^{228,229} In the synthesis, the monomers were heated at 200°C for 15 h in dimethyl sulfoxide in air. With this experimental conditions, the formation of imines is followed by the attack of the imine double bond by primary amines, leading to the formation of a final amina framework. Finally, after washing the precipitated material, a pale yellow powder was obtained.

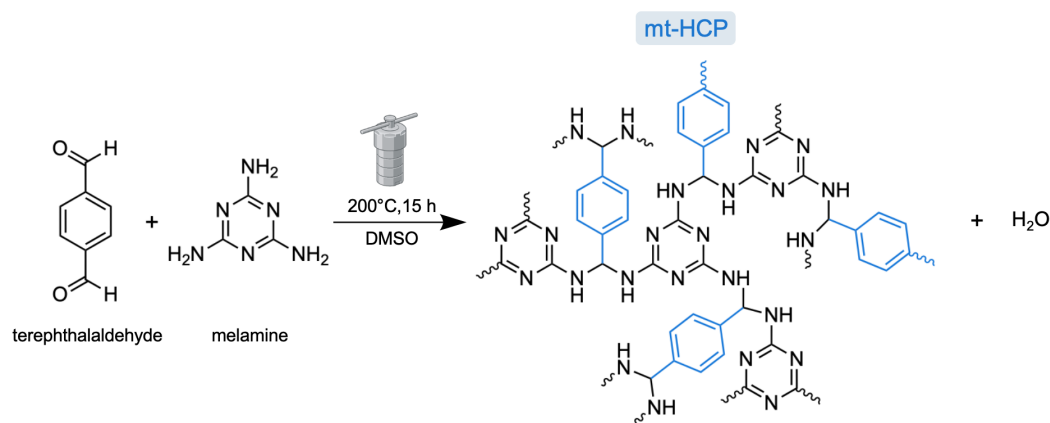


FIGURE 5.3: Schematic representation of the synthetic procedure and structure network of melamine-terephthalaldehyde derived hyper-crosslinked polymer (**mt-HCP**).

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of **mt-HCP** are reported in Figure 5.4. They reveal elongated interconnected spherical nanoparticles, suggesting a networked arrangement.

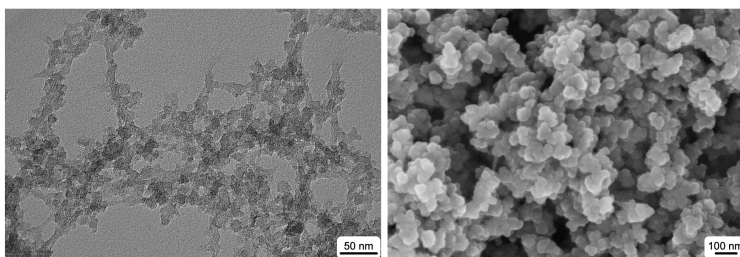


FIGURE 5.4: TEM (left) and SEM right images of **mt-HCP**.

Attenuated total reflection infrared (ATR-IR) spectroscopy was performed to first evaluate **mt-HCP** (Figure 5.5). The fingerprint of the primary amine from melamine, namely

the NH_2 stretching at around 3470 cm^{-1} , 3420 cm^{-1} and NH_2 bending at 1650 cm^{-1} , are not detected. Moreover, the peak at 1650 cm^{-1} characteristic of $\text{C}=\text{O}$ stretching of terephthalaldehyde is absent. Thus, the condensation between the amino and aldehyde groups of the monomers has taken place effectively. The two distinctive signals at approximately 1550 cm^{-1} and 1480 cm^{-1} are assigned to the $\text{C}=\text{N}$ vibration of triazine rings. Weak signals around 1600 cm^{-1} are also visible, which may suggest the presence of traces of imine functionalities, although the overall structure remains predominantly aminated. Thermogravimetric analysis (TGA) under nitrogen flow reveals an initial weight loss around 200°C , likely due to the evaporation of solvents trapped within the pores (Figure 5.5). A second smaller weight loss occurs around 330°C , which could be attributed to the decomposition of weakly bound or terminal functional groups. The HCPs' main structure remains stable up to 450°C , beyond which the significant weight loss corresponds to the degradation of the triazine units within the framework.

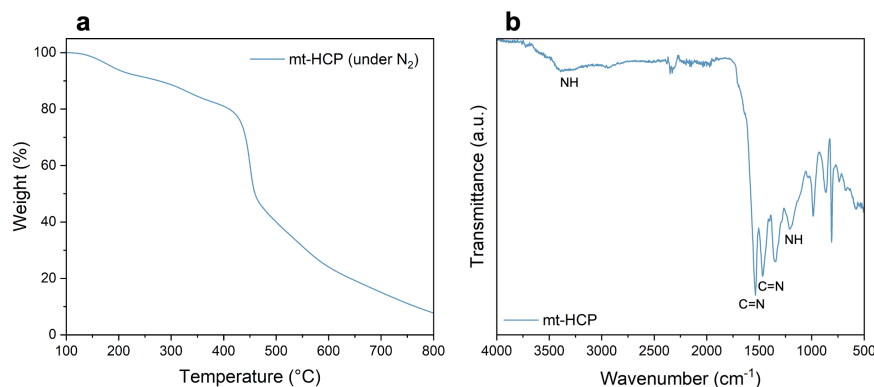


FIGURE 5.5: (a) TGA curve under N_2 atmosphere; (b) ATR-IR spectrum of **mt-HCP**.

The **mt-HCP** material was subsequently subjected to thermal treatment at different pyrolysis temperature under controlled argon flow, with the purpose of obtaining nitrogen-rich electrocatalysts with enhanced conductivity. The pyrolysis temperatures of 400°C , 600°C and 800°C were selected, resulting in the formation of three materials with different properties, labelled **HCP-400**, **HCP-600** and **HCP-800**, respectively. The structural evolution of **mt-HCP** as a function of temperature was investigated, and it was observed that various material's key characteristics, including composition, morphology, porosity, conductivity, and, ultimately, catalytic activity, are highly dependent on the chosen pyrolysis temperature.

TEM analysis of all the three thermalized HCP-based materials is shown in Figure 5.6. In comparison with the **mt-HCP**, the structure obtained from the 400°C treatment appears more coalescent and displays a globular morphology, with particles forming larger, more

cohesive units. At higher temperatures, the structure begins to lose its definition, particularly for **HCP-800**, where the shape becomes more irregular, yet it is possible to recognize large spherical-shaped particles.

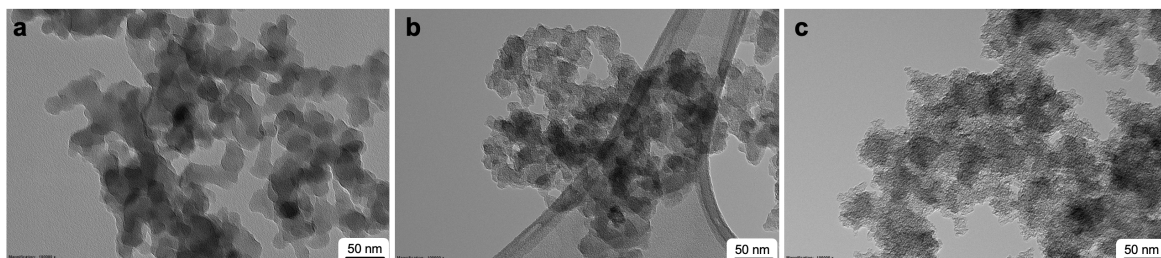


FIGURE 5.6: TEM and SEM images of (a) **HCP-400**, (b) **HCP-600**, (c) **HCP-800**.

X-ray diffractograms of **mt-HCP** and its derivatives indicates that the structure is predominantly amorphous (Figure 5.7b), even though **HCP-800** exhibit a low-intensity reflection related to graphitic carbon (002) at approximately 26.7° , so that the thermal treatment generates crystalline domains in the material. This change in graphitization degree of the thermally-treated materials has been further evaluated by Raman spectroscopy (Figure 5.7a). For the higher pyrolysis temperature (600 and 800°C), two overlapping peaks, the so-called D (1350 cm^{-1}) and G band (1580 cm^{-1}) typical of carbon-based material containing graphitic domains, are detectable. On the other hand, the Raman spectrum of **HCP-400** presents a broad and flattened G band with a very low-intensity D band shoulder, indication of a highly disordered, predominantly amorphous carbon structure with minimal graphitic domains.

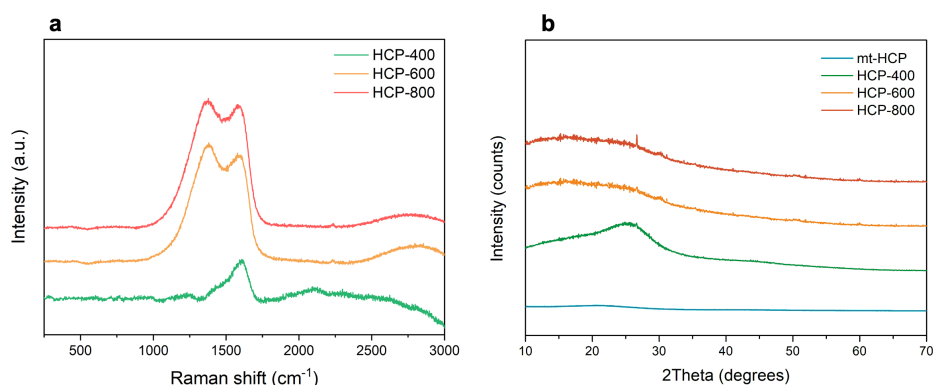


FIGURE 5.7: Raman spectra (a) and XR diffractogram (b) of **HCP-400**, **HCP-600**, **HCP-800**.

XPS analysis provided valuable insights into the carbon-based structure of the materials. The deconvolution of the N1s XPS spectrum of **mt-HCP** reveals the characteristic signal of

triazine (C=N–C) and the contribution of N–H functionalities from the HCP network (Figure 5.8). The C1s peak can be deconvoluted into three main contributions, corresponding to C=C, C–N, and N–C=N, as expected from the reported structure in Figure 5.3. Upon thermal treatment, this pristine material gradually acquires more graphitic nature, as shown in the XPS spectra of the three thermalized materials. **HCP-400** exhibits a more coordinated network compared to **mt-HCP**, due to the presence of an additional contribution of graphitic nitrogen (N(C)₃) at 400.7 eV and a decreased component of secondary amines/pyrrolic nitrogens (NH(C)₂) at 399.7. In this structure, the dominant N component (peak area = 54.7%) at 398.5 eV is assigned to the pyridinic nitrogen characteristic of the triazines. In the C1s high-resolution spectrum of **HCP-400**, although graphitic carbon is clearly present, it is not the predominant component; instead, the C=N–C bond makes a significant contribution. The atomic percentages of C and N remain almost unchanged compared to the pristine HCP, with a C/N ratio of 1.7. In contrast, the C1s spectra of both **HCP-600** and **HCP-800** present a dominant peak deconvolution pattern attributed to graphitic carbon. Moreover, for these two materials, the C/N ratio increases significantly, reaching 3.7 for **HCP-600** and 6.6 for **HCP-800**. Despite this, the N1s spectrum of **HCP-600** still retains some component characteristic of triazine-based structures, whereas **HCP-800** displays a definite enhancement of the graphitic nitrogen signal. Interestingly, **HCP-800** presents an additional N contribution which may be arising from generation of NO_x moieties. The shift in nitrogen configuration, especially the ratio $N_{\text{pyrrolic}}/N_{\text{pyridinic}}$ may have a considerable impact on ORR activity, as discussed in Chapter 1.

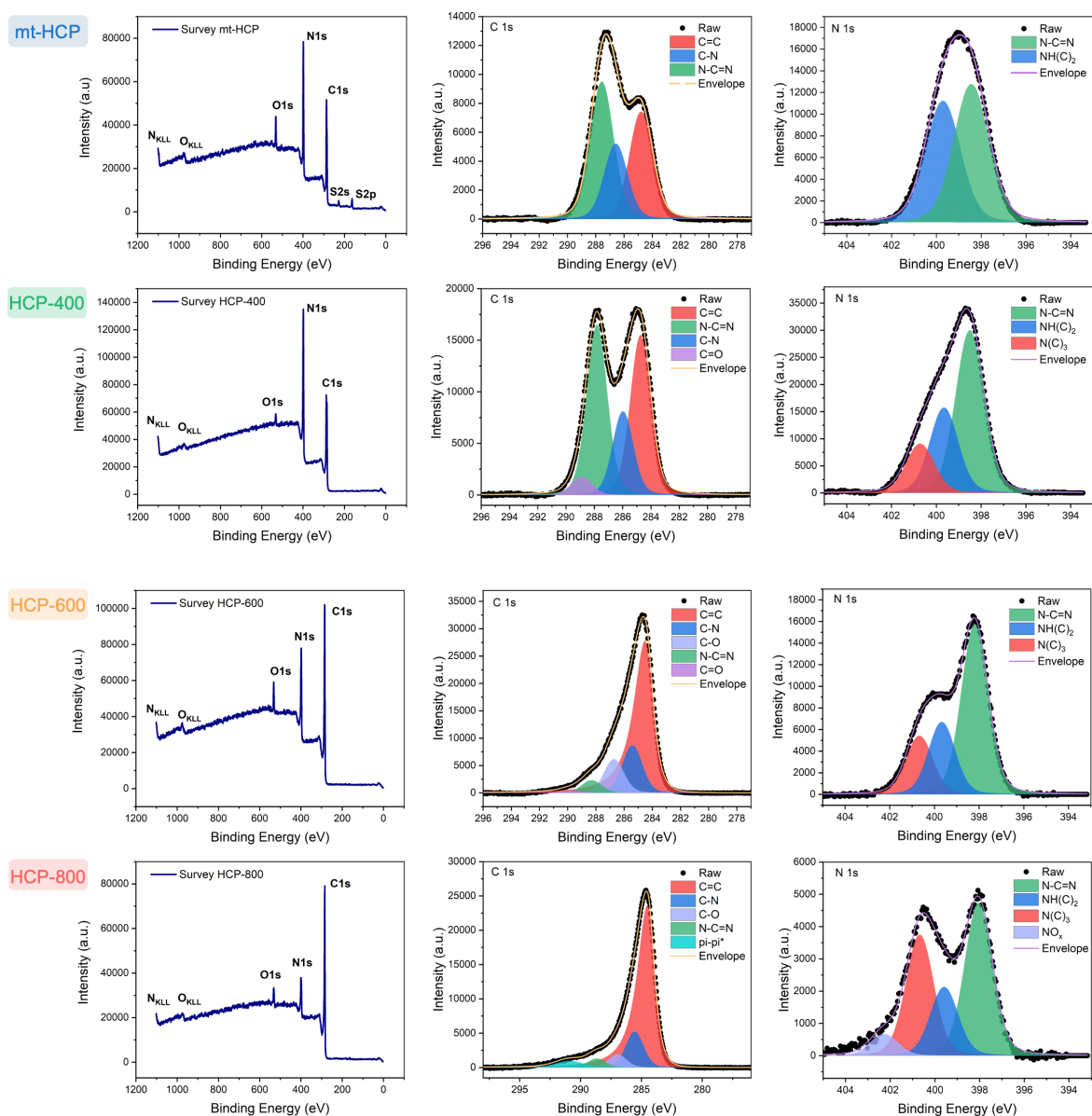


FIGURE 5.8: XPS analysis (survey, C1s and N1s HR spectra) of the HCP materials.

TABLE 5.1: Atomic percentages of HCP materials from XPS data.

Sample	C / at%	N / at%	O / at%	C/N
mt-HCP	60.8	34.5	4.7	1.7
HCP-400	60.2	38.9	1.8	1.7
HCP-600	75.7	20.4	3.9	3.7
HCP-800	84.2	12.8	3.0	6.6

The textural properties were investigated by means of nitrogen physisorption measurements at the temperature of liquid nitrogen. Pristine **mt-HCP** exhibits a typical type IV isotherm with a hysteresis loop at high nitrogen pressures and a steep uptake at very low P/P^0 , indicating a micro-mesoporous framework (Figure 5.9). It possesses a relatively high Brunauer–Emmett–Teller (BET) specific surface area of $596 \text{ m}^2 \text{ g}^{-1}$, a considerable total pore volume of $1.15 \text{ cm}^3 \text{ g}^{-1}$ and a pore size maximum of 20.5 nm. Furthermore, t-plot analysis indicates a notable contribution from micropores, with a calculated micropore volume of $0.13 \text{ cm}^3 \text{ g}^{-1}$ (Table 5.2). Following pyrolysis at different temperatures, the textural features of the electrocatalysts were significantly modulated. Specifically, after treatment at 400°C , the micropores collapse, leaving a mesoporous material with a BET surface area of $114 \text{ m}^2 \text{ g}^{-1}$. In contrast, higher temperatures lead to the restructuring of microporous features. As a result, **HCP-600** exhibits an improved BET surface area and a substantial contribution of micropores, with a micropore volume of $0.14 \text{ cm}^3 \text{ g}^{-1}$. Finally, after thermal treatment at 800°C , the resulting material presents a isotherm type I, indicating a fully microporous material, with a Langmuir surface area of $356 \text{ m}^2 \text{ g}^{-1}$. Due to the diverse textural properties of the materials, both desorption and absorption pore size distributions are provided for completeness in Figure 5.9. The pristine HCP material exhibits a broad distribution of micropores along with narrow mesopores. **HCP-400** and **HCP-600** display comparable distribution, with pore diameter maximum in the range of 50 nm.

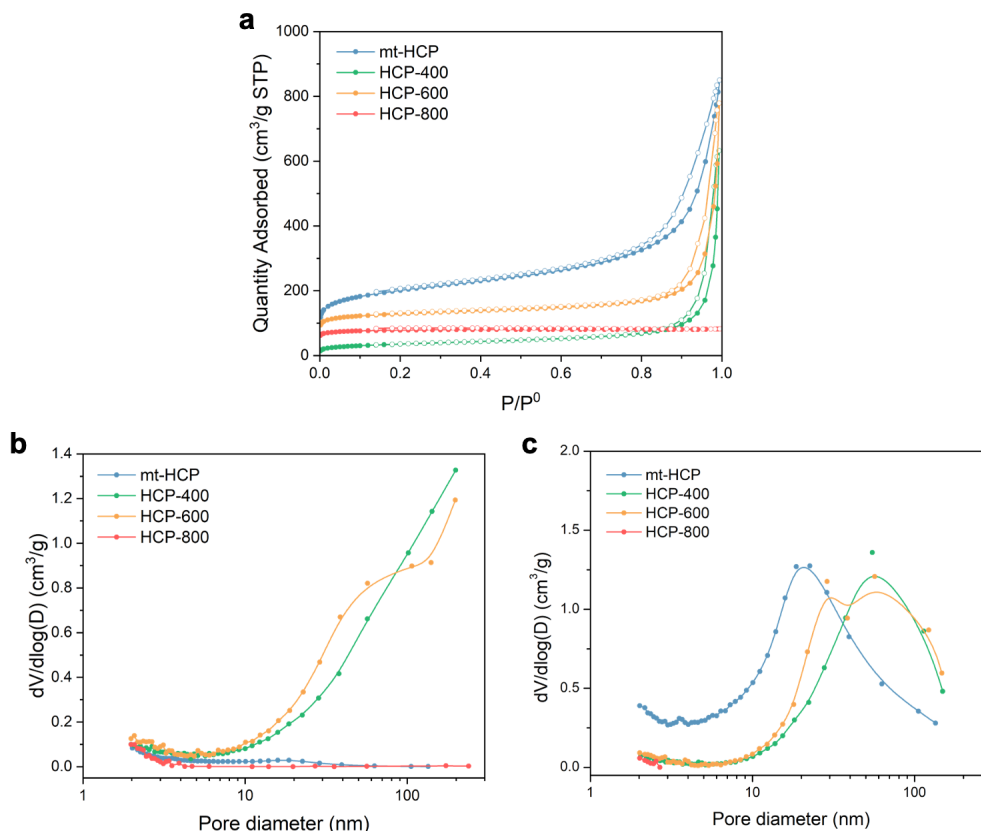


FIGURE 5.9: (s) N_2 isotherms, (b) adsorption and (c) desorption BJH pore size distributions of the HCP-based materials.

TABLE 5.2: Calculated surface areas, external surface areas, pore volumes and micropore volumes derived from nitrogen physisorption data for HCP-based materials.

Sample	BET surface area ($m^2 g^{-1}$)	Langmuir surface area ($m^2 g^{-1}$)	External surface area ($m^2 g^{-1}$)	Cumulative pore volume ($cm^3 g^{-1}$)	Micropore volume ($cm^3 g^{-1}$)
mt-HCP	596	–	411	1.15	0.13
HCP-400	114	–	108	0.95	0.01
HCP-600	353	–	138	1.4	0.14
HCP-800	–	356	46	–	0.10

In addition to the surface areas determined by N_2 physisorption, the electrochemical surface area (ECSA) offers a more meaningful measure of material activity under electrocatalytic conditions. ECSA values, presented in Figure 5.10 and Table 5.3, reveal significant differences among the catalysts treated at different temperatures. For **HCP-400**, the

ECSA and corresponding roughness factor (RF) indicate limited electrochemical activity, with a relatively low ECSA of 0.63 cm^2 . However, as the treatment temperature increases, a marked enhancement in ECSA is observed, with **HCP-800** achieving an outstanding ECSA of 121.50 cm^2 . This suggests that the higher treatment temperatures induce structural or compositional changes that significantly improve the electrochemical surface activity of the HCP-based electrocatalysts.

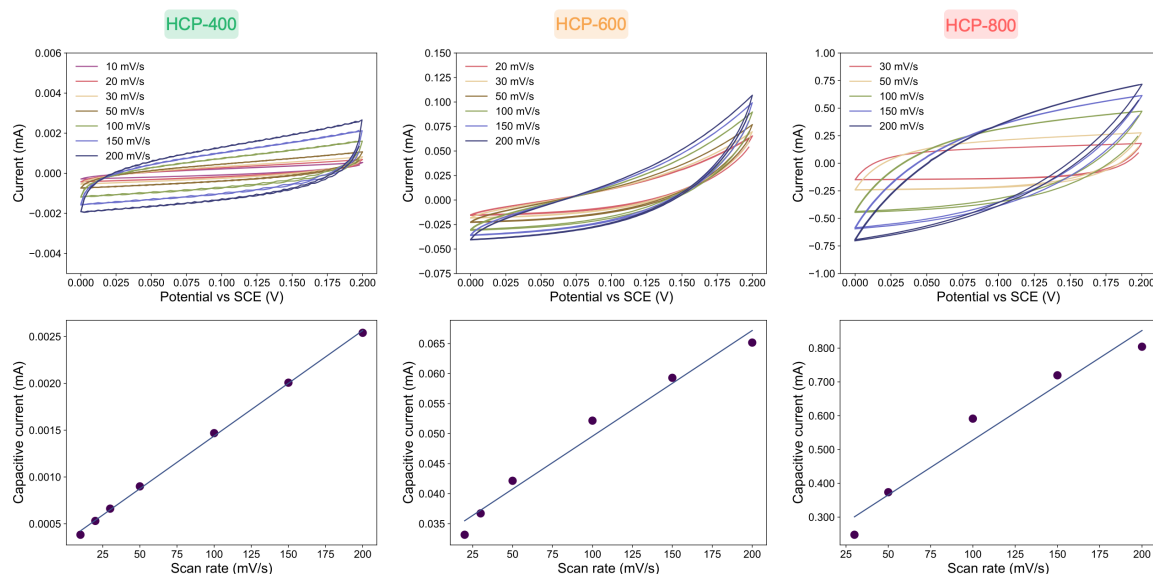


FIGURE 5.10: ECSA calculations obtained for the HCP-based materials in KOH 0.1 M electrolyte under Ar-saturated conditions.

TABLE 5.3: Double-layer capacitance (C_{dl}), roughness factor (RF) and electrochemical surface area (ECSA) for the HCP-based materials obtained from ECSA calculations reported in Figure 5.10.

Sample	C_{dl} (mF)	RF	ECSA (cm^2)
HCP-400	$1.13 \cdot 10^{-8}$	3.22	0.63
HCP-600	$1.76 \cdot 10^{-7}$	33.64	6.59
HCP-800	$3.24 \cdot 10^{-6}$	619.92	121.50

The ORR catalytic activities of the thermally-treated HCP materials were evaluated using linear sweep voltammetry (LSV) in 0.1 M KOH electrolyte (pH 12.8) at a scan rate of 5 mV s^{-1} . Figure 5.11 compares the performance of the materials in both Ar- and O_2 -saturated conditions. The increase in current under O_2 -saturated conditions, relative to the inert Ar atmosphere, confirms the catalytic activity of the materials towards ORR. Notably, **HCP-800** demonstrates a more positive onset potential (0.75 V vs RHE) compared to **HCP-400** (0.61 V) and **HCP-600** (0.59 V), along with higher current densities, consistent with the

ECSA evaluation and presumably resulting from the higher graphitization degree. As a side note, noticeable current contribution is observed under Ar conditions for **HCP-600** and more prominently for **HCP-800**, which could be attributed to non-faradaic processes.

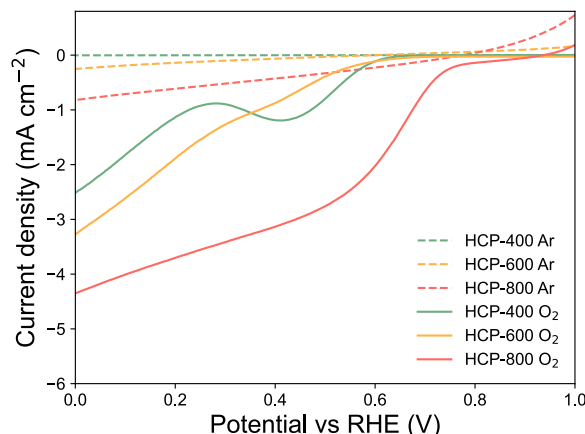
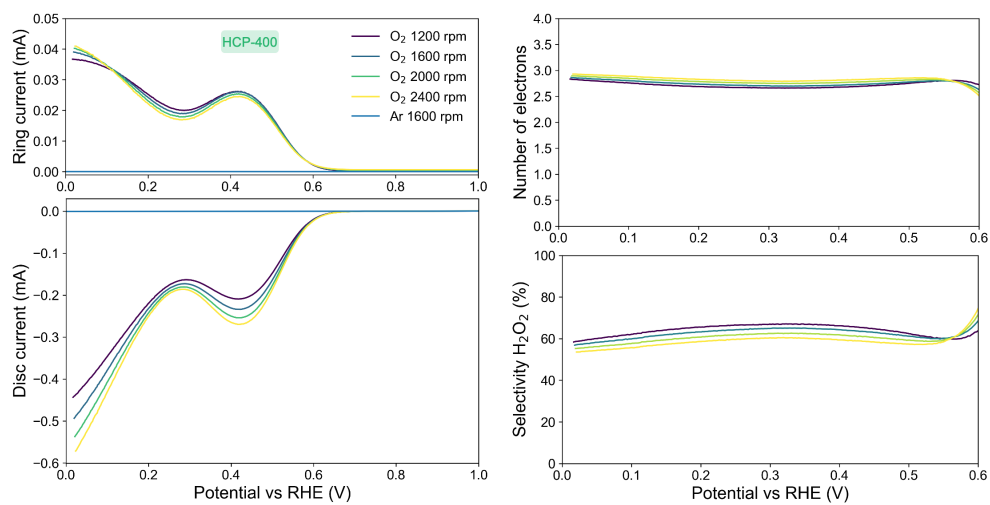


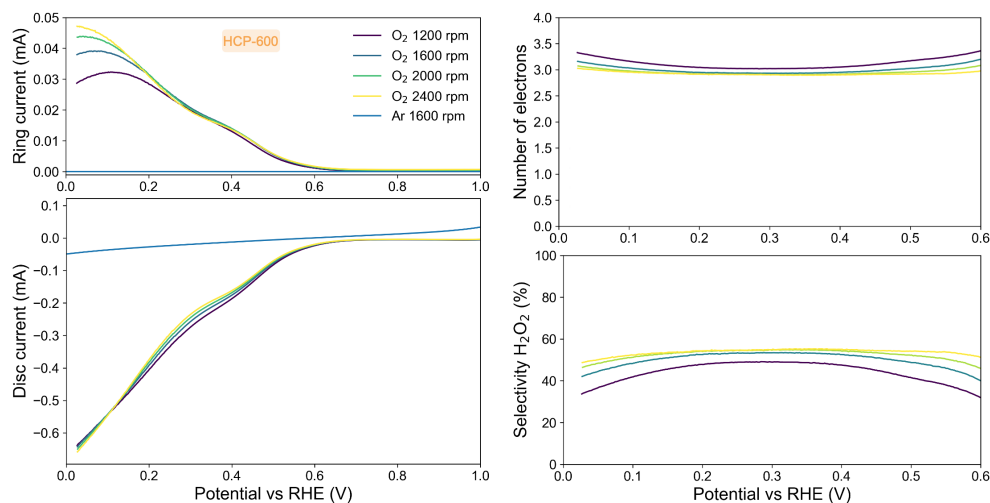
FIGURE 5.11: LSV curves obtained for the HCP-based materials at 1600 rpm, 5 mV s^{-1} in KOH 0.1 M electrolyte under Ar- and O_2 -saturated conditions.

The catalytic selectivity of the materials was investigated using rotating ring disk electrode (RRDE) analysis *via* LSV in hydrodynamic mode, allowing for the evaluation of the number of electrons involved in the oxygen reduction process. LSV measurements were performed at varying rotation speeds (1200, 1600, 2000, and 2400 rpm) in alkaline electrolyte, and the resulting disc and ring currents, along with the calculated number of electrons and selectivity towards H_2O_2 , are presented in Figure 5.12 for each material. While the disc current increases with the pyrolysis temperature, as already discussed, the selectivity towards H_2O_2 follows the opposite trend. **HCP-400** exhibits the highest selectivity for the 2-electron pathway, with the number of electrons involved reaching up to 2.71 at 0.35 V vs RHE, and a H_2O_2 selectivity ranging from 58% to 65% across the investigated potential window. In contrast, **HCP-600** shows an increased electron transfer number, with a minimum of 2.95, while **HCP-800** favors the 4-electron ORR pathway, reaching a maximum H_2O_2 selectivity of only 30%. The enhanced selectivity for H_2O_2 observed in **HCP-400** could be attributed to its higher nitrogen content, as revealed by XPS analysis, as well as the distinct distribution of nitrogen species. Specifically, this material exhibits a higher $N_{\text{pyrrolic}}/N_{\text{pyridinic}}$ ratio (0.52) compared to **HCP-600** and **HCP-800** (respectively 0.43 and 0.45). Furthermore, the two electrocatalysts differ significantly in terms of porosity. Although it is challenging to quantify the exact contribution of porosity, the extensive microporosity of the HCP-derived materials may negatively influence the 2-electron reduction pathway, potentially decreasing H_2O_2 production. It is widely recognized that the porosity of electrocatalyst largely influences the ORR selectivity as it affects the diffusion of the reagents and products to the active sites and

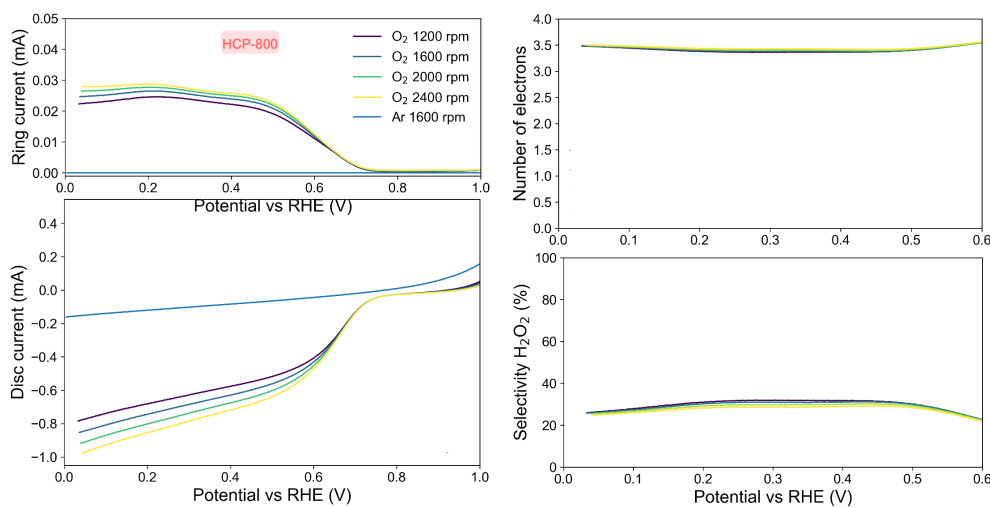
the kinetics of the ORR process.²³⁰ The clear correlation between pore size distribution and ORR selectivity is complex to establish. For instance, several studies showed that active ORR sites located in micropores can facilitate the further reduction of H_2O_2 to H_2O . On the other hand, other work reported that microporosity is instead a beneficial factor contributing to H_2O_2 selectivity.^{26,212,231,232}



(A) LSV curves with RRDE of HCP-400.



(B) LSV curves with RRDE of HCP-600.



(C) LSV curves with RRDE of HCP-800.

FIGURE 5.12: LSV curves obtained for the HCP-based materials at 1600 rpm, 5 mV s^{-1} in KOH 0.1 M electrolyte under Ar- and O_2 -saturated conditions.

TABLE 5.4: Number of electrons and selectivity for H_2O_2 calculated from RRDE tests in alkaline electrolyte for HCP-derived materials.

Sample	Potential (V vs RHE)	Number of electrons	Selectivity H_2O_2
HCP-400	0.35	2.71	65
HCP-600	0.35	2.95	53
HCP-800	0.35	3.41	30

Important information on the activity and selectivity aspects that relate to conductivity of the material and mass transfer of the reagents can be acquired through electrochemical impedance spectroscopy (EIS). To assess the electrochemical behavior and highlight the main differences between the HCP-derived materials during the ORR, EIS measurements and were performed in O_2 -saturated 0.1 M KOH electrolyte under an applied potential of 0.0 V vs RHE. In Figure 5.13, the Nyquist plots for **HCP-600** and particularly **HCP-800** display significantly lower polarization resistance values compared to **HCP-400**. Notably, the ohmic resistance of **HCP-600** is 79.2 Ω , significantly higher than **HCP-400** (34.3 Ω) and **HCP-800** (39.2 Ω), implying a lower electrical conductivity. This observation is somehow unexpected, as intuitively the conductivity of a carbon material should proportionally increase with the graphitization degree (which grows with the temperature of the pyrolysis treatment). However, such a higher resistance may be attributed to the complex porosity of the **HCP-600** sample, which features both mesopores and micropores. The specific configuration of these pores may likely increase the non-conductive regions in the material. The Nyquist plot analysis for **HCP-400** reveals a three time constant shape, with two overlapping charge transfer contributions at higher frequencies, evidenced by the presence of non-symmetrical semicircles, and a distinct diffusion process at low frequencies (Table 5.5). **HCP-400** shows significantly higher charge transfer resistance (R_1+R_2) compared to the other catalysts. However, the resistance associated with the diffusion process is lower than that of **HCP-600**. Additionally, the diffusion resistance in **HCP-800** is considerably more pronounced, as shown by the strong Warburg impedance behavior at low frequencies, indicating higher resistance to mass transport compared to the other two materials. The increased diffusion resistance with rising pyrolysis temperature could be attributed to the development of microporosity in the material structure. This limitation in mass transport could influence the selectivity between the 2-electron and 4-electron ORR pathways. The micropores may, in fact, partially retain intermediate species or H_2O_2 product, promoting further reduction and thereby favoring the $(2+2)e^-$ pathway over the $2e^-$ or direct $4e^-$ process. This interpretation aligns with RRDE investigations, where the selectivity for H_2O_2 is more pronounced for **HCP-400**, which exhibits a mesoporous structure without any microporosity.

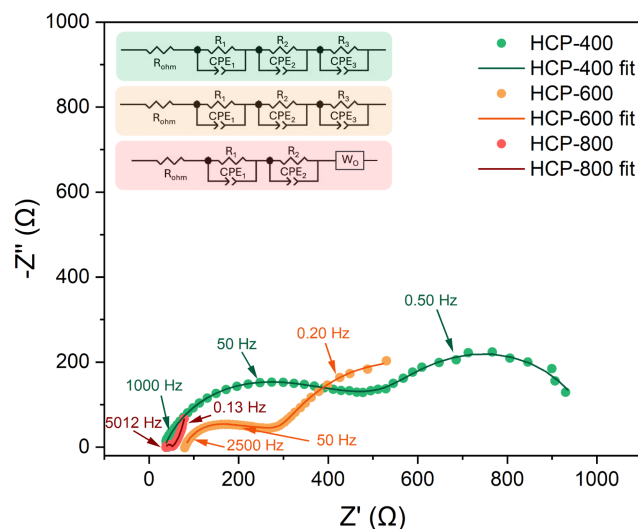


FIGURE 5.13: EIS spectra under applied potential 0.0 V vs RHE curves of HCP-based materials in KOH 0.1 M electrolyte under O₂ atmosphere.

TABLE 5.5: Fitted parameters from EIS data for the HCP-derived materials under applied potential 0.0 V vs RHE.

Sample	R_{el} (Ω)	R_1 (Ω)	R_2 (Ω)	R_3 (Ω)
HCP-400	34.3	215.2	327.1	419.6
HCP-600	79.2	85.2	139.3	538.7
HCP-800	39.2	11.6	87.5	–

HCP-400 was investigated more in detail through EIS under various reductive potentials. In Figure 5.14, the Nyquist plots of **HCP-400** in Ar and O₂ atmosphere at OPC are shown in the left panel for comparison. A higher electrochemical activity is evident when transitioning from an Ar to a O₂ atmosphere, evidenced by a decreased polarization resistance in O₂. The right panel of Figure 5.14 displays the EIS spectra recorded at different applied potentials, as graphically illustrated in the inset plot. The LSV curve exhibits a distinct peak at 0.42 V vs RHE, which may correspond to the one-electron reduction of O₂ to O₂^{•−}.^{233,234} The Nyquist plot at this peak potential shows a notably higher polarization resistance, with both charge transfer and diffusion contributions significantly increased compared to those observed at other applied potentials. This suggests that the reduction process at 0.42 V may be partially linked to the adsorption of the formed reduced species, which hinders the charge transfer and diffusion processes. Recent reports assigned similar reduction peak to the one-electron reduction of activated O₂ into superoxide radical, a species that could be exploited for wastewater pollutants' degradation or organic synthesis.²³⁵ However, further assessments are currently ongoing to confirm this hypothesis.

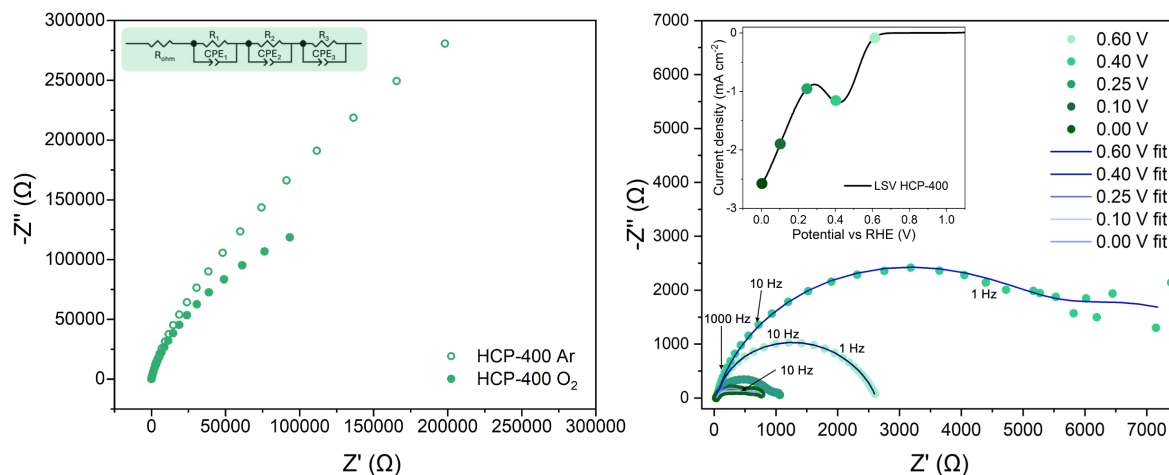


FIGURE 5.14: EIS spectra of HCP-400 in KOH 0.1 M electrolyte under Ar and O₂ atmosphere at OCP (left) and EIS spectra of HCP-400 at different applied potentials.

Due to its higher activity for H₂O₂ production, the material **HCP-400** was studied using RRDE tests in neutral (0.1 M KNO₃ electrolyte) and acidic (0.1 M H₂SO₄ electrolyte) environments (Figure 5.15). In acidic conditions, the onset potential shifts significantly to more negative values (-0.11 V vs RHE). Additionally, H₂O₂ selectivity drops, with an average selectivity of 29% over the range of investigated potentials. In this electrolyte, a side reaction, most likely HER, was also detected. In contrast, the neutral environment showed improved selectivity for the 2-electron process across the potential range, with H₂O₂ selectivity reaching up to 77% at 0.09 V vs RHE. This enhanced selectivity for H₂O₂ in neutral conditions suggests that **HCP-400** holds promise as a potential catalyst for H₂O₂ production in applications such as wastewater treatment or biomedical processes.

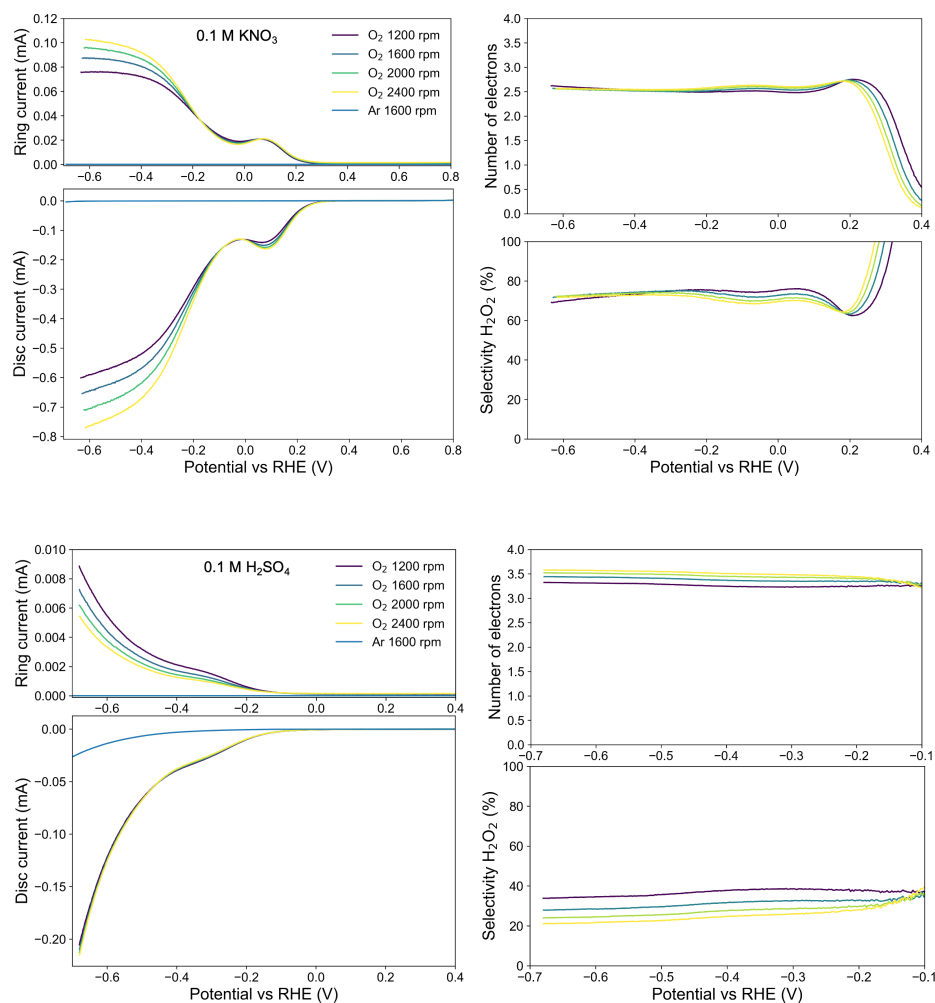


FIGURE 5.15: ORR polarization curves of **HCP-400** in neutral and acidic electrolyte at various rotation speeds, 5 mV s^{-1} under Ar- and O_2 -saturated conditions.

TABLE 5.6: Maximum H_2O_2 selectivity at specific applied potentials across different electrolyte pH values for **HCP-400**.

Electrolyte	Potential (RHE)	Number of electrons	Selectivity H_2O_2
Alkaline	0.35	2.71	65
Neutral	0.09	2.48	77
Acidic	-0.12	3.41	30

5.4 Conclusions and Outlooks

In this chapter, N-doped metal-free electrocatalysts for the oxygen reduction reaction (ORR) were developed, starting from a hyper-crosslinked polymer synthesized through a facile solvothermal approach from melamine and terephthalaldehyde. The obtained (**mt-HCP**) is characterized by an aminal-polymeric framework based on triazine structures. Thermal treatment at high temperatures is a crucial step in activating **mt-HCP** as an ORR electrocatalyst. A series of HCP-derived, nitrogen-rich materials have been synthesized at different pyrolysis temperatures (400°C, 600°C, 800°C), leveraging the well-defined structure of the pristine **mt-HCP**. The resulting HCP-based materials exhibit diverse atomic compositions, nitrogen species distributions, textural properties, and degrees of graphitization, as extensively characterized through nitrogen physisorption, XPS, Raman spectroscopy, and XRD. ORR performance, assessed through RRDE analysis in an alkaline environment, was found to increase significantly with rising pyrolysis temperatures. This improvement is attributed to a greater presence of graphitic nitrogen and carbon domains, which leads to enhanced current density, more positive onset potential, and an exceptional increase in electrochemical surface area (ECSA), particularly for **HCP-800**. However, **HCP-800** exhibits the lowest selectivity for the 2-electron ORR pathway, with a maximum H₂O₂ selectivity of 30%. In contrast, **HCP-400** retains much of the polymeric network's original structure, with a nitrogen content as high as 38.9 at% and a minimal graphitic N component. Despite producing lower current density and exhibit higher charge transfer resistance compared to **HCP-600** and **HCP-800**, **HCP-400** demonstrates the highest selectivity for H₂O₂, achieving selectivities of 65% and 77% in alkaline and neutral electrolytes, respectively. However, the higher nitrogen atomic percentage and N distribution alone does not fully explain the performance differences. EIS analysis suggests that the microporosity present in **HCP-600**, and more significantly in **HCP-800**, negatively affects mass transport during ORR catalysis, increasing the likelihood of inducing a (2+2)-electron mechanism, which favors H₂O as the main product.

In conclusion, the use of hyper-crosslinked polymer **mt-HCP** as starting synthetic platform enables the assembly of metal-free ORR electrocatalysts through thermal treatment, offering specific and tunable properties. The development of metal-free materials derived from porous organic polymers with well-defined structures is still a novel and not fully investigated approach and holds great promise.

5.5 Experimental Section

Materials. Dimethylsulfoxide > 99.7%, melamine 99%, terephthalaldehyde 99%, potassium hydroxide 99.99%, potassium nitrate > 99%, isopropanol 99.9%, H₂SO₄ 99.999%, and Nafion 117 (5% solution in lower aliphatic alcohols and water) were purchased from Sigma-Aldrich.

All electrochemical experiments were performed with Milli-Q water obtained by using a Direct-Q (Millipore) water purification system.

Synthetic procedure of HCP-based materials.

The following procedure were followed for the preparation of the HCP-based materials:

mt-HCP: 408 mg (3.24 mmol) of melamine and 652 mg (4.86 mmol) of terephthalaldehyde were dissolved in 20 mL of dimethylsulfoxide (DMSO) through sonication in a 40 mL teflon-liner. The solution in a teflon-lined autoclave was heated at 200°C for 15 hours. The obtained precipitate was extensively washed with DMSO, acetone and dichloromethane through multiple cycles of sonication and filtration (filter Millipore 0.45 μm). The obtained light yellow powder was dried at 120°C for 24 h.

HCP-400: 150 mg of **mt-HCP** was heated in a boat-shaped alumina crucible at 400°C for 2 h with a ramping time of 2°C min⁻¹ under argon flow.

HCP-600: 150 mg of **mt-HCP** was heated in a boat-shaped alumina crucible at 600°C for 2 h with a ramping time of 2°C min⁻¹ under argon flow.

HCP-800: 150 mg of **mt-HCP** was heated in a boat-shaped alumina crucible at 800°C for 2 h with a ramping time of 2°C min⁻¹ under argon flow.

Characterization. Raman spectra were recorded on a inVia Renishaw spectrometer equipped with a Nd:YAG laser using an excitation wavelength of 532 nm. Thermogravimetric analysis (TGA) was carried out on a TA Discovery TGA 550 instrument with a heating rate of 10 °C min⁻¹ under N₂ flow. IR spectra were recorded in attenuated total reflectance (ATR) mode on a Shimadzu IRAffinity-1S spectrophotometer equipped with a QATR 10 accessory. TEM analyses were performed using a Philips EM 208 microscope operating at 100 kV and equipped with an 11 MP bottom-mounted CCD Olympus Quemesa camera. Textural properties were analyzed by N₂ physisorption at the liquid nitrogen temperature using a Micrometrics ASAP 2020 automatic analyzer. All the NPs were degassed at 120 °C for 12 h at 10 μmHg . The specific surface area was obtained by applying the Brunauer–Emmett–Teller (BET) method equation and Langmuir equation. Pore size distribution was determined applying the Barrett, Joyner, and Halenda (BJH) method equation to the adsorption and desorption branch of the isotherms. Powder X-ray diffraction analysis was performed on a Malvern PANalytical Empyrean Series 3 with Cu Long Fine Focus spot High Resolution tube comprehensive of Ni β filter, detector 1Der, over a 2θ range of 10–100° with a step size of 0.17°. The phase determination was performed through ICDD database.

Electrochemical measurements. Electrochemical tests were carried out at room temperature on an Autolab 302N electrochemical workstation (Metrohm, Autolab). Saturated Calomel Electrode (SCE) was used as reference electrode, while Pt wire was used as counter electrode. As working electrode, Rotating Ring Disk Electrode (RRDE, Metrohm) with both a circular Glassy Carbon (GC) surface of 0.196 cm² geometric area, with the addition in RRDE

of a platinum ring. The ink for the working electrode was prepared as follows: 10 mg of catalyst were dispersed in 0.220 g of water, 0.112 g of ethanol, and 0.084 g of a Nafion solution. The resulting ink was sonicated for 90 minutes and drop-casted onto the glassy carbon electrode (7 μ l). The as-prepared electrode was then dried at room temperature overnight. Electrochemical active surface area (ECSA) and Roughness factor (RF) values were evaluated *via* the capacitive current near OCP at different scan speeds and determined using the following equation:

$$\text{ECSA} = \text{RF} \cdot S$$

$$R_f = \frac{C_{dl}(\text{catalyst})}{C_{dl}(\text{smooth glassy carbon})}$$

where RF denotes the roughness factor defined as the ratio of the double layer capacitance (C_{dl}) of the working electrode with the drop-casted material to that of the corresponding smooth glassy carbon electrode employed for this measurements. S denotes the geometrical surface area of the glassy carbon (0.196 cm^2). The C_{dl} values were determined by establishing a linear relationship of the difference in anodic and cathodic current densities $\delta j = (j_{\text{anodic}} - j_{\text{cathodic}})$. Electrochemical impedance spectroscopy (EIS) measurements were performed using a frequency response analyzer (FRA, AutoLab 302 N, Metrohm) at room temperature. EIS spectra were recorded at both OCP and under applied reductive potential under pure Ar or O₂ atmosphere with a 10 mV amplitude voltage perturbation in the maximum frequency range from 100 kHz to 1 Hz. The EIS fitting analysis was performed employing Python package impedance.py.²³⁶

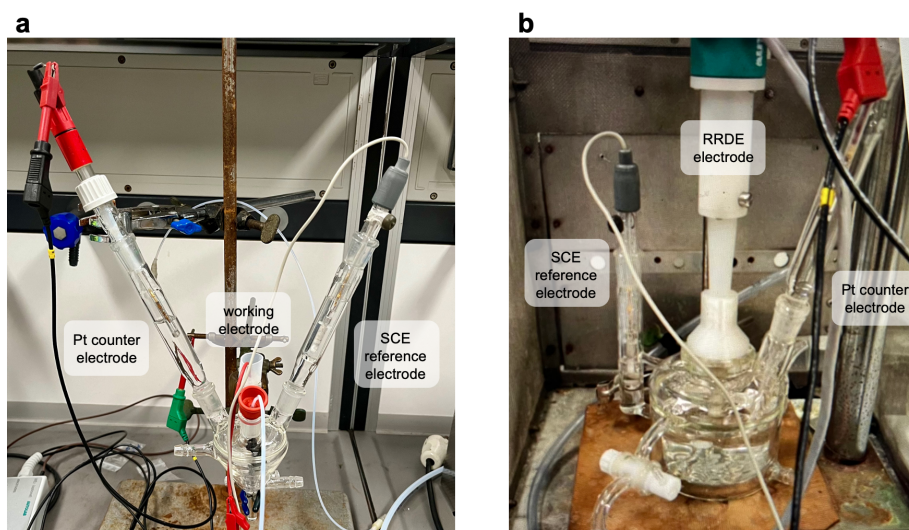


FIGURE 5.16: (a) Single cell set-up with SCE reference electrode, Pt wire counter electrode and glassy carbon working electrode with 0.196 cm^2 geometric area, employed for ECSA calculations, and (b) single cell setup housing a RRDE GC/Pt tip, SCE electrode in a Luggin capillary, and a Pt wire counter electrode in a bridge equipped with a Vycor frit.

Chapter 6

Outlooks and Perspectives

The path to a sustainable society is one of the today's main challenges, marked by a transition away from finite, scarce resources. Yet, the urgency of change demands accelerated innovation across diverse fields. This thesis explores sustainable alternatives through photocatalysis and electrocatalysis for the production of chemicals taking advantage from the integration of carbon nanostructures (CNSs). CNSs are a class of materials that presents several useful properties, and therefore hold promise for reducing dependence on the metal-based systems, prevalent in industry. CNS-based catalysts offer a pathway to better harness catalytic mechanisms, potentially achieving both effectiveness and environmental alignment. However, to reach the standards required for industry, substantial progress is needed to enhance their efficiency, stability and versatility. Integrative strategies, such as coupling these catalysts with complementary processes, could further improve the sustainability of the approaches discussed in this thesis. This concluding section is intended to provide future perspectives and suggestions for the projects discussed. In particular, Chapter 3 discusses a Ni/CN dual catalytic system, where a heterogeneous catalyst is coupled with a homogeneous transition metal complex. Recently, this approach has been shifting toward a fully heterogeneous system, with Ni embedded directly into the CN structure.^{111–113} This strategy offers significant advantages in terms of recyclability, allowing for the reuse of both the carbon-based catalyst and the metal component. However, it also presents a number of drawbacks, above all the Ni leaching and deactivation. A better interaction between CN and Ni could mitigate these issues, resulting in a more recyclable system. Thus, the strategy proposed in this chapter, where the CN photocatalyst is modified using a cost-effective methodology, could help develop fully heterogeneous Ni/CN catalysts with enhanced stability. It may further help the development of more robust single-atom catalysts for this application, maximizing metal use, as each atom can virtually sustain the catalysis. This stability is essential for scaling up stages from a lab-scale batch reactor to larger scales, particularly in flow reactor designs.²³⁷

Chapter 4 presents the CO₂ electroreduction into formic acid using a type of CNS (carbon nanohorns) to reduce the reliance on a critical metal such as bismuth, developing an inorganic-organic nanohybrid material. The cathodic CO₂RR is typically paired with the

anodic oxygen evolution reaction, as shown in the catalytic tests reported in this project, although this pairing is both thermodynamically and kinetically challenging. Therefore, coupling CO₂ conversion with value-added anodic reactions (e.g. alcohol oxidation, biomass oxidation, wastewater contaminant oxidation) can enhance the energy efficiency of the cell while producing valuable products from both compartments of the electrolyzer.²³⁸

The last experimental chapter presents a study on tuning the properties of carbon-based electrocatalysts using hyper-crosslinked polymers as precursors. This investigation aligns with a broader research branch on metal-free catalysts for ORR. The production of H₂O₂ from ORR is also promising for applications within the electro-Fenton process, which generates hydroxyl radicals using Fe species to degrade organic pollutants. By leveraging the *in situ* synthesis of H₂O₂ via the 2-electron ORR in contaminated wastewater, this approach represents a more advanced technology for wastewater treatment. Furthermore, exploring the use of catalytically formed superoxide radicals by ORR catalysts could pave the way for improved pollutant removal, as recent studies have suggested.²³⁵

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