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PhD in

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**Development and production of Bimetallic Nanomaterials by means
of a Spinning disc reactor for Enviromental and industrial
applications.**

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Abstract:

This PhD thesis reports about an in-depth study on the synthesis, characterization and the application of bimetallic nanomaterials, focusing on their potential use for environmental remediation and energy conversion. The research emphasizes the development of Fe, Ni and Al bimetallic oxides and Layered Double Hydroxides (LDHs) nanoparticles using advanced synthesis techniques, including Spinning Disc Reactor (SDR) technology and the employment of hydrothermal methods. Together, these techniques allowed to produce nanomaterials with a precisely controlled sizes, shape and surface properties, which are crucial for catalytic performance optimization. A significant part of the research involves the integration of these kind of bimetallic oxides with graphitic carbon nitride (g-C₃N₄) leading to composite catalysts. The adopted hybrid approach aims to enhance the photocatalytic properties of the material, in particular for the degradation of persistent organic pollutants in water and for energy conversion processes such as solar-driven hydrogen production. The obtained composites demonstrated a superior light absorption and charge separation efficiency, leading to enhanced photocatalytic activities compared to conventional materials.

Furthermore, the thesis explores the doping of these bimetallic oxides with noble metals such as silver (Ag). Noble metal doping was found to significantly improve the catalytic activity, particularly in photocatalytic and electrochemical applications, such as the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR). The presence of noble metals promotes electron transfer and introduced additional active sites, thereby improving the overall efficiency of these catalytic processes.

Comprehensive characterization of the synthesized nanomaterials was performed using a range of different techniques, including transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and electrochemical analyses. These characterizations confirmed the structural integrity and enhanced properties of the nanomaterials, underpinning their high catalytic performances. The research was able to demonstrate that these bimetallic nanomaterials qualifies for practical applications in the field of environmental remediation, such as water purification, and in energy technologies,

including water splitting and hydrogen production. Moreover, the findings was developed with insight to a potential scaling up of the proposed synthesis methods for industrial applications and suggest more future research directions, in exploring new metal combinations and green synthesis techniques to further enhance the environmental sustainability and performance of these nanomaterials.

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Chapter 1 Introduction

1.1 Nanomaterials

Nanomaterials are materials that have at least one dimension at the nanoscale (1-100 nm), including nanoparticles, nanowires, nanoplates and nanocomposites. At these dimensions, nanomaterials often exhibit properties that are substantially different from their bulk counterparts, primarily due to quantum confinement effects, increased surface area and enhanced surface reactivity. These unique properties enable nanomaterials to play a crucial role in advancing technology across various fields, including electronics, energy storage, medicine, and environmental remediation [1]. The high surface area-to-volume ratio of nanomaterials is one of their most significant attributes. This property increases the number of active sites available for chemical reactions, making nanomaterials particularly useful in catalysis. Additionally, the quantum effects that occur at the nanoscale can lead to altered optical, electronic, and magnetic behaviors, which are beneficial in applications such as photovoltaics, sensors, and imaging technologies [2].

There are several types of nanomaterials, including zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) nanomaterials. Zero-dimensional nanomaterials, such as quantum dots, are confined in all three spatial dimensions, leading to pronounced quantum effects. One-dimensional nanomaterials, such as nanowires and nanotubes, are confined in two dimensions, while two-dimensional nanomaterials, such as graphene and transition metal dichalcogenides (TMDs), are confined in one dimension. Three-dimensional nanomaterials, such as nanocomposites and nanoporous materials, exhibit interconnected structures that provide both surface area and mechanical robustness [3]. Nanoparticles are among the most studied nanomaterials due to their versatility and potential in various applications. Metallic nanoparticles, for instance, have been widely researched for their catalytic properties, as well as their roles in medicine as drug delivery agents and in diagnostic imaging. Semiconductor nanoparticles, such as cadmium selenide (CdSe) quantum dots, have been used in optoelectronic devices due to their size-tunable optical properties [4]. Another significant class of nanomaterials is carbon-based nanomaterials, including

fullerenes, carbon nanotubes (CNTs), and graphene. These materials have attracted significant attention due to their exceptional mechanical strength, electrical conductivity, and thermal stability. Graphene, in particular, has revolutionized fields such as flexible electronics, energy storage, and photodetectors due to its two-dimensional structure and extraordinary electron mobility [5].

Nanomaterials are also used in biomedical applications. Nanoparticles, such as gold and silver nanoparticles, are employed in cancer therapy, where they serve as carriers for drug delivery or as agents for photothermal therapy. Their small size allows them to penetrate biological barriers and deliver therapeutic agents directly to target cells. Furthermore, magnetic nanoparticles are used in magnetic resonance imaging (MRI) for enhanced contrast, enabling early detection of diseases [6]. Despite their promising applications, nanomaterials also pose potential risks, particularly regarding their environmental and health impacts. Due to their small size, nanomaterials can penetrate biological membranes and accumulate in tissues, raising concerns about their long-term toxicity. Research is ongoing to understand the biocompatibility and environmental behavior of nanomaterials, with a focus on developing safer and more sustainable nanomaterials [7]. In fact, nanomaterials have opened new avenues in science and engineering, with their unique properties driving advancements in numerous fields. As synthesis techniques continue to evolve, the ability to tailor nanomaterials for specific applications will expand their use even further, while ongoing research seeks to mitigate the potential risks associated with their use.

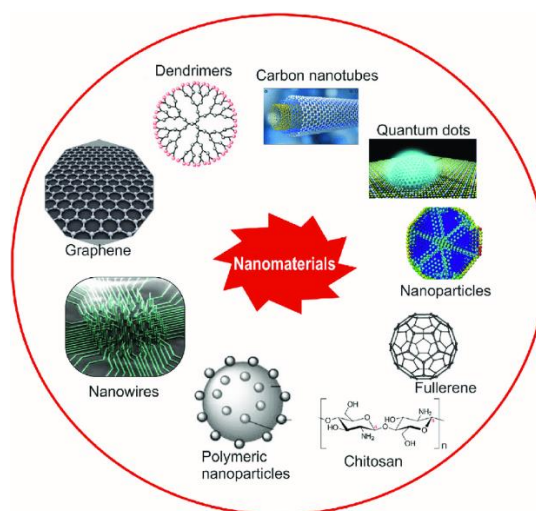


Fig. 1. 1 Various types of Nanomaterials

1.2 Catalysis

Catalysis is a fundamental process in chemistry that involves increasing the rate of a chemical reaction by introducing a substance known as a catalyst, which is not consumed in the reaction itself. Catalysts lower the activation energy required for a reaction to occur, enabling the reaction to proceed more quickly or under milder conditions. Catalysis is essential in various industries, including petrochemicals, pharmaceuticals, and environmental technologies, making it a critical area of study in chemical engineering and materials science [8]. Nanomaterials have proven to be highly effective catalysts due to their high surface area and ability to expose a large number of active sites for chemical reactions. This characteristic is particularly important in heterogeneous catalysis, where the catalyst and reactants are in different phases (e.g., solid catalyst with liquid or gaseous reactants). The unique electronic properties of nanomaterials, such as quantum effects and surface plasmon resonance, can further enhance their catalytic activity by facilitating electron transfer during chemical reactions [9].

One of the most well-known applications of catalysis involving nanomaterials is in the automotive industry, where platinum and palladium nanoparticles are used in catalytic converters to reduce harmful emissions. These nanoparticles catalyze the oxidation of carbon monoxide (CO) into carbon dioxide (CO₂) and the reduction of nitrogen oxides (NO_x) into nitrogen gas (N₂), thereby helping to reduce air pollution. The high surface area of these nanoparticles allows for more efficient catalysis, even at low temperatures [10]. In the chemical industry, nanomaterials are used as catalysts for important reactions such as hydrogenation, oxidation, and polymerization. For instance, palladium nanoparticles are widely used in carbon-carbon coupling reactions, such as the Suzuki-Miyaura and Heck reactions, which are essential in the synthesis of pharmaceuticals and fine chemicals. The small size of the nanoparticles allows for greater interaction with the reactants, leading to higher yields and selectivity [11].

Photocatalysis is another area where nanomaterials have shown great potential. In photocatalytic reactions, light is used to activate a catalyst, typically a semiconductor material, which then drives a chemical reaction. Titanium dioxide (TiO₂) nanoparticles are widely used in photocatalysis for environmental applications such as water purification and air cleaning. When exposed to UV light, TiO₂ generates reactive oxygen species that can oxidize and break

down organic pollutants into less harmful substances. This process has been extensively researched for applications in wastewater treatment and air purification systems [12].

Nanomaterials have also been employed as electrocatalysts in energy conversion technologies such as fuel cells and water splitting. In proton exchange membrane fuel cells (PEMFCs), platinum nanoparticles are used as electrocatalysts to facilitate the oxygen reduction reaction (ORR) at the cathode, which is a key reaction in the generation of electricity from hydrogen. Due to the high cost of platinum, research has focused on developing alternative catalysts, including bimetallic nanoparticles and transition metal oxides, which offer enhanced catalytic performance at a lower cost [13].

In the emerging field of biomass conversion, nanocatalysts are being developed to transform biomass into valuable chemicals and fuels. For example, nanomaterials such as nickel and cobalt nanoparticles are being explored as catalysts for the conversion of lignocellulosic biomass into biofuels and bio-based chemicals. These processes are seen as key to the development of a sustainable bioeconomy, as they offer a renewable alternative to fossil fuels [14]. While nanomaterials have demonstrated impressive catalytic performance, challenges remain in terms of stability, scalability, and recyclability. In many catalytic processes, nanoparticles tend to aggregate, which can reduce their surface area and catalytic activity over time. To address this issue, researchers are exploring methods to stabilize nanoparticles, such as supporting them on porous materials or encapsulating them in protective shells. Moreover, the scalability of nanomaterial synthesis remains a challenge, particularly for industrial applications that require large quantities of catalysts [15]. As the field of catalysis continues to evolve, nanomaterials are expected to play an increasingly important role in the development of new catalytic systems that are more efficient, cost-effective, and environmentally friendly. Ongoing research is focused on understanding the fundamental mechanisms of catalysis at the nanoscale, as well as developing new materials and synthesis techniques to optimize their performance.

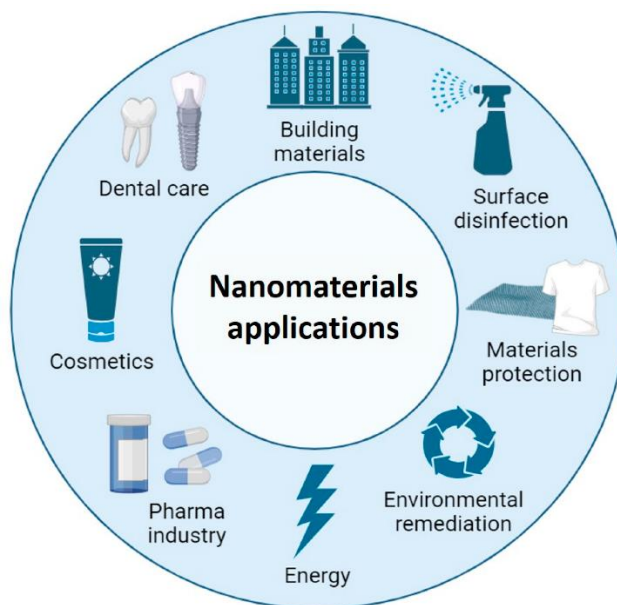


Fig. 1.2 Applications of Nanomaterials

1.3 Types of Catalysis

Catalysis is broadly classified into three major categories: homogeneous catalysis, heterogeneous catalysis and enzymatic catalysis. Each of these types of catalysis plays a critical role in chemical processes, from industrial manufacturing to energy conversion and environmental remediation. The distinctions between these types are based on the phase of the catalyst relative to the reactants and the mechanisms by which the catalysts operate.

1.3.1 Homogeneous Catalysis

Homogeneous catalysis occurs when the catalyst and the reactants are in the same phase, typically in a liquid solution. This type of catalysis is widely used in organic synthesis, polymerization reactions, and the production of fine chemicals. In homogeneous catalysis, the catalyst interacts directly with the reactants on a molecular level, often leading to high selectivity and efficiency. One of the classic examples of homogeneous catalysis is the hydroformylation reaction, where a soluble transition metal catalyst is used to convert alkenes into aldehydes, a key step in the production of detergents, plastics, and pharmaceuticals [13]. Nanomaterials have been incorporated into homogeneous catalysis to further enhance reaction rates and selectivity. For instance, metal-organic frameworks (MOFs) and single-atom catalysts (SACs) have been developed to create highly efficient homogeneous catalytic

systems. MOFs, which consist of metal ions coordinated to organic ligands, offer a high degree of tunability in terms of pore size and chemical functionality, making them ideal for catalysis in homogeneous systems [14]. SACs, on the other hand, consist of isolated metal atoms dispersed on a support, providing active sites with well-defined coordination environments, which enhance catalytic performance in homogeneous reactions [15].

Despite the advantages of homogeneous catalysis, including high activity and selectivity, one of the main challenges is the difficulty in separating and recycling the catalyst after the reaction. This can lead to issues of catalyst contamination in the final product and increased operational costs, particularly when expensive metals like platinum or palladium are used [16]. To address this challenge, researchers have been exploring the development of hybrid systems that combine the benefits of homogeneous and heterogeneous catalysis. For example, immobilizing homogeneous catalysts on solid supports, such as nanomaterials or polymer matrices, allows for easier catalyst recovery and reuse [17].

1.3.2 Heterogeneous Catalysis

Heterogeneous catalysis occurs when the catalyst is in a different phase than the reactants, typically a solid catalyst interacting with liquid or gaseous reactants. This form of catalysis is widely used in industrial processes, including oil refining, chemical production, and environmental applications such as exhaust gas treatment. Heterogeneous catalysts offer several advantages, including ease of separation from the reaction mixture, recyclability, and stability under a wide range of reaction conditions [18].

Nanomaterials play a crucial role in heterogeneous catalysis due to their high surface area and tunable surface properties. Metal nanoparticles, metal oxides, and carbon-based nanomaterials are frequently employed as heterogeneous catalysts. For example, platinum and palladium nanoparticles are used in catalytic converters to facilitate the oxidation of harmful gases like carbon monoxide (CO) and hydrocarbons, converting them into less harmful carbon dioxide (CO₂) and water [19]. The small size of these nanoparticles allows for a large number of active sites, improving the overall efficiency of the catalytic process.

Another important area of heterogeneous catalysis is the use of nanomaterials in energy conversion technologies, such as fuel cells and electrolyzers. Nanostructured catalysts, such as Pt/C (platinum on carbon) and RuO₂ (ruthenium oxide), are employed to enhance the

performance of electrochemical reactions involved in hydrogen production and oxygen reduction. These catalysts help reduce the overpotential required for the reactions, thereby improving the energy efficiency of the systems [20]. In addition, nanomaterials such as zeolites and mesoporous silicas are used as catalysts in petrochemical processes to convert crude oil into valuable fuels and chemicals [21]. The tunability of nanomaterials makes them ideal for tailoring the properties of heterogeneous catalysts. For instance, researchers have developed bimetallic and alloy nanoparticles to achieve synergistic effects that enhance catalytic activity and stability. Gold-palladium (Au-Pd) and platinum-ruthenium (Pt-Ru) nanoparticles are examples of bimetallic catalysts that have shown superior performance in reactions such as alcohol oxidation and hydrogenation compared to their monometallic counterparts [22]. By carefully controlling the composition and structure of these nanomaterials, it is possible to optimize their catalytic properties for specific reactions.

1.3.3 Enzymatic Catalysis

Enzymatic catalysis, also known as biocatalysis, involves the use of biological molecules, typically enzymes, to catalyze chemical reactions. Enzymes are highly specific and efficient catalysts that operate under mild conditions, such as room temperature and neutral pH, making them ideal for applications in the pharmaceutical, food, and biofuel industries. Enzymatic catalysis offers several advantages, including high selectivity, the ability to catalyze complex reactions, and the potential for sustainable and environmentally friendly processes [23]. Nanomaterials have been increasingly integrated into enzymatic catalysis to enhance enzyme activity, stability, and reusability. For example, enzymes can be immobilized on nanomaterials such as graphene, silica nanoparticles, and magnetic nanoparticles, which help protect the enzyme from denaturation while maintaining its catalytic activity. This immobilization also allows for easier recovery and reuse of the enzyme, reducing the cost of the catalytic process [24]. Magnetic nanoparticles, in particular, offer the advantage of easy separation from the reaction mixture using an external magnetic field, which simplifies the recycling of the enzyme [25].

Furthermore, nanomaterials can be used to create enzyme mimics, known as nanozymes. These nanomaterials exhibit enzyme-like activities and can catalyze reactions similar to natural enzymes. For instance, cerium oxide (CeO₂) nanoparticles have been shown to mimic

the activity of catalase, an enzyme that breaks down hydrogen peroxide into water and oxygen. Nanozymes have the potential to be used in medical diagnostics, environmental remediation, and industrial catalysis due to their stability, robustness, and low cost compared to natural enzymes [26].

1.3.4 Hybrid Catalysis and Emerging Trends

As the field of catalysis continues to evolve, researchers are increasingly exploring hybrid catalytic systems that combine the strengths of different types of catalysis. For example, photocatalytic and electrocatalytic systems that integrate both homogeneous and heterogeneous catalysts are being developed to improve the efficiency of reactions such as water splitting and CO₂ reduction [27]. These hybrid systems leverage the advantages of nanomaterials to create more efficient and sustainable catalytic processes. Another emerging trend is the development of multi-functional catalysts that can perform multiple reactions in a single process. For instance, bifunctional catalysts composed of nanomaterials such as palladium and copper have been used to simultaneously catalyze hydrogenation and oxidation reactions, reducing the number of steps required in chemical synthesis and improving overall process efficiency [28].

1.4 Synthesis Techniques for Nanomaterials

Nanomaterial synthesis is pivotal to the field of nanotechnology, as the properties of nanomaterials—such as size, shape, and composition—are highly dependent on the method used to create them. The synthesis techniques for nanomaterials can broadly be classified into top-down and bottom-up approaches. These methods differ fundamentally in their mechanisms for creating nanoscale structures, and each has its own advantages and limitations depending on the desired characteristics of the nanomaterial and the intended application.

1.4.1 Top-Down Approaches

Top-down approaches involve breaking down bulk materials into nanoscale structures through mechanical, chemical, or physical processes. The focus is on reducing the size of the material to the nanoscale by applying external forces, such as mechanical milling, etching, or ablation. These techniques are often simpler and more cost-effective for producing large quantities of nanomaterials. However, they can suffer from drawbacks, including poor control

over particle uniformity and surface structure, as well as the potential for introducing defects into the material [29]. One of the most common top-down techniques is mechanical milling, where bulk materials are ground into nanoparticles. This method is widely used in the production of metal oxides and other nanocomposites. Another example is laser ablation, a process that uses high-energy laser pulses to vaporize material from a solid target, forming nanoparticles with well-defined sizes and shapes [30]. Despite the limitations of top-down approaches, they are often favored for their scalability and simplicity, especially in industrial applications.

1.4.2 Bottom-Up Approaches

In contrast, bottom-up approaches involve assembling nanomaterials from atomic or molecular precursors. This method allows for greater control over the composition, size, and morphology of the nanomaterials, as the structure is built from the ground up through chemical reactions, self-assembly, or molecular deposition techniques. Bottom-up approaches are particularly advantageous for producing high-quality, defect-free nanomaterials with precise control over their properties, making them ideal for applications in catalysis, electronics, and medicine [31]. Bottom-up techniques such as chemical vapor deposition (CVD) and sol-gel synthesis are widely used for creating nanomaterials with specific characteristics. These methods enable the production of nanomaterials with highly uniform structures and tailored surface properties, which are crucial for their performance in advanced technological applications. Bottom-up approaches also include hydrothermal synthesis, electrochemical deposition, and self-assembly, each of which provides unique advantages for specific types of nanomaterials [32].

Both top-down and bottom-up methods are integral to the field of nanomaterial synthesis, and the choice of method often depends on the desired properties of the final material and its intended use. With these foundational approaches in mind, we now explore the specific techniques that fall under each category, highlighting their mechanisms, applications, and recent advancements.

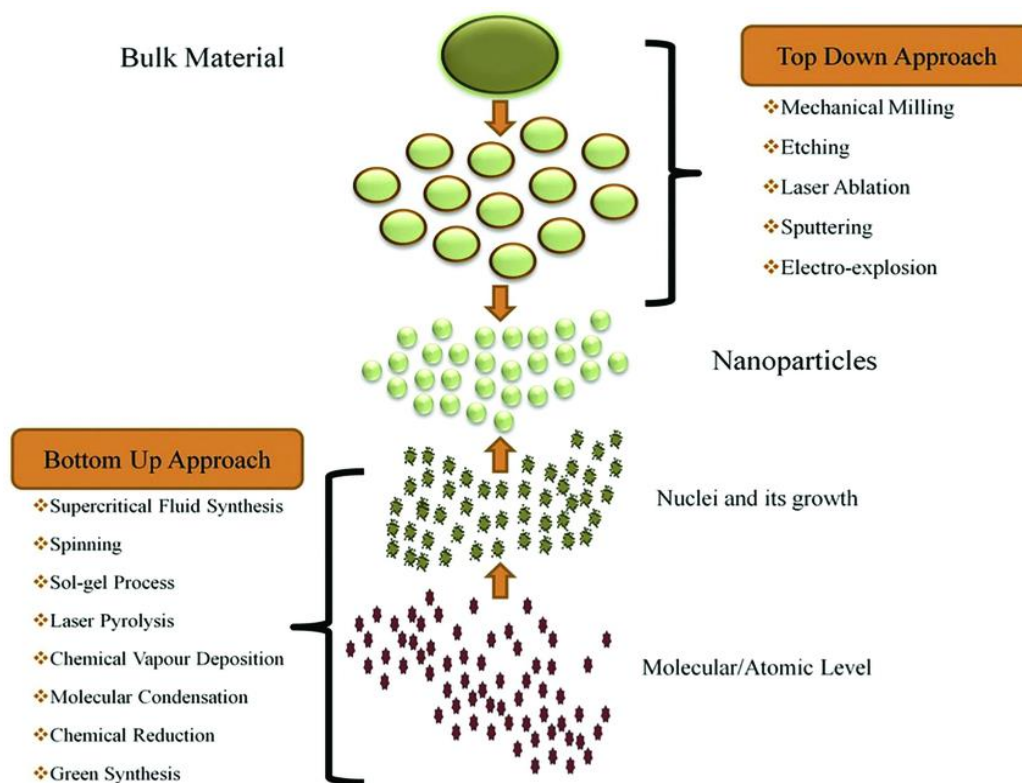


Fig. 1.3 Synthesis techniques for nanomaterials

1.4.3 Mechanical Milling

Mechanical milling is a top-down technique that involves grinding bulk materials into fine powders using high-energy mills. This method is widely used to produce metal oxide nanoparticles and nanocomposites. Mechanical milling is effective for large-scale production, but the particles produced often have a wide size distribution and irregular shapes, which can affect their performance in certain applications [33]. However, the technique remains popular due to its simplicity and scalability, particularly in industrial settings.

1.4.4 Laser Ablation

Laser ablation is a powerful technique for producing nanoparticles from solid targets using high-energy laser pulses. This process can create nanoparticles with controlled sizes and shapes, making it ideal for applications in catalysis, medicine, and environmental remediation. Laser ablation is often used to synthesize metallic nanoparticles, such as gold and silver, which are valued for their catalytic and optical properties [34]. The ability to precisely control the laser parameters allows for fine-tuning of the particle characteristics, though the technique requires specialized equipment and can be limited in terms of production scale.

1.4.5 Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) is one of the most widely used bottom-up techniques for synthesizing nanomaterials. In this process, gaseous precursors are decomposed at high temperatures, leading to the deposition of a thin film of nanomaterial on a substrate. CVD is particularly effective for producing carbon nanomaterials, such as carbon nanotubes (CNTs) and graphene, as well as metal and semiconductor nanomaterials. The method offers excellent control over film thickness, composition, and morphology, making it ideal for applications in electronics, catalysis, and energy storage [35].

1.4.6 Sol-Gel Synthesis

Sol-gel synthesis is a versatile bottom-up approach for producing metal oxide nanoparticles. The process involves the hydrolysis and condensation of metal alkoxides or metal salts to form a colloidal solution (sol), which then forms a gel-like network. After drying and calcination, nanoparticles are produced. This method is particularly useful for creating nanomaterials such as titanium dioxide (TiO_2), which are widely used in catalysis and photocatalysis due to their high surface area and tunable properties [36]. The sol-gel process allows for the incorporation of dopants and the creation of complex nanostructures, making it highly adaptable to different applications.

1.4.7 Hydrothermal and Solvothermal Synthesis

Hydrothermal and solvothermal synthesis involve chemical reactions in a sealed reactor under elevated temperatures and pressures. Hydrothermal synthesis uses water as the solvent, while solvothermal synthesis employs organic solvents. These methods are particularly useful for producing crystalline nanoparticles with well-controlled sizes and shapes, such as zinc oxide (ZnO) and iron oxide (Fe_2O_3) [37]. The ability to manipulate the reaction environment allows for precise control over particle morphology and crystal structure, making these techniques highly effective for applications in catalysis, energy storage, and environmental remediation.

1.4.8 Electrochemical Deposition

Electrochemical deposition is a method that involves reducing metal ions from a solution onto a conductive substrate, leading to the formation of nanostructures such as nanowires and nanotubes. This bottom-up technique is widely used for synthesizing nanomaterials for

energy storage devices, including supercapacitors and batteries. Electrochemical deposition offers precise control over the thickness and morphology of the nanomaterials, making it an attractive option for producing high-purity nanostructures with specific properties [38].

1.4.9 Spinning Disc Reactor (SDR) Technology

Spinning Disc Reactor (SDR) technologies is an emerging bottom-up technique that utilizes centrifugal forces to rapidly mix and react chemical precursors on a rotating disc. This process enables the continuous production of uniform nanoparticles with controlled size and morphology. SDR technology is particularly effective for synthesizing metallic and bimetallic nanoparticles, which are used in catalysis, drug delivery, and environmental applications [39]. The rapid mixing and nucleation provided by SDR technology result in high yields and uniform products, making it a promising approach for scaling up nanomaterial production.

1.4.10 Plasma-Assisted Synthesis

Plasma-assisted synthesis involves using plasma to generate reactive species, such as ions, radicals, and electrons, which drive the formation of nanomaterials. This technique allows for the production of nanomaterials at lower temperatures than conventional methods, making it suitable for synthesizing materials on temperature-sensitive substrates. Plasma-assisted synthesis is commonly used for producing carbon nanomaterials, metal nanoparticles, and nanodiamonds with high purity and tunable properties [40]. The method is versatile and offers significant control over the final product's composition and structure.

1.4.11 Self-Assembly Techniques

Self-assembly techniques rely on the spontaneous organization of molecules or nanoparticles into ordered structures through non-covalent interactions, such as van der Waals forces, hydrogen bonding, and electrostatic interactions. These methods are particularly useful for creating nanoscale materials with specific architectures, such as nanoparticle arrays and nanostructured films. Self-assembly is highly effective for applications in nanophotonics, catalysis, and drug delivery, where the arrangement of nanomaterials is critical for their functionality [41].

1.4.12 Green Synthesis Techniques

Green synthesis techniques emphasize the use of environmentally friendly materials and processes to produce nanomaterials. This approach minimizes the use of toxic chemicals and harsh conditions by utilizing natural reducing agents, such as plant extracts, microbes, and enzymes, to synthesize nanoparticles. Green synthesis methods have been successfully employed to produce metal nanoparticles, including silver and gold nanoparticles, with minimal environmental impact [42]. These techniques are gaining popularity as researchers focus on sustainability and reducing the ecological footprint of nanomaterial production.

1.5 Application of Nanomaterials

Nanomaterials have a wide array of applications that leverage their unique properties, such as high surface area, quantum confinement, and tunable optical, electrical, and chemical characteristics. These applications span across various fields, including catalysis, energy storage, medicine, environmental protection, electronics, and more. The versatility of nanomaterials allows for their integration into both existing technologies and the development of innovative new solutions to global challenges.

1.5.1 Catalysis and Chemical Processing

One of the most significant applications of nanomaterials is in catalysis, where their high surface area and enhanced reactivity provide substantial advantages over traditional materials. Nanocatalysts are employed in both homogeneous and heterogeneous catalytic processes to accelerate reactions in chemical manufacturing, environmental remediation, and energy conversion [43]. For instance, metal nanoparticles, such as platinum (Pt), palladium (Pd), and gold (Au), are commonly used as catalysts in industrial chemical reactions, including hydrogenation, oxidation, and carbon-carbon coupling reactions [44]. Nanocatalysts are particularly effective in environmental applications, where they are used to degrade pollutants in air, water, and soil. Titanium dioxide (TiO₂) nanoparticles, for example, are widely used as photocatalysts in water purification systems. When exposed to ultraviolet (UV) light, TiO₂ nanoparticles generate reactive oxygen species (ROS), which break down harmful organic compounds, such as pesticides and pharmaceutical residues, into less toxic substances [45]. This photocatalytic process has become an essential technology for sustainable environmental management.

In addition to single-metal nanocatalysts, bimetallic nanomaterials have shown enhanced catalytic properties due to synergistic effects between the two metals. Bimetallic nanoparticles, such as platinum-palladium (Pt-Pd) and gold-silver (Au-Ag), are employed in fuel cells to improve the efficiency of oxygen reduction reactions (ORR) and hydrogen oxidation reactions (HOR) [46]. These reactions are critical for energy generation in fuel cells and other renewable energy technologies.

1.5.2 Energy Storage and Conversion

Nanomaterials have transformed the energy storage and conversion landscape by improving the performance of devices such as batteries, supercapacitors, and solar cells. Their small size and high surface area make nanomaterials ideal candidates for enhancing the efficiency, capacity, and lifespan of energy storage systems. For example, lithium-ion batteries (LIBs) have benefited from the incorporation of nanomaterials like graphene, silicon nanoparticles, and carbon nanotubes (CNTs) into electrode materials, which increase the charge capacity and improve charge-discharge rates [47]. Supercapacitors, which are energy storage devices that provide high power density and fast charge-discharge capabilities, also rely on nanomaterials to boost performance. Nanomaterials such as transition metal oxides (e.g., MnO_2 and RuO_2) and carbon-based nanomaterials (e.g., activated carbon and graphene) are used in supercapacitors to increase the surface area of the electrodes, allowing for greater charge storage and enhanced cycling stability [48]. These advancements have paved the way for the development of portable electronics, electric vehicles, and renewable energy systems.

In the field of energy conversion, nanomaterials are integral to the operation of solar cells, particularly in the design of next-generation photovoltaics such as dye-sensitized solar cells (DSSCs) and perovskite solar cells. Nanomaterials like quantum dots, perovskite nanocrystals, and metal oxides are employed to improve light absorption, charge transport, and electron mobility within the solar cells, resulting in higher power conversion efficiencies [49]. For example, quantum dots can be tuned to absorb different wavelengths of light, making them highly effective in capturing solar energy across the visible spectrum.

1.5.3 Biomedical Applications

Nanomaterials have made significant strides in the biomedical field, where their small size, biocompatibility, and functionalizability make them valuable tools in diagnostics, drug delivery, and therapeutics. One of the most prominent applications of nanomaterials in medicine is in cancer therapy. Nanoparticles, such as gold nanoparticles (AuNPs) and liposomes, are used to deliver drugs directly to tumor cells, enhancing the efficacy of treatment while minimizing damage to healthy tissues [50]. This targeted drug delivery reduces the side effects commonly associated with conventional chemotherapy.

In addition to drug delivery, nanomaterials are used in imaging and diagnostics. Magnetic nanoparticles, such as iron oxide (Fe_3O_4) nanoparticles, are employed in magnetic resonance imaging (MRI) as contrast agents to improve the visualization of tumors and other abnormalities in the body. Similarly, gold nanoparticles are used in optical imaging and biosensing applications due to their strong surface plasmon resonance properties, which enhance signal sensitivity in diagnostic assays [51].

Nanomaterials also play a key role in tissue engineering and regenerative medicine. For example, nanofibrous scaffolds made from biodegradable polymers are used to support the growth and differentiation of cells in tissue regeneration. These nanoscaffolds mimic the extracellular matrix, providing structural support and promoting cell adhesion, proliferation, and differentiation in the repair of damaged tissues, such as bone, cartilage, and skin [52].

1.5.4 Environmental Remediation

Environmental applications of nanomaterials are gaining momentum as researchers seek sustainable solutions to pollution and resource depletion. Nanomaterials are used in water treatment, air purification, and soil remediation due to their ability to adsorb, degrade, or transform pollutants. For instance, nanomaterials like zero-valent iron (nZVI) nanoparticles are employed in the remediation of contaminated groundwater and soils, where they reduce toxic metals and degrade chlorinated organic compounds [53]. These processes help to detoxify pollutants and restore contaminated environments. Nanomaterials are also used in air purification systems to capture and degrade airborne pollutants, such as volatile organic compounds (VOCs) and particulate matter. Metal oxide nanomaterials, such as zinc oxide

(ZnO) and manganese oxide (MnO_2), are used as catalysts to oxidize harmful gases like carbon monoxide (CO) and nitrogen oxides (NO_x) into less harmful substances [54]. These catalytic reactions contribute to cleaner air and reduce the impact of industrial emissions on the environment.

1.5.5 Electronics and Photonics

In the electronics and photonics industries, nanomaterials have enabled the development of smaller, faster, and more efficient devices. Graphene and carbon nanotubes (CNTs), for example, are used in the fabrication of transistors, sensors, and flexible electronic components due to their exceptional electrical conductivity and mechanical strength. These nanomaterials allow for the creation of lightweight and flexible electronics, which have applications in wearable devices, displays, and solar cells [55]. Nanophotonics, the study of light behavior at the nanoscale, has also benefited from the use of nanomaterials. Plasmonic nanoparticles, such as gold and silver, are employed in photonic devices to manipulate light at the nanoscale, enabling the development of highly sensitive sensors, optical waveguides, and enhanced imaging systems [56]. These nanophotonic applications are critical in fields such as telecommunications, data storage, and medical diagnostics.

1.5.6 Agriculture and Food Industry

Nanomaterials are increasingly being explored for their potential applications in agriculture and the food industry. In agriculture, nanomaterials are used to improve the efficiency of fertilizers and pesticides by enabling controlled release and targeted delivery to plants, which reduces waste and minimizes the environmental impact of agricultural practices. Nanomaterials such as silver nanoparticles and chitosan nanocomposites are being studied for their antimicrobial properties, which can help protect crops from pests and diseases [57].

In the food industry, nanomaterials are used to improve food packaging by enhancing the barrier properties of packaging materials and extending the shelf life of food products. Nanomaterials like clay nanoparticles and nanocellulose are incorporated into packaging films to improve their mechanical strength, moisture resistance, and antimicrobial activity [58]. These innovations are helping to reduce food spoilage and waste while maintaining food safety and quality.

1.6 Bimetallic Nanomaterials: An Overview

Bimetallic nanomaterials, composed of two distinct metal elements, offer unique and enhanced properties due to the synergistic effects between the metals. These materials are particularly advantageous in applications such as catalysis, energy storage, and environmental remediation. Among bimetallic nanomaterials, Layered Double Hydroxides (LDHs) have garnered significant attention due to their versatile chemical structures and tunable properties. LDHs, also known as hydrotalcite-like materials, are a subclass of lamellar compounds that contain layers of metal hydroxides with exchangeable interlayer anions [59].

1.6.1 Layered Double Hydroxide Bimetallic Materials

Layered double hydroxides (LDHs) are represented by the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{n+}(A^{n-})_x/n \cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, and A^{n-} is an interlayer anion. The structure of LDHs is derived from that of brucite ($Mg(OH)_2$), where some divalent cations are substituted by trivalent cations, leading to positively charged layers. To maintain charge neutrality, anions such as carbonate (CO_3^{2-}), nitrate (NO_3^-), or chloride (Cl^-) are incorporated into the interlayer spaces along with water molecules [60].

The versatility of LDHs stems from their ability to accommodate a wide variety of metal cations, making them ideal for creating bimetallic nanomaterials. Common metal combinations in LDHs include Mg-Al, Ni-Al, Zn-Al, and Co-Al. The combination of different metals in the layers can lead to enhanced catalytic, electrical, and thermal properties, which are exploited in applications such as catalysis, energy storage, and environmental remediation [61]. LDH bimetallic materials have garnered significant interest in heterogeneous catalysis due to their high surface area, tunable acid-base properties, and the ability to undergo calcination to form mixed metal oxides with excellent catalytic activity. The presence of both divalent and trivalent metal cations in the LDH structure allows for the optimization of catalytic properties by adjusting the metal ratio and composition [62].

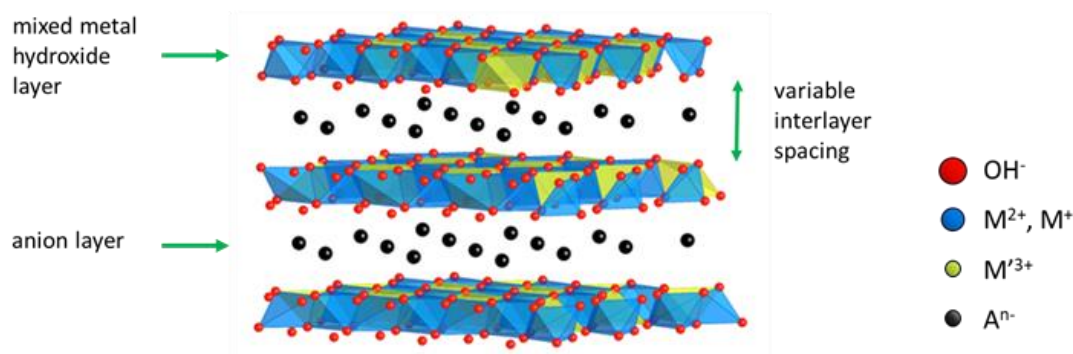


Fig. 1.2 Layered double hydroxide structure

One of the notable features of LDHs is their ability to be transformed into mixed metal oxides through thermal decomposition. This process, known as calcination, removes the interlayer water and anions, resulting in the formation of highly active metal oxides with a large surface area and uniform distribution of metal sites. These mixed oxides have found widespread use in oxidation, reduction, and acid-base catalysis, as well as in the removal of pollutants from water and air [63].

1.6.2 Synthesis of LDH Bimetallic Materials

The synthesis of LDH bimetallic materials typically involves co-precipitation, hydrothermal methods, or sol-gel techniques. The most common approach is co-precipitation, where metal salts of the desired divalent and trivalent metals are co-precipitated by the addition of a base (such as NaOH or Na₂CO₃) at controlled pH and temperature conditions. This method allows for the fine-tuning of the metal composition and the formation of highly crystalline LDH structures [64].

Hydrothermal synthesis is another method used to enhance the crystallinity and uniformity of LDHs. In this process, the metal salts are dissolved in an aqueous solution, followed by precipitation under high-temperature and high-pressure conditions in a sealed reactor. The hydrothermal method results in well-ordered LDHs with enhanced thermal stability and catalytic activity [65].

Following synthesis, the as-prepared LDH bimetallic materials can be further modified by calcination to produce mixed metal oxides. The choice of metal cations, the ratio between

them, and the calcination temperature determine the properties of the resulting oxides, including their surface area, porosity, and catalytic behavior.

1.6.3 Layered Double Hydroxide Oxides

Upon calcination, LDHs decompose into layered double hydroxide oxides or mixed metal oxides, which exhibit enhanced catalytic, electrical, and optical properties compared to their precursor materials. The calcination process typically occurs at temperatures ranging from 400 to 800°C, depending on the desired characteristics of the final oxide material. During calcination, the interlayer water and anions are eliminated, and the metal hydroxide layers are transformed into oxide phases, often forming spinel or perovskite-like structures depending on the composition of the LDH [66]. The resulting oxides are characterized by a high surface area, mesoporosity, and well-dispersed active metal sites, which make them highly effective in catalytic applications. For example, mixed metal oxides derived from Mg-Al and Ni-Al LDHs are widely used as catalysts in processes such as CO₂ reforming of methane, catalytic cracking of hydrocarbons, and the oxidative dehydrogenation of alkanes [67]. The catalytic activity of these oxides is often superior to that of conventional catalysts due to the uniform distribution of metal ions and the presence of multiple oxidation states, which facilitate redox reactions.

In addition to their catalytic applications, LDH-derived oxides are used in energy storage devices, such as supercapacitors and batteries. The layered structure of LDHs can enhance the diffusion of ions and electrons, making them ideal materials for electrodes in energy storage systems. For instance, Ni-Al and Co-Al LDH oxides have been explored as electrode materials for supercapacitors due to their high specific capacitance and excellent cycling stability [68]. Furthermore, LDH-derived oxides have found applications in environmental remediation, particularly in the removal of heavy metals and other pollutants from water. The high surface area and active metal sites of these oxides allow for efficient adsorption and degradation of contaminants. For example, mixed metal oxides derived from Zn-Al and Cu-Al LDHs have been shown to effectively remove arsenic and lead from water through adsorption and catalytic oxidation [69].

1.7 Applications of Bimetallic Nanomaterials

Bimetallic nanomaterials have become a cornerstone in multiple high-impact applications due to their ability to combine the distinct properties of two different metals. Their synergistic interactions lead to enhanced catalytic, electronic, optical, and magnetic properties, which are beneficial across numerous fields such as catalysis, energy storage, environmental protection, and biomedicine. The diversity and tunability of bimetallic nanomaterials make them superior to their monometallic counterparts for many industrial, environmental, and technological applications.

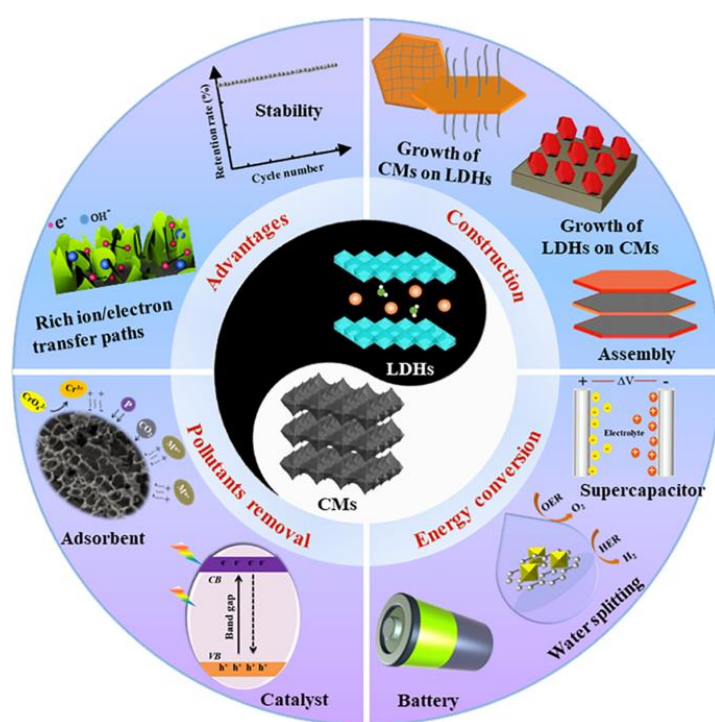


Fig. 1.3 Application of LDH and its oxides

1.7.1 Catalysis

Bimetallic nanomaterials are extensively utilized in catalysis, where the combination of two metals often results in improved catalytic performance due to electronic and geometric effects. Bimetallic catalysts are particularly valuable in heterogeneous catalytic processes for industrial and environmental applications. One of the most studied examples is platinum-palladium (Pt-Pd) bimetallic nanoparticles, which are employed in hydrogenation and oxidation reactions. These nanoparticles demonstrate enhanced catalytic activity, selectivity, and resistance to deactivation compared to monometallic catalysts, particularly in fuel cells

for the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) [70]. Another critical application of bimetallic catalysts is in automotive catalytic converters, which utilize platinum-rhodium (Pt-Rh) and platinum-palladium (Pt-Pd) bimetallic nanoparticles to facilitate the oxidation of carbon monoxide (CO) and hydrocarbons, as well as the reduction of nitrogen oxides (NO_x) into less harmful gases [71]. These catalysts help reduce vehicle emissions and have become integral components in reducing the environmental impact of internal combustion engines.

In the field of environmental catalysis, bimetallic iron-nickel (Fe-Ni) and iron-palladium (Fe-Pd) nanoparticles have been widely used for the degradation of chlorinated organic compounds in contaminated groundwater. The bimetallic systems exhibit enhanced reductive dechlorination properties due to the combined effects of the two metals, enabling faster and more complete degradation of pollutants such as trichloroethylene (TCE) and perchloroethylene (PCE) [72].

1.7.2 Energy Storage and Conversion

Bimetallic nanomaterials have emerged as key players in energy storage and conversion technologies, particularly in batteries, supercapacitors, and fuel cells. The combination of two metals allows for the fine-tuning of electrochemical properties such as charge capacity, electron transfer rates, and cycling stability. For instance, nickel-cobalt (Ni-Co) bimetallic oxides are used as electrode materials in supercapacitors, offering high specific capacitance, excellent cycling stability, and fast charge-discharge capabilities. These properties make them ideal for applications in portable electronics and electric vehicles [73].

In lithium-ion batteries (LIBs), bimetallic nanoparticles, such as cobalt-nickel (Co-Ni) and iron-cobalt (Fe-Co), are used to enhance the performance of battery electrodes. These materials provide improved cycling stability and higher energy density compared to traditional electrode materials. The bimetallic combinations help to optimize lithium-ion diffusion and electron transport, which are crucial for maintaining battery efficiency over long periods [74]. Fuel cells, which convert chemical energy into electrical energy, also benefit from the use of bimetallic catalysts. Platinum-ruthenium (Pt-Ru) and platinum-palladium (Pt-Pd) catalysts are commonly used in proton-exchange membrane fuel cells (PEMFCs) to reduce the

overpotential for the ORR and HOR. These bimetallic catalysts improve the overall efficiency of the fuel cells while enhancing their resistance to deactivation by impurities such as carbon monoxide (CO) [75].

1.7.3 Environmental Remediation

Bimetallic nanomaterials are extensively employed in environmental remediation applications due to their enhanced reactivity and ability to interact with various contaminants. In water treatment, bimetallic nanoparticles such as iron-copper (Fe-Cu) and iron-palladium (Fe-Pd) are used for the removal of toxic heavy metals, including lead (Pb) and arsenic (As), as well as for the catalytic degradation of organic pollutants. The enhanced reactivity of these bimetallic systems stems from the synergistic effects between the two metals, which facilitate more efficient adsorption and reduction processes [76].

Bimetallic nanoparticles are also used in the treatment of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) in air purification systems. For instance, platinum-rhodium (Pt-Rh) catalysts are utilized in automotive and industrial catalytic converters to reduce harmful emissions by converting toxic gases into less harmful products. These bimetallic systems are critical for reducing the environmental impact of industrial emissions and improving air quality [77].

In addition to their catalytic activity, bimetallic nanomaterials are used in soil remediation. For example, bimetallic iron-based nanoparticles are employed to degrade persistent organic pollutants (POPs) in contaminated soils. The presence of a secondary metal enhances the reductive capacity of iron, allowing for more efficient degradation of contaminants such as polychlorinated biphenyls (PCBs) and dioxins [78].

1.7.4 Biomedical Applications

Bimetallic nanomaterials hold significant potential in the biomedical field, where their unique properties are harnessed for drug delivery, imaging, and therapeutic applications. One of the most promising uses of bimetallic nanoparticles in medicine is in drug delivery systems. Gold-silver (Au-Ag) and gold-palladium (Au-Pd) nanoparticles are used to deliver therapeutic agents directly to target tissues or cells. These nanoparticles can be functionalized with ligands

or antibodies to enhance their targeting capabilities, ensuring that the drug is released specifically at the disease site, thus minimizing side effects [79]. In diagnostics, bimetallic nanoparticles such as gold-silver (Au-Ag) are used in surface-enhanced Raman scattering (SERS) for highly sensitive detection of biomolecules. The strong plasmonic properties of bimetallic nanoparticles enhance the signal strength of Raman scattering, making them ideal for use in molecular diagnostics and medical imaging [80].

Bimetallic nanoparticles also show promise in cancer therapy, particularly in photothermal therapy. Gold-palladium (Au-Pd) and gold-silver (Au-Ag) nanoparticles absorb light and convert it into heat, which can be used to selectively kill cancer cells while sparing healthy tissues. These bimetallic systems offer superior thermal conductivity and biocompatibility compared to single-metal nanoparticles, enhancing their effectiveness in treating tumors [81].

1.7.5 Electronics and Photonics

Bimetallic nanomaterials are critical components in the development of next-generation electronics and photonics due to their unique electrical and optical properties. Gold-copper (Au-Cu) and silver-palladium (Ag-Pd) nanoparticles, for example, are used in the fabrication of conductive inks for flexible electronics, enabling the production of wearable devices and printed sensors. These materials offer high electrical conductivity and mechanical flexibility, making them suitable for use in a wide range of electronic applications [82]. In the photonics industry, bimetallic nanoparticles such as gold-silver (Au-Ag) are used to enhance the performance of optical devices through their plasmonic properties. These nanoparticles exhibit strong surface plasmon resonance (SPR), which allows them to manipulate light at the nanoscale, leading to the development of highly sensitive optical sensors and improved imaging techniques. Bimetallic nanomaterials are also used in metamaterials, which are engineered to have unique properties not found in natural materials, such as negative refractive indices and the ability to control light propagation [83].

In summary, bimetallic nanomaterials have a wide range of applications across various industries, including catalysis, energy, environment, medicine, and electronics. Their enhanced properties, derived from the combination of two metals, allow for superior performance and functionality in processes ranging from energy conversion to environmental

remediation and biomedical interventions. Ongoing research into the synthesis and application of bimetallic nanomaterials continues to drive advancements in these fields, making them indispensable in modern technology.

1.8 Research Objectives

The primary objective of this research is to develop advanced bimetallic oxide nanomaterials and Layered Double Hydroxides (LDHs) integrated with composite catalysts such as graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) and doped with noble metals like silver (Ag). This study aims to improve the performance of these nanomaterials in environmental and energy applications, including catalysis, pollutant degradation, and energy conversion systems.

The research objectives are outlined as follows:

1. Synthesis of Bimetallic Oxides (Fe, Ni, and Al) and LDH-Based Nanomaterials:

The first objective of the research is to synthesize bimetallic oxide nanomaterials using Fe, Ni, and Al, as well as Layered Double Hydroxides (LDHs) as precursors. These materials are known for their exceptional catalytic properties and tunable surface characteristics. The research will focus on optimizing the synthesis process to achieve controlled size, shape, and morphology of the bimetallic oxides and LDHs. The synthesis will incorporate scalable techniques such as hydrothermal synthesis and co-precipitation to produce highly uniform and stable nanomaterials. Special emphasis will be placed on creating mixed oxides derived from Fe-Ni-Al LDHs, which are expected to show superior catalytic activity in environmental and energy-related processes [82].

2. Incorporation of Composite Catalysts Such as Graphitic Carbon Nitride ($g\text{-C}_3\text{N}_4$):

The second objective is to integrate the synthesized bimetallic oxides and LDHs with composite catalysts such as graphitic carbon nitride ($g\text{-C}_3\text{N}_4$). $g\text{-C}_3\text{N}_4$ has gained significant attention due to its high photocatalytic activity, excellent chemical stability, and ability to form heterostructures with other nanomaterials. By combining $g\text{-C}_3\text{N}_4$ with bimetallic oxides, the research aims to enhance the catalytic efficiency of the composite materials, particularly in photocatalysis and environmental remediation applications. The synergistic effects between

g-C₃N₄ and bimetallic oxides are expected to improve light absorption, charge separation, and reaction rates in photocatalytic processes [83].

3. Doping with Noble Metals (Ag or Au) to Enhance Catalytic Performance:

The third objective is to explore the doping of bimetallic oxides and LDH-based composites with noble metals such as silver (Ag) and gold (Au). Noble metal doping is known to significantly enhance the catalytic properties of nanomaterials by introducing new active sites and improving electron transfer processes. Ag and Au nanoparticles will be doped onto the surface of the bimetallic oxides and LDH composites to further increase their catalytic performance in reactions such as hydrogen evolution reactions (HER), oxygen reduction reactions (ORR), and pollutant degradation. The research will focus on optimizing the doping process to achieve uniform dispersion of the noble metal nanoparticles and maximize their interaction with the bimetallic oxides [84].

4. Characterization of Synthesized Nanomaterials:

Following the synthesis and doping processes, the next objective is to comprehensively characterize the resulting nanomaterials. Techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) will be used to investigate the structural and chemical properties of the bimetallic oxides, LDH composites, and noble metal-doped nanomaterials. The characterization will focus on understanding the impact of metal composition, particle size, and doping concentration on the catalytic activity and stability of the materials. Additionally, electrochemical analysis will be conducted to evaluate the performance of these nanomaterials in energy storage and conversion systems [85].

5. Evaluation of Catalytic Performance in Environmental and Energy Applications:

The fifth objective is to evaluate the catalytic performance of the synthesized nanomaterials in environmental and energy applications. For environmental applications, the research will focus on the degradation of organic pollutants such as dyes, pharmaceuticals, and chlorinated hydrocarbons in water. The photocatalytic activity of the g-C₃N₄ composites and the impact of noble metal doping on the degradation efficiency will be assessed. In energy applications,

the research will test the effectiveness of the nanomaterials as catalysts in fuel cells and supercapacitors, particularly in reactions like ORR and HER. The goal is to optimize the catalytic properties of the materials to enhance their performance in sustainable energy systems [86].

6. Optimization of Synthesis Parameters for Scale-Up:

The final objective of this research is to optimize the synthesis parameters for the large-scale production of bimetallic oxides, LDH composites, and noble metal-doped nanomaterials. This will involve identifying the key factors that influence the scalability of the synthesis process, such as precursor concentration, reaction temperature, and reaction time. The optimization will focus on ensuring that the large-scale production of these materials can be achieved without compromising their catalytic performance and stability. The ultimate goal is to develop a scalable and cost-effective method for producing high-performance nanomaterials suitable for industrial applications in catalysis, environmental protection, and renewable energy [87].

1.9 Overall Significance of the Research

The successful completion of these research objectives is expected to lead to the development of novel bimetallic oxides and LDH-based nanomaterials with enhanced catalytic properties. By integrating g-C₃N₄ and doping with noble metals such as Ag or Au, the research aims to create advanced catalysts that are highly effective in environmental remediation and energy conversion. The insights gained from this research could have significant implications for the design of next-generation nanomaterials with applications in clean energy technologies, water purification and sustainable industrial processes.

This thesis is structured into six chapters that collectively address the research conducted on bimetallic nanomaterials, including their synthesis, characterization, and applications in environmental and energy-related fields.

The introduction provides the context and motivation behind the research, highlighting the importance of bimetallic nanomaterials in tackling challenges such as environmental

remediation and energy conversion. It also outlines the research objectives and the overall structure of the thesis.

The second chapter delves into the experimental methodologies and instrumentation used. This includes the synthesis of bimetallic oxides (Fe, Ni, and Al) and Layered Double Hydroxides (LDHs), as well as the incorporation of graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) and noble metals like silver (Ag) and gold (Au) to enhance catalytic properties. Various synthesis techniques such as hydrothermal methods and co-precipitation are detailed, along with the characterization of the synthesized nanomaterials using tools like TEM, SEM, XRD, XPS, ICP-MS, and electrochemical analyses. Additionally, the performance of these nanomaterials in environmental and energy-related tests is discussed.

The next three chapters comprise manuscripts that have either been published or submitted for publication. These chapters present the core findings of the research. The first manuscript focuses on the synthesis and characterization of bimetallic oxides, specifically their applications in water treatment. The second manuscript explores the synergistic effects of integrating bimetallic nanomaterials with $\text{g-C}_3\text{N}_4$ for photocatalytic degradation of pollutants. The third manuscript discusses the enhancement of catalytic and electrochemical performance through the doping of bimetallic nanomaterials with Ag or Au, particularly in water splitting and organic degradation.

The final chapter concludes the thesis by summarizing the research findings and reflecting on the significance of the results. It emphasizes the development of high-performance bimetallic nanomaterials with potential applications in both environmental and energy sectors. The conclusion also suggests future research directions, such as further optimization of synthesis methods and broader applications in sustainable technologies.

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Chapter 2: Methodology

2.1 Concept of Process Intensification

Process Intensification (PI) is a vital engineering strategy aimed at making substantial improvements in manufacturing and processing. The primary goal of PI is to enhance the efficiency, cost-effectiveness, and environmental sustainability of chemical processes. This can be achieved through the development of novel apparatus and processing techniques that lead to dramatic reductions in energy consumption, reactor volume, and waste generation, while simultaneously improving productivity and safety. PI began to gain traction in the late 20th century as industries recognized the need to meet growing economic and environmental challenges. Its core principles include increasing the efficiency of the energy used in reactions, reducing the physical footprint of processing equipment, and minimizing by-products and waste. PI is increasingly applied to various sectors, including chemical manufacturing, pharmaceuticals, and environmental engineering, where the synthesis and application of nanomaterials play a significant role [1].

One of the key approaches in PI is the use of intensified reactors, such as Spinning Disc Reactors (SDRs), microreactors, and compact heat exchangers. These reactors enable better control of reaction conditions such as temperature and mixing, which are crucial for producing nanomaterials with consistent properties. For example, SDRs are specifically designed to enhance mass and heat transfer through high shear rates, allowing for faster and more controlled chemical reactions [2]. PI techniques are increasingly favored in nanomaterials synthesis due to their ability to address issues related to scale-up, reproducibility, and reaction time. Traditional methods of nanomaterials synthesis often require large-scale reactors, long reaction times, and high energy inputs. By contrast, PI methods can significantly reduce the size of the reactors and the energy required while improving the consistency and quality of the nanomaterials produced [3]. For example,

nanomaterials such as metal oxides and carbon-based materials have been successfully synthesized using intensified methods with superior properties for catalysis and environmental remediation [4]. Furthermore, PI allows for a more sustainable approach to chemical processing. The reduction in energy consumption and waste production aligns with the growing demand for greener technologies in industries. In nanomaterials synthesis, process intensification can facilitate the use of less toxic solvents and reagents, or even enable solvent-free processes [5]. These approaches not only minimize the environmental impact but also often lead to higher yields of more uniform nanomaterials.

In addition, the rapid development of PI methods has allowed for advancements in process modeling and simulation, further optimizing the conditions for nanomaterials synthesis. By integrating process intensification with computational tools, researchers can predict reaction outcomes, scale processes more efficiently, and design more compact, efficient reactors [6]. This has been particularly useful in industries where precision and control over the synthesis of nanomaterials are critical, such as in the production of catalysts for hydrogen generation or in the development of novel materials for energy storage [7]. Process Intensification also supports the advancement of renewable energy technologies, such as hydrogen production. For instance, intensified processes can be used to produce hydrogen more efficiently from water splitting or other catalytic reactions involving nanomaterials [8]. These processes can be made more sustainable by optimizing reactor designs and operating conditions to maximize hydrogen yield while minimizing energy input [9]. In fact, Process Intensification represents a transformative approach in chemical engineering, with far-reaching applications in nanomaterials synthesis. The principles of PI—such as improving mass and heat transfer, reducing equipment size, and lowering energy consumption—are key to developing more sustainable, cost-effective, and efficient processes in nanotechnology and other industries. As the field continues to evolve, PI is expected to play an even larger role in driving innovation in materials science, energy production, and environmental sustainability [10].

2.2 Spinning Disc Reactor (SDR)

The Spinning Disc Reactor (SDR) represents a novel and advanced process intensification technology that has found widespread applications in chemical processing, particularly in the

synthesis of nanomaterials. The SDR relies on the rapid rotation of a disc to create a thin liquid film, enabling enhanced mixing, mass transfer, and heat transfer, all of which are critical for achieving efficient chemical reactions with high precision. This makes the SDR particularly well-suited for the synthesis of nanomaterials, where control over particle size and distribution is paramount.

The core of the SDR system is a rapidly rotating disc, typically positioned horizontally. When liquid reagents are introduced at the center of the spinning disc, centrifugal forces drive the liquid outward, forming a thin film that spreads radially across the disc surface. This thin liquid film enables significant improvements in heat and mass transfer rates compared to conventional reactors. The enhanced mass transfer is a direct consequence of the high shear forces generated by the rapid rotation of the disc, which breaks up the liquid and facilitates efficient mixing of the reactants [11]. The formation of this thin film is critical to the functioning of the SDR, as it provides an increased surface-area-to-volume ratio, leading to faster reaction kinetics. This characteristic is especially important for reactions such as precipitation, crystallization, and nanoparticle formation, where precise control over the rate of nucleation and growth is necessary to produce nanoparticles with uniform size and morphology [12]. Additionally, the high rates of mass and heat transfer allow for improved temperature control, reducing the likelihood of localized overheating or incomplete reactions, which are common challenges in bulk-phase reactors [13].

One of the major advantages of the SDR in nanomaterial synthesis is the ability to tailor particle size distribution. The intense shear forces and rapid mixing on the spinning disc help to avoid agglomeration, a common issue in traditional reactors where nanoparticles tend to clump together due to Brownian motion or van der Waals forces. By preventing agglomeration, the SDR ensures that nanoparticles are more evenly distributed and remain within a narrower size range [14]. This has been demonstrated in the synthesis of metallic and metal oxide nanoparticles, such as silver, gold, and zinc oxide, which are widely used in applications ranging from catalysis to biomedical devices [15]. Moreover, SDRs offer flexibility in scaling up chemical reactions. Unlike conventional batch reactors, where scaling up often leads to challenges in maintaining uniform reaction conditions, the SDR can be scaled

by increasing the disc size or stacking multiple discs. This modular scalability allows for increased production capacity without compromising the quality of the synthesized nanomaterials [16]. For instance, the synthesis of titanium dioxide (TiO_2) nanoparticles using an SDR has been shown to result in consistent particle sizes and high purity, even when scaled up for industrial applications [17].

From an environmental standpoint, SDRs are also more sustainable than many traditional reactors. The improved heat transfer and rapid mixing allow for reactions to proceed at lower temperatures and with shorter reaction times, reducing energy consumption. Furthermore, the reduced reactor volume and faster reaction times lead to less solvent usage and waste generation, aligning with green chemistry principles [18]. The ability to perform continuous reactions in SDRs, rather than batch processes, also contributes to higher overall process efficiency and lower environmental impact [19].

Another key aspect of SDR technology is its versatility in handling different types of reactions. The SDR has been successfully employed in a wide variety of chemical processes, including polymerization, crystallization, and catalysis. In the field of nanomaterials, SDRs have been particularly effective in producing nanoparticles for applications in photocatalysis, sensors, and energy storage. For example, zinc oxide nanoparticles synthesized using SDRs have been utilized in dye-sensitized solar cells, where their uniform size and enhanced surface area contribute to improved efficiency [20].

Despite these advantages, the use of SDRs is not without challenges. One of the primary issues is the potential for fouling on the surface of the disc, particularly when working with reactants that produce solid precipitates or highly viscous materials. This fouling can affect the flow dynamics and reduce the efficiency of the reactor over time. To mitigate this, researchers have explored various disc materials and surface coatings to reduce fouling and facilitate easy cleaning [21]. Additionally, careful control of the reaction conditions, such as disc rotation speed and liquid feed rate, can help to minimize fouling and maintain reactor performance [22]. In summary, the Spinning Disc Reactor is a powerful tool for the intensification of chemical processes, particularly in the field of nanomaterials synthesis. Its ability to enhance

mass and heat transfer, reduce reaction times, and improve control over particle size distribution makes it an attractive option for both academic research and industrial production. As the demand for advanced nanomaterials continues to grow, SDR technology is likely to play an increasingly important role in the development of new materials and scalable synthesis processes.

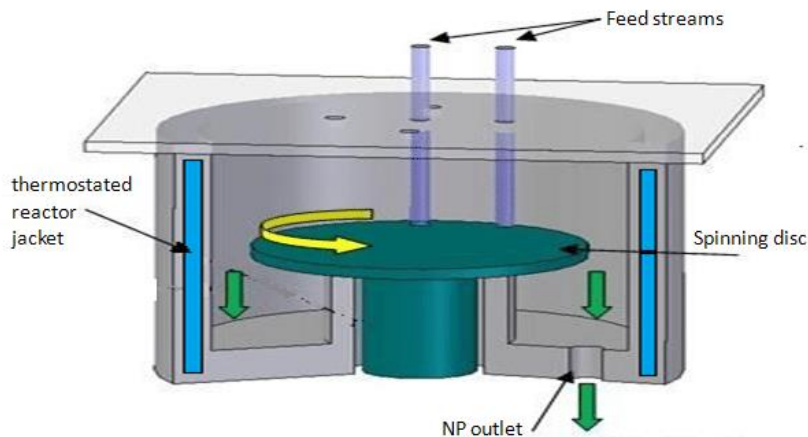


Fig 2.1 Spinning disc reactor schematic diagram

2.3 Factors Affecting the Process Parameters The performance and efficiency of a Spinning Disc Reactor (SDR) are governed by several critical factors, which influence the reaction kinetics, mass and heat transfer, and ultimately, the quality of the synthesized nanomaterials. Understanding and optimizing these process parameters are key to fully harnessing the benefits of SDR technology, particularly in nanomaterial synthesis. The primary factors that affect the performance of SDRs include disc speed, flow rate, liquid viscosity, disc surface properties, and temperature. Each of these parameters interacts with the others to impact the overall efficiency and output of the reaction.

2.3.1 Disc Speed

Disc speed is one of the most significant parameters in an SDR, as it directly influences the centrifugal forces acting on the liquid film and, consequently, the thickness of the film. As the disc speed increases, the liquid film becomes thinner, which enhances the mass and heat transfer rates across the disc surface. Thin films promote faster reaction kinetics by decreasing the diffusion distance for reactants and facilitating more efficient mixing [23]. However, excessively high disc speeds can lead to turbulence in the liquid film, which can destabilize the process and negatively affect the control over particle size and morphology during

nanomaterial synthesis [24]. Therefore, optimizing disc speed is essential to maintaining a balance between improved mixing and the stability of the reaction environment.

2.3.2 Flow Rate

The flow rate of the liquid introduced onto the spinning disc is another critical parameter that must be carefully controlled. The flow rate affects the residence time of the reactants on the disc, which in turn influences the extent of the reaction. Higher flow rates result in shorter residence times, which can reduce the overall yield of the reaction if the reactants do not have sufficient time to fully convert. Conversely, very low flow rates may lead to inefficient use of the reactor's surface area and potential fouling as reactants accumulate on the disc [25]. In the context of nanomaterial synthesis, controlling the flow rate is crucial for ensuring that nucleation and growth of nanoparticles occur under optimal conditions, leading to uniform particle sizes and shapes.

2.3.3 Liquid Viscosity

The viscosity of the liquid reactants also plays an important role in determining the behavior of the thin film on the spinning disc. High-viscosity liquids tend to form thicker films, which can reduce the mass and heat transfer efficiency of the reactor. In contrast, low-viscosity liquids create thinner films that allow for more rapid diffusion of reactants and faster heat dissipation [26]. However, care must be taken when working with low-viscosity liquids, as excessively thin films can become unstable and break up due to centrifugal forces, leading to inconsistent reaction conditions. The choice of solvents and additives can be used to adjust the viscosity of the reaction mixture, helping to fine-tune the film thickness and improve the performance of the SDR [27].

2.3.4 Disc Surface Properties

The material and surface texture of the spinning disc are also important factors that can influence the behavior of the liquid film. Smooth discs promote the formation of uniform thin films, which are ideal for maximizing mass and heat transfer rates. However, rough or textured surfaces can introduce turbulence into the liquid film, which may enhance mixing in some cases but can also lead to uneven film thickness and reduce the efficiency of the reaction [28]. In nanomaterial synthesis, where precise control over reaction conditions is required, smooth discs are generally preferred to ensure consistency in particle size and morphology.

Additionally, coatings or modifications to the disc surface can be employed to reduce fouling and prevent the buildup of solid precipitates during the reaction [29].

2.3.5 Temperature

Temperature control is a critical factor in SDR operations, particularly in exothermic or endothermic reactions. The thin film environment of an SDR facilitates rapid heat exchange between the liquid film and the disc surface, allowing for precise temperature control throughout the reaction [30]. In nanomaterial synthesis, maintaining a stable temperature is crucial for controlling the nucleation and growth of nanoparticles, as fluctuations in temperature can lead to variations in particle size, shape, and crystal structure. For example, the synthesis of metal oxide nanoparticles typically requires a high degree of temperature control to ensure the formation of the desired crystalline phase and to prevent the growth of amorphous or undesired phases [31]. The efficient heat transfer properties of the SDR help to minimize temperature gradients and maintain consistent reaction conditions.

2.3.6 Reagent Concentration

The concentration of the reactants introduced onto the spinning disc also plays a significant role in determining the outcome of the reaction. High concentrations of reactants can lead to rapid nucleation and growth of nanoparticles, but they also increase the risk of agglomeration if not carefully controlled [32]. Conversely, low concentrations may result in slower reaction rates and lower yields, but they offer better control over particle size and distribution. In SDRs, the ability to rapidly mix reactants in the thin film environment allows for better control over concentration gradients, reducing the likelihood of localized over-concentration and improving the overall quality of the nanomaterials produced [33].

2.3.7 Fouling and Maintenance

One of the challenges associated with SDR operation is fouling, particularly in processes where solid by-products or precipitates are formed. Fouling occurs when these solids deposit on the surface of the disc, reducing the efficiency of the reactor by obstructing the flow of liquid and interfering with the formation of the thin film. Strategies to minimize fouling include the use of anti-fouling coatings on the disc surface, periodic cleaning cycles, and careful control of the reaction conditions to prevent excessive solid formation [34]. Regular

maintenance is essential to ensure that the reactor continues to operate efficiently and to avoid interruptions in the process. In conclusion, the performance of the Spinning Disc Reactor is influenced by a complex interplay of factors, including disc speed, flow rate, liquid viscosity, disc surface properties, temperature, and reagent concentration. Optimizing these parameters is essential for achieving the desired outcomes in nanomaterial synthesis, where control over particle size, morphology, and phase composition is critical. By carefully tuning these factors, researchers can maximize the efficiency of the SDR and produce high-quality nanomaterials with greater consistency and precision.

2.4 Models and Equations of SDR Process

Several models have been proposed to describe the fluid dynamics and the thickness of the liquid film on a rotating disc, which are critical for understanding the behavior of the Spinning Disc Reactor (SDR). These models provide insight into how variables such as disc speed, flow rate, and viscosity affect the reaction environment, particularly for nanomaterial synthesis. Solving the governing equations for fluid flow, heat transfer, and mass transfer in an SDR is a complex task that often requires the use of computational fluid dynamics (CFD) software to obtain accurate predictions of flow behavior, temperature distribution, and reaction rates [35]. One of the foundational models for describing the thickness of the liquid film on the spinning disc was proposed by Lepehin and Riabchuk and later extended by Nusselt. These models provide a semi-empirical relationship for predicting the thickness of the liquid film, $\delta(r)$, at a given radial position r from the center of the disc. The thickness of the film is an essential parameter because it governs the heat and mass transfer rates, which in turn influence the reaction kinetics and particle size distribution during nanoparticle synthesis [36].

The thickness of the liquid film, $\delta(r)$, is given by the following equation:

$$\delta(r) = 0.886 Q^{0.348} \nu^{0.328} r^{-0.7} \omega^{-0.676} \quad (1.1)$$

where Q is the flow rate of the liquid (in m^3s^{-1}), ω is the angular velocity of the disc (in rad.s^{-1}), r is the radial distance from the centre of the disc (in m), and ν is the kinematic viscosity of the

liquid (in m^2s^{-1}) [37]. In practical operation, the flow rate Q , angular velocity ω , and viscosity ν are typically set as fixed values, remaining constant over time for a given reaction.

This thin film formed on the disc allows for rapid heat and mass transfer, enhancing the micromixing of reagents and enabling faster reaction rates, which are crucial for the synthesis of nanomaterials. The radial variation of film thickness also means that reaction conditions can vary across the disc, with thinner films near the disc's periphery providing more intense mixing and heat transfer [38].

The liquid film at a given radius r will uptake kinetic energy from the spinning disc, which is transferred to the fluid as specific dispersed power, $\epsilon(r)$, expressed by the following equation:

$$\epsilon(r) = 2\tau(r)^{-1} [(\omega^2 r_b^2 - \nu(r_b)^2) - (\omega^2 r_a^2 - \nu(r_a)^2)] \quad (1.2)$$

where where $r_b > r_a$, τ (s) is the residence time, r (m) the radial distance of the injection point of the reactant from the disk centre and $\nu(r)$ (m s^{-1}) the radial velocity of the liquid film [39].

The residence time $\tau(r)$ and radial velocity $\nu(r)$ can be further evaluated by the following relationships:

$$\tau(r) = (81\pi^2\nu)^{1/3} (16\omega^2 Q^2)^{-1/3} (r_b^{4/3} - r_a^{4/3}) \quad (1.3)$$

$$\nu(r_a) = (3\nu)^{-1} r_a \omega^2 \delta^2 \quad (1.4)$$

The specific power dissipation $\epsilon(r)$ represents the energy imparted to the fluid by the disc's rotation. This energy creates conditions for intense micromixing within the thin liquid film, which is especially favorable for nanoparticle synthesis. The higher the specific energy dissipation, the more effective the local mixing between reagent solutions becomes. This promotes nucleation and particle growth while reducing the size of the nanoparticles produced due to the enhanced mixing conditions and shorter micromixing times [40].

Micromixing time is a crucial parameter in determining the outcome of the reaction, particularly in terms of the size distribution of nanoparticles. Shorter micromixing times lead

to higher local concentrations of reactants, accelerating nucleation rates and reducing particle size. Consequently, controlling the process parameters such as angular velocity, flow rate, and radial distance allows for precise manipulation of the reaction environment, which is critical for tailoring nanoparticle characteristics such as size and morphology [41].

This model highlights the delicate balance required to optimize SDR processes for nanomaterial synthesis. A high specific energy dissipation improves micromixing, leading to smaller nanoparticle sizes and more uniform distributions. However, excessive energy input can also induce turbulence and disrupt the stability of the liquid film, potentially leading to non-uniform reactions and variable product quality. Thus, the use of CFD simulations is often employed to fine-tune these parameters, allowing for optimal reactor design and operation that maximizes reaction efficiency while maintaining control over nanoparticle properties [42].

In conclusion, the models and equations governing the Spinning Disc Reactor process provide valuable insights into the fluid dynamics, heat transfer, and mass transfer within the reactor. By understanding and applying these models, researchers can optimize the performance of SDRs for a wide range of applications, particularly in the synthesis of nanomaterials. The ability to manipulate process parameters through precise control over film thickness, energy dissipation, and micromixing conditions allows for enhanced control over reaction outcomes, leading to the production of high-quality nanomaterials with tailored properties.

2.5 Co-precipitation of Bimetallic CoFe Oxide Catalyst

The co-precipitation method is a widely used approach for the synthesis of bimetallic CoFe oxide catalysts due to its simplicity, scalability, and effective control over the stoichiometry of the metal components. This process involves the simultaneous precipitation of cobalt (Co) and iron (Fe) ions from a homogeneous solution, typically in the form of metal nitrates or sulfates, by the addition of a precipitating agent such as sodium hydroxide (NaOH) or ammonium hydroxide (NH₄OH). The co-precipitation technique allows for the intimate mixing of the metal ions at the atomic level, which is crucial for the formation of a uniform bimetallic oxide phase and enhances the catalytic performance of the material [43]. In the co-precipitation method, the choice of precursors, pH, temperature, and aging time significantly influence the physicochemical properties of the resulting CoFe oxide catalysts. The process generally begins with the dissolution of cobalt and iron salts in water to form a clear solution. The pH of the

solution is then adjusted by the controlled addition of the precipitating agent, which induces the formation of metal hydroxide precipitates. The co-precipitated hydroxides are aged for a specific period, filtered, washed, and finally calcined at high temperatures to convert the hydroxides into the desired bimetallic oxide phase.

The calcination step plays a crucial role in determining the crystallinity, phase composition, and surface area of the catalyst. During this thermal treatment, the hydroxide species undergo decomposition, resulting in the formation of crystalline CoFe oxide with well-defined morphologies. The specific surface area of the catalyst can be tuned by controlling the calcination temperature, which directly impacts the catalytic activity for various applications such as oxygen evolution reactions (OER), hydrogen evolution reactions (HER), and other redox processes [44]. Several studies have demonstrated the advantages of bimetallic CoFe oxides synthesized by co-precipitation in catalytic applications. The synergistic interaction between Co and Fe in the oxide lattice improves the electron transfer and catalytic performance compared to their monometallic counterparts. Furthermore, the homogeneous dispersion of active sites within the catalyst enhances the overall efficiency in catalytic processes [45].

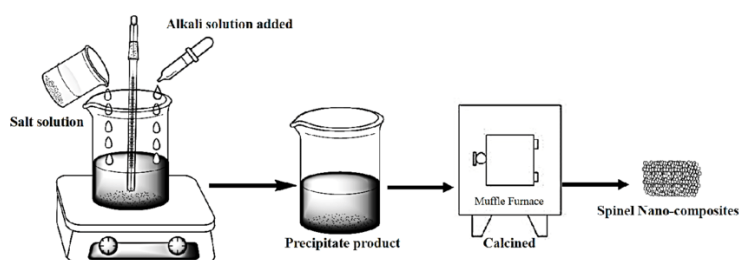


Fig 2.2 Co-precipitation method

2.6 Hydrothermal Method for LDH

The hydrothermal method is a versatile and effective technique for the synthesis of layered double hydroxides (LDHs), which are materials composed of positively charged brucite-like layers and interlayer anions. The hydrothermal process involves the crystallization of materials from aqueous solutions under elevated temperature and pressure, typically in a sealed autoclave. This method provides precise control over the size, morphology, and

crystallinity of LDH materials, making it suitable for a wide range of applications including catalysis, adsorption, and drug delivery [46].

In a typical hydrothermal synthesis of LDHs, metal salts, such as nitrates or chlorides, are dissolved in water along with a base such as NaOH to form a precursor solution. This solution is then transferred into an autoclave and subjected to elevated temperatures (usually between 120°C and 200°C) for several hours. Under these conditions, the metal ions undergo hydrolysis and nucleation, followed by the growth of LDH crystals. The hydrothermal environment promotes the formation of highly crystalline LDH materials with well-defined morphologies [47].

The hydrothermal method offers several advantages over conventional synthesis techniques, such as higher crystallinity, better control over particle size, and the ability to produce materials with unique morphologies such as nanoplates, nanorods, and nanotubes. Moreover, the mild reaction conditions in hydrothermal synthesis are suitable for incorporating thermally sensitive organic molecules or dopants into the LDH structure without decomposition [48]. LDHs synthesized by the hydrothermal method have been extensively studied for their potential in environmental remediation, energy storage, and as catalysts for various chemical reactions. The ability to tune the composition and structure of LDHs by adjusting the hydrothermal conditions makes this method highly attractive for the development of advanced materials with tailored properties [49].

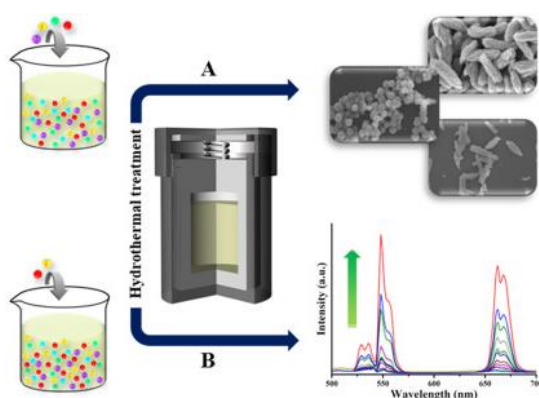


Fig 2.3 Hydrothermal Method of NPs synthesis

2.7 Photoreduction for Ag Doping

Photoreduction is an efficient and environmentally friendly method for doping metal oxides with noble metals such as silver (Ag). The process involves the reduction of metal ions in the presence of light and a photocatalyst, typically under mild reaction conditions. This technique has gained significant attention due to its ability to produce highly dispersed metal nanoparticles on the surface of the host material, leading to enhanced catalytic, optical, and electronic properties [50].

In a typical photoreduction process for Ag doping, a solution of a silver precursor, such as silver nitrate (AgNO_3), is mixed with the metal oxide substrate in the presence of a photocatalyst, such as titanium dioxide (TiO_2). Upon exposure to ultraviolet (UV) light, the photocatalyst generates electron-hole pairs. The photogenerated electrons reduce the Ag^+ ions to metallic Ag nanoparticles, which are deposited onto the surface of the metal oxide. The size, distribution, and loading of Ag nanoparticles can be controlled by adjusting the concentration of the silver precursor, the intensity of the light source, and the reaction time [51]. The photoreduction method offers several advantages for Ag doping, including simplicity, the use of non-toxic reagents, and the ability to perform the reaction under ambient conditions. Moreover, the use of light as a driving force for the reduction reaction eliminates the need for high temperatures or reducing agents, making the process more sustainable [52]. Ag-doped metal oxides synthesized by photoreduction have shown enhanced performance in various applications such as photocatalysis, antimicrobial coatings, and sensors [53].

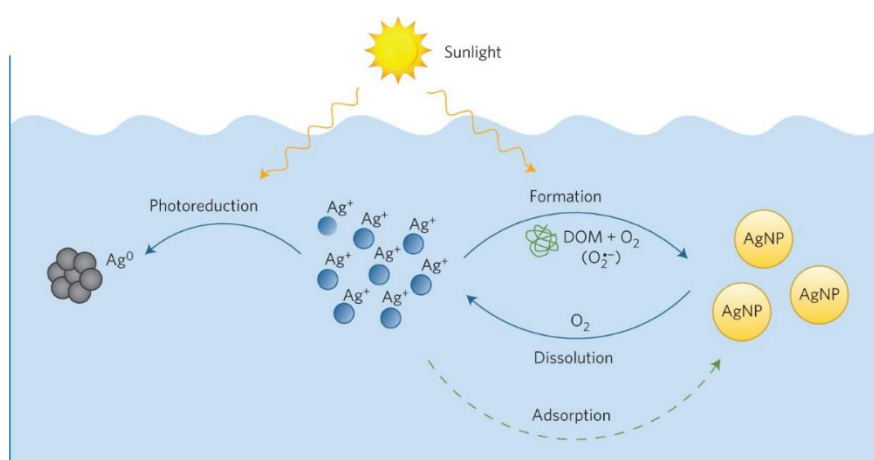


Fig 2.4 Photoreduction method of Ag

2.8 Testing Setup for Photocatalytic Water Splitting Hydrogen Production

Photocatalytic water splitting has emerged as a promising technology for sustainable hydrogen production, utilizing solar energy to convert water (H_2O) into hydrogen (H_2) and oxygen (O_2). The testing setup for this process is critical to evaluating the efficiency and performance of various photocatalysts. A typical experimental configuration for photocatalytic hydrogen production includes a reaction vessel, a light source, a photocatalyst, a sacrificial agent, a gas collection system, and analytical instruments for monitoring gas evolution and catalytic activity [54].

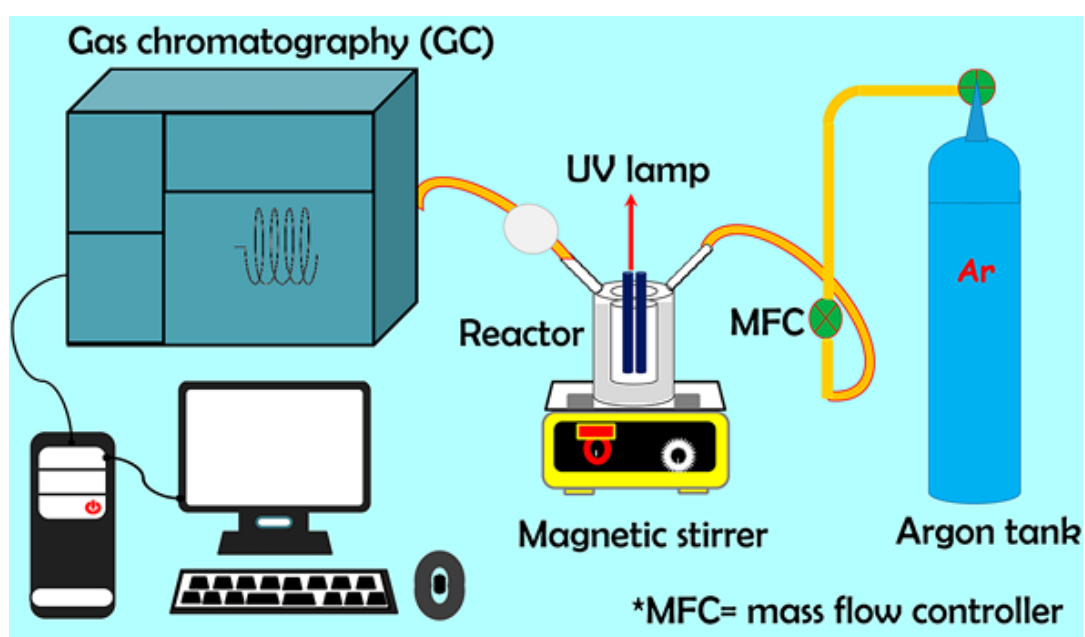


Fig 2.5 Photocatalytic water splitting setup

2.8.1 Reaction Vessel

The reaction vessel, often referred to as a photoreactor, is designed to hold the aqueous solution of the photocatalyst and ensure uniform exposure to light. The reactor is typically constructed of quartz or glass, materials that allow the transmission of UV-visible light, which is necessary for photocatalyst activation. The vessel can either be a batch reactor or a continuous flow reactor, depending on the experimental requirements. In a batch reactor, the reaction mixture remains static, and the gas produced during water splitting accumulates in the headspace. This setup is simple and allows for easy monitoring of gas production over time. In contrast, a continuous flow reactor involves a steady flow of water or electrolyte solution through the reactor, making it suitable for large-scale or industrial applications [55].

2.8.2 Light Source

The light source is a crucial component in photocatalytic hydrogen production. The efficiency of the process largely depends on the ability of the photocatalyst to absorb light and generate electron-hole pairs that drive the water-splitting reaction. Most testing setups use UV or visible light sources, depending on the bandgap of the photocatalyst. For photocatalysts such as TiO_2 , which require UV light, mercury or xenon arc lamps are commonly used. These lamps can emit light in a wide spectrum, with intense UV radiation capable of activating the photocatalyst. For visible-light-active photocatalysts, such as those based on doped semiconductors or composite materials (e.g., CdS , $\text{g-C}_3\text{N}_4$), halogen or LED lamps are employed. Solar simulators are also frequently used to mimic sunlight and evaluate the performance of photocatalysts under conditions that resemble natural solar irradiation [56]. The intensity and wavelength of the light are controlled to ensure that the photocatalyst is activated at its optimal conditions. The intensity of the light is typically calibrated to 100 mW/cm^2 , which corresponds to standard sunlight under AM 1.5G conditions.

2.8.3 Photocatalyst and Sacrificial Agent

The photocatalyst is the heart of the system, typically comprising a semiconductor material that absorbs light and generates charge carriers (electrons and holes). Materials such as TiO_2 , ZnO , WO_3 , CdS , and various metal oxides are widely used as photocatalysts due to their ability to absorb light and catalyze the water-splitting reaction. In some cases, photocatalysts are doped with noble metals (e.g., Pt , Au , Ag) or combined with other materials to enhance their activity, charge separation efficiency, and stability [57]. To improve hydrogen production efficiency, a sacrificial agent is often added to the system. Sacrificial agents, such as methanol, ethanol, or sodium sulfide (Na_2S), act as electron donors, preventing the recombination of photogenerated electrons and holes. This ensures that the electrons can effectively reduce protons (H^+) in the water to generate hydrogen gas, while the sacrificial agent is oxidized by the holes [58].

2.8.4 Gas Collection and Measurement

Gas collection is a vital aspect of the experimental setup, enabling accurate measurement of the amount of hydrogen produced. One of the simplest methods for gas collection is water displacement, where the evolved gases are captured in an inverted graduated cylinder or burette submerged in water. As hydrogen gas is produced, it displaces the water in the

cylinder, allowing for quantification of the gas volume. More sophisticated setups employ gas chromatography (GC) to analyze the composition and purity of the evolved gases. GC allows for precise determination of the hydrogen-to-oxygen ratio and the detection of any impurities, ensuring that the photocatalytic process is proceeding efficiently. Additionally, pressure sensors and mass flow meters can be used to monitor the rate of gas evolution in real-time, providing valuable data on the kinetics of hydrogen production [59].

2.8.5 Monitoring and Control Systems

To ensure accurate and reproducible results, the testing setup for photocatalytic water splitting often includes monitoring and control systems. A potentiostat may be employed to monitor the electrochemical parameters of the system, such as potential and current. For photoelectrochemical water splitting, where an external bias is applied to the system, the potentiostat controls the applied voltage and measures the photocurrent generated by the photocatalyst under illumination. Furthermore, temperature control is essential in photocatalytic experiments, as temperature variations can significantly influence reaction kinetics. Thermocouples or temperature sensors are used to monitor the reaction temperature, ensuring that it remains constant throughout the experiment. In some cases, a water bath or cooling system is used to maintain the temperature within a desired range, preventing overheating and degradation of the photocatalyst [60].

2.8.6 Data Acquisition and Analysis

Accurate data acquisition is critical for evaluating the performance of photocatalysts in water-splitting reactions. Real-time monitoring of gas evolution, light intensity, and reaction conditions allows researchers to assess the efficiency and stability of the photocatalyst. Data logging systems, often integrated with computer software, record all relevant parameters such as gas volume, light intensity, temperature, and electrochemical signals. Post-experiment analysis typically involves calculating the apparent quantum efficiency (AQE) and the solar-to-hydrogen (STH) efficiency of the photocatalytic system. These metrics are essential for comparing the performance of different photocatalysts and optimizing the system for higher hydrogen production yields [61]. Overall, the testing setup for photocatalytic water splitting is a complex but essential part of hydrogen production research. By combining controlled light sources, efficient photocatalysts, and precise measurement tools, researchers can

systematically evaluate and improve the photocatalytic systems designed for sustainable hydrogen generation.

2.9 Testing Setup for Organic Degradation

Organic degradation testing is commonly used to evaluate the efficiency of catalysts in breaking down organic pollutants in water, such as dyes, pharmaceuticals, and other industrial chemicals. The typical testing setup for organic degradation experiments involves a reactor, an organic pollutant solution, a catalyst, a light source (for photocatalytic degradation), and instruments to measure the concentration of organic pollutants over time. For photocatalytic organic degradation, a common setup includes a photoreactor with a quartz window to allow light penetration, ensuring efficient interaction between the catalyst and the light source. The reactor contains an aqueous solution of the organic pollutant, typically at concentrations ranging from 10 to 100 mg/L. The catalyst, such as TiO₂, ZnO, or doped metal oxides, is suspended in the solution. UV or visible light, depending on the catalytic material, is used to activate the photocatalyst [61].

The light source in photocatalytic systems is usually a mercury lamp, xenon arc lamp, or a solar simulator, depending on the specific wavelength required to excite the photocatalyst. The intensity and duration of light exposure are carefully controlled to study the degradation kinetics of the organic pollutants. The reactor can either be a batch reactor, where the reaction occurs in a single batch of solution, or a continuous flow reactor, where the polluted water continuously flows through the system [62]. Analytical techniques such as UV-visible spectroscopy and high-performance liquid chromatography (HPLC) are often employed to monitor the concentration of organic pollutants in the solution. UV-visible spectroscopy allows for real-time monitoring of the absorbance changes of the pollutant at characteristic wavelengths, while HPLC provides more detailed information on the degradation products and intermediates [63]. The effectiveness of the catalyst is evaluated based on the degradation efficiency, which is calculated by comparing the initial and final concentrations of the pollutant. Kinetic studies are also performed to determine the rate constants and reaction mechanisms involved in the degradation process. Advanced setups may also include instruments for measuring the chemical oxygen demand (COD) and total organic carbon (TOC), which provide additional insights into the degree of organic degradation achieved by

the catalyst [64]. The testing setup for organic degradation is essential for understanding the catalytic properties of materials and their potential application in environmental remediation. Through systematic experimentation, researchers can optimize catalyst performance and develop more effective systems for the removal of harmful organic compounds from water [65].

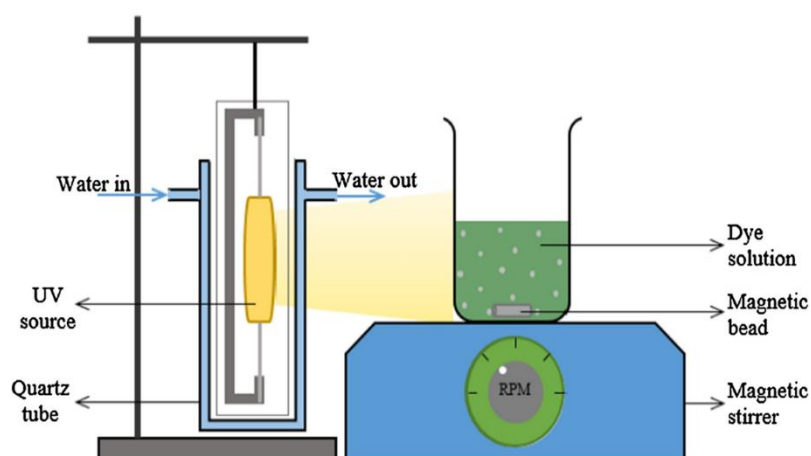


Fig 2.6 Organic dye degradation setup

2.9 Characterization Equipment

Characterization techniques are crucial in catalysis research to gain insights into the physical and chemical properties of catalysts, which directly affect their performance. Each technique serves a unique purpose and provides specific information about the catalyst's structure, morphology, surface area, and electronic properties. This section outlines the purpose, working principle, and application of several commonly used characterization techniques in catalysis, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electron microscopy, surface area measurements (BET), UV-visible spectroscopy (DRS), gas chromatography-mass spectrometry (GC-MS), and photoluminescence spectroscopy (PL).

2.9.1 X-Ray Powder Diffraction (XRD)

X-ray diffraction (XRD) is employed to determine the crystal structure, phase composition, and crystallite size of catalysts. It provides essential information about the arrangement of atoms in a material, the presence of different crystalline phases, and the level of crystallinity. In catalysis, understanding these structural properties is critical for correlating the catalyst's

performance with its crystalline form and identifying the active phases responsible for catalytic activity.

XRD is based on the diffraction of X-rays by the periodic atomic planes in a crystal. When a crystalline material is irradiated with X-rays, these rays are scattered by the atoms in the crystal lattice. If the scattering satisfies Bragg's law,

$$n\lambda=2d\sin\theta$$

where λ is the X-ray wavelength, d is the distance between atomic planes, and θ is the angle of incidence, the scattered waves interfere constructively, producing a diffraction pattern [66].

This pattern is characteristic of the crystal structure and can be analyzed to identify the material's phase and determine lattice parameters. XRD is widely used to identify the phases present in a catalyst, such as different metal oxides, sulfides, or zeolites. This is crucial because the catalytic properties often depend on the specific phases. For instance, different phases of titania (anatase, rutile) or alumina (gamma, alpha) exhibit different catalytic behaviors. XRD can also provide information about the crystallite size through peak broadening analysis using the Scherrer equation. In heterogeneous catalysis, smaller crystallite sizes can enhance the catalytic activity by increasing the available surface area for reactions [67].

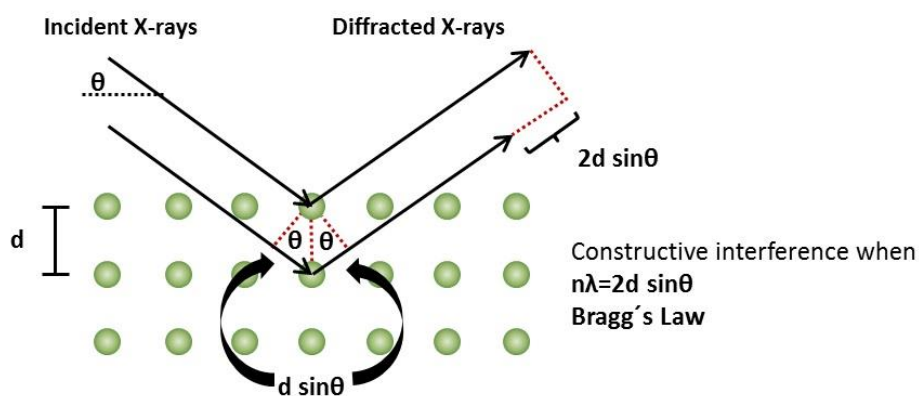


Fig 2.7 X-ray diffraction working principle

2.9.2 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is primarily used to analyze the surface chemistry of catalysts. It provides information on the elemental composition, oxidation states, and chemical bonding environments of atoms at the surface of the material. Since catalysis often

occurs at the surface of the catalyst, XPS is invaluable for understanding how surface properties, such as the presence of active sites, influence catalytic performance.

XPS works by irradiating a sample with X-rays, which causes the ejection of core-level electrons from the atoms in the sample. The kinetic energy of these ejected electrons is measured, and their binding energy is calculated using the equation

$$E_b = h\nu - E_k$$

where $h\nu$ is the photon energy, and E_k is the kinetic energy of the electron. The binding energy is unique to each element and its oxidation state, allowing the identification of elements and their chemical environments at the surface [68].

XPS is used to investigate the surface composition of catalysts, including the oxidation states of metal centers, the presence of dopants, and the surface coverage of adsorbed species such as oxygen, hydrogen, or carbon species. For example, in metal-supported catalysts, XPS can distinguish between metallic and oxidized forms of the metal, which is critical for understanding redox reactions in catalysis. In catalysts such as palladium or platinum, the oxidation state of the metal influences its catalytic behavior in reactions like hydrogenation or oxidation [69].

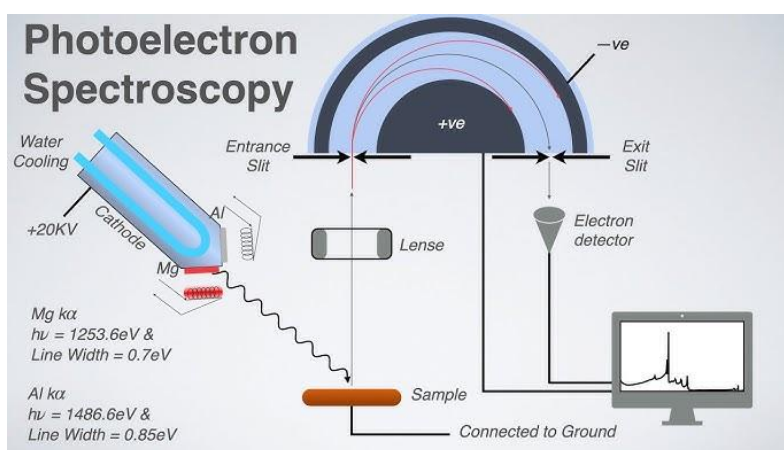


Fig 2.8 XPS working principle

2.9.3 Electron Microscopy (SEM and TEM)

Electron microscopy is used to visualize the morphology, size, and distribution of catalyst particles. It provides high-resolution images that reveal the surface texture, shape, and

internal structure of catalysts. This is important for optimizing catalyst design, as properties such as particle size and distribution significantly affect catalytic performance.

SEM: Scanning electron microscopy (SEM) involves scanning a focused electron beam across the surface of a sample. The interaction between the electron beam and the surface atoms generates signals (secondary and backscattered electrons) that are used to create detailed images of the sample's surface morphology [70].

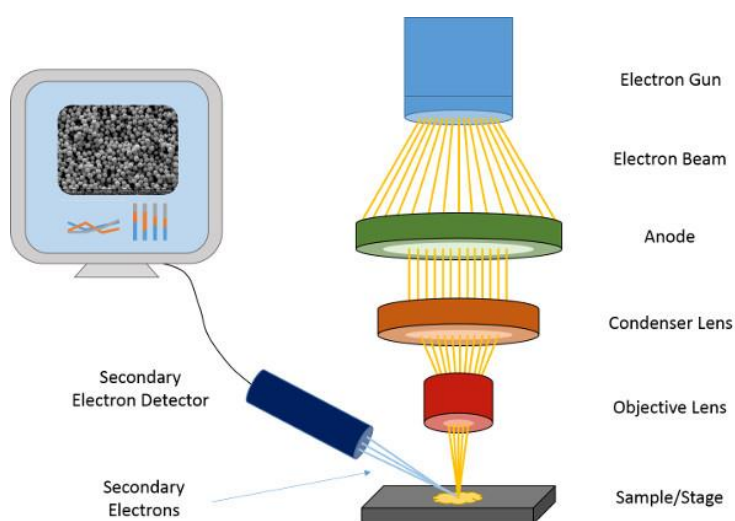


Fig 2.9 SEM Working principle

TEM: Transmission electron microscopy (TEM) involves passing a high-energy electron beam through an ultrathin sample. The electrons that pass through the sample are used to form an image, revealing the internal structure at the atomic level. TEM can also provide diffraction patterns, which offer information about the crystallinity and orientation of particles [71].

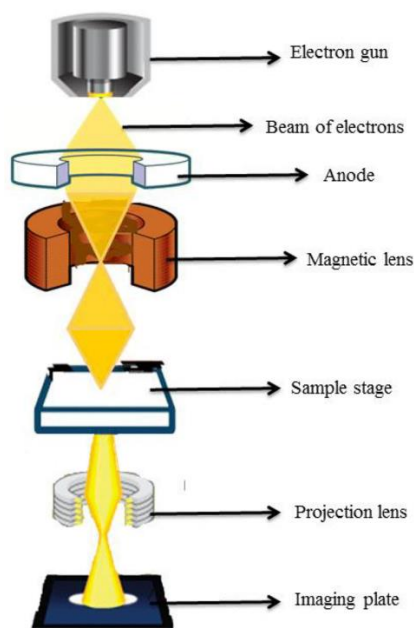


Fig 2.10 Working principle of TEM

SEM is commonly used to study the surface morphology of catalysts, including the size and shape of nanoparticles or porous structures. For instance, SEM can be used to examine the distribution of metal nanoparticles on a support material, which affects the availability of active sites for catalysis. TEM, particularly high-resolution TEM (HRTEM), is used to investigate the internal structure of nanoparticles, the presence of defects, and the interfaces between different phases in composite catalysts. These structural insights help in optimizing the synthesis process to achieve better dispersion of active sites and enhanced catalytic efficiency [71].

2.9.4 Surface Area Measurements (BET)

The Brunauer-Emmett-Teller (BET) method is used to determine the specific surface area and porosity of catalysts. The surface area is a key factor in catalysis, as a higher surface area generally provides more active sites for catalytic reactions, leading to increased efficiency. The BET method measures the amount of gas (usually nitrogen) adsorbed onto the surface of a material at cryogenic temperatures. The amount of gas adsorbed at different pressures is used to construct an adsorption isotherm, which can be analyzed using the BET equation to calculate the specific surface area. The pore size distribution and total pore volume can also be derived from the adsorption-desorption isotherm [72]. BET surface area measurements are crucial for characterizing porous catalysts such as zeolites, metal-organic frameworks (MOFs),

and activated carbons. Catalysts with a high surface area provide more active sites for reactants to adsorb and react, improving their catalytic performance. For example, in hydrodesulfurization (HDS) catalysts, the surface area and pore structure determine the accessibility of reactants to active metal sites, influencing the overall reaction rate [73].

2.9.5 UV-VIS Spectroscopy (DRS)

UV-visible diffuse reflectance spectroscopy (DRS) is used to investigate the optical properties of catalysts, including their light absorption characteristics and electronic transitions. This technique is especially useful for studying catalysts that are involved in light-driven processes or those with electronic transitions relevant to their catalytic activity.

In DRS, a beam of light is directed at the surface of a powdered sample, and the reflected light is collected. The diffuse reflectance is converted into absorption data, which can be analyzed to determine the material's electronic band structure, including its bandgap energy for semiconductors or ligand-field transitions for metal complexes [74].

UV-visible spectroscopy is commonly used to study metal oxides, metal nanoparticles, and metal complexes that act as catalysts. For instance, DRS can determine the bandgap energy of semiconductor catalysts, which is important for photocatalytic reactions. In non-photocatalytic systems, UV-visible spectroscopy can monitor changes in the oxidation states of transition metals during catalytic cycles, providing insights into redox processes [75].

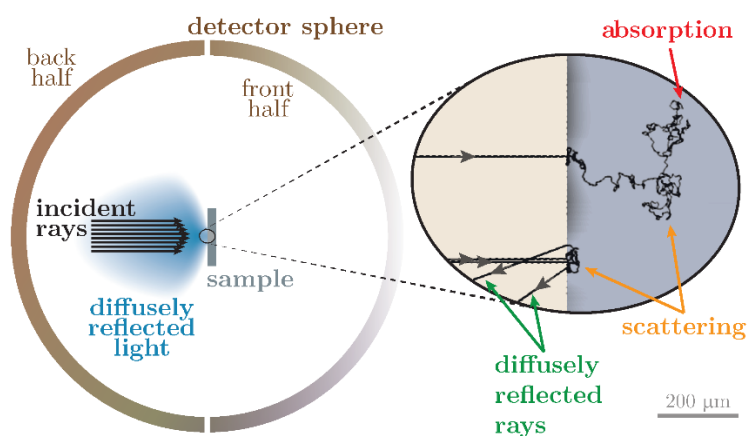


Fig 2.11 UV DRS spectroscopy

2.9.6 Gas Chromatography-Mass Spectrometry (GC-MS)

Gas chromatography-mass spectrometry (GC-MS) is used to separate, identify, and quantify the products of catalytic reactions. It is particularly valuable in studying reaction mechanisms, conversion rates, and selectivity in gas-phase or liquid-phase catalytic processes.

GC separates the components of a mixture based on their volatility and interaction with the stationary phase in the GC column. Once separated, the compounds enter the mass spectrometer, where they are ionized and fragmented. The resulting ions are detected based on their mass-to-charge ratio, providing structural information about the molecules [76].

GC-MS is widely used in catalysis to analyze reaction products, particularly in processes such as hydrocarbon reforming, Fischer-Tropsch synthesis, and oxidation reactions. By identifying and quantifying the products, researchers can determine the efficiency of the catalyst, the selectivity toward desired products, and any by-products formed during the reaction. This information is crucial for optimizing reaction conditions and catalyst composition [77].

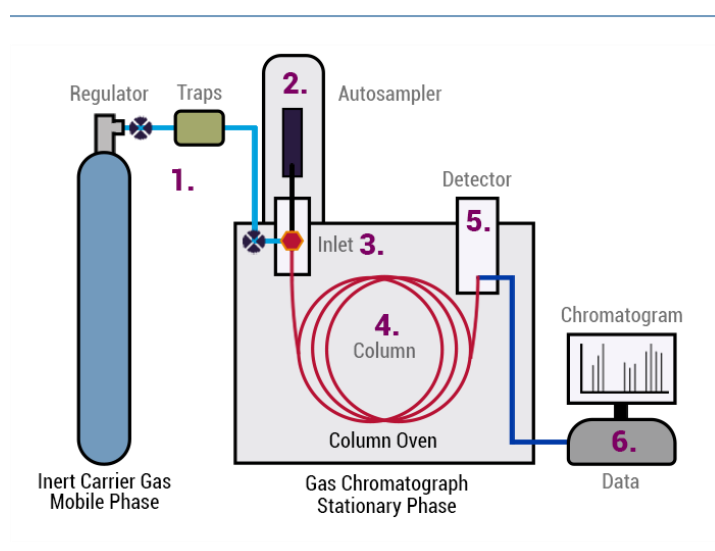


Fig 2.12 GC working principle

2.9.7 Photoluminescence Spectroscopy (PL)

Photoluminescence (PL) spectroscopy is used to study the electronic structure and defects within catalysts. It provides insights into the recombination of charge carriers (electrons and holes) and the presence of defects or impurities that can influence catalytic performance, especially in semiconductors and metal complexes.

In PL spectroscopy, a material is excited by a light source, which promotes electrons from the ground state to an excited state. As the electrons relax back to the ground state, they emit light.

The wavelength and intensity of the emitted light provide information about the energy levels, defects, and recombination processes within the material [78].

PL spectroscopy is particularly useful in studying catalysts that rely on electronic transitions, such as semiconductors. For example, in metal oxide catalysts, PL can reveal the efficiency of charge carrier separation, which is important for redox reactions. A lower PL intensity indicates fewer recombination events, suggesting more efficient charge separation and higher catalytic activity. PL is also used to study the impact of doping or surface modifications on the electronic properties of catalysts [79].

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Chapter 3: Production and characterization of Cobalt ferrite nanoparticles by means of a Spinning Disk Reactor

3.1 Abstract

Cobalt ferrite (CoFe_2O_4) nanoparticles have gained significant attention in recent years due to their unique magnetic and catalytic properties, making them promising candidates in environmental remediation. In this work the synthesis of CoFe_2O_4 nanoparticles was performed via co-precipitation method at room temperature by means of a Spinning Disk Reactor (SDR). The obtained results were benchmarked against the same obtained by using a conventional Stirred Tank Reactor (STR) in terms of crystallinity, particle size, particle size distribution, surface area, and magnetization efficiency. Along with that, the photocatalytic degradation capacity of the obtained product toward the organic dye methylene blue under UV and Visible light irradiation was also investigated. UV and visible light photocatalytic efficiency of the SDR and STR nanoparticles were 98.7% and 88% respectively and it degraded the methylene blue dye in 120 min. Moreover, the photocatalyst was tested for multiple cycles to check photocatalyst stability and recyclability.

3.2 Introduction

In the last decades, interest for photocatalytic degradation of organic pollutants in wastewater and groundwater by means of the use of semiconductor compounds has increased much becoming one of the most promising green chemistry technologies available to tackle water decontamination; in particular, visible-light-induced photocatalysts which are capable to use solar energy and reaching interesting efficiency values. This result may be achieved by employing transition-metal ferrite nanoparticles, that are metal oxides with a spinel structure, consisting of two different metal cations bonded together to oxygen atoms. This structure exhibits unique magnetic and electric properties, making the material available for biomedical, solar cell and catalysis use [1]. Due to their biocompatibility and catalytic properties, Cobalt ferrite nanoparticles (CFO) are attracting considerable attention when used as a photocatalytic material. Moreover, the excellent magnetic properties of this material allow the recovery and reuse of the same by magnetic traps with ease and without significant loss of their catalytic efficiency [2]. The synthesis of CFO may be performed in several ways, such as by hydrothermal method [3], by sol-gel method [4], by micro-emulsion [5] or by thermal decomposition [6]. The main drawback of these techniques is the use of an extended amount of organic and toxic solvents or surfactants, representing an environmental hazard during their production process leading also to high production costs. The development of a green, cheap, fast and reproducible method for the preparation of industrial amounts of single-phase ferrite nanoparticles is therefore welcome [7]. An alternative technique might be the co-precipitation of the metal hydroxides from their precursor salts solution, characterized by a short reaction time at low reaction temperature. Key parameters for the outcome of the reaction are the reaction temperature, the mixing conditions and pH of the reactants. A good control on these parameters appears to be essential to achieve controlled sized nanoparticles production.

In the last years, the spinning disk reactor (SDR) technology was used and validated as a profitable equipment, capable of intensifying the continuous production monodispersed nanoparticles of controllable size with a reduced energy consumption and productivity rates interesting to industrial purpose [8]. Indeed, the same equipment was successfully used to produce many different nanomaterials such as titanium dioxide [9], silver [10] and

hydroxyapatite [11] nanoparticles. On the disk it was observed that micromixing conditions and residence time are critical parameters to achieve the production of nanoparticles, since they have a direct impact on both nucleation and crystal growth kinetics, respectively [12]. A high micro mixing condition leads to the formation and a local distribution of supersaturation conditions in the medium, capable to trigger the nucleation process of crystallites; a smaller residence time do not allow following crystal growth, keeping the crystallites small in size [13] [11]. The SDR is indeed capable to achieve high micro mixing conditions connected to very small residence time values, making the production of nanoparticles by precipitation possible [14].

In this work, a SDR was used to produce Cobalt ferrite nanoparticles (CFO) by adopting a co-precipitation method at room temperature. The obtained results were compared to those obtained by means of a conventional stirred tank reactor (STR), in terms of crystallinity, particle size, particle size distribution, surface area and magnetization efficiency. At the end, the produced material was checked towards a photocatalytic removal of methylene blue under UV and Visible light conditions for many cycles, thus validating the overall approach.

3.3 Materials And Methods

Cobalt ferrite nanoparticles (CFO) were synthesized by co-precipitation method without the use of surfactants. All the reagents for the synthesis were supplied by Sigma Aldrich and were of analytical grade: iron (III) nitrate nonahydrate (99.9 % purity), Cobalt (II) nitrate hexahydrate (99.8 % purity) and sodium hydroxide (pellets, 98% purity). All the aqueous solutions were prepared by adopting milli-Q water.

Metal precursors including iron (III) nitrate (Fe^{3+}), and Cobalt (II) nitrate (Co^{2+}) with the Fe^{3+} : Co^{2+} molar ratio of 2 : 1 were solubilized in 50 mL of water and stirred for 30 minutes at room temperature. Parallel to this, a 3 M NaOH solution was prepared by dissolving 3 g of NaOH pellet in 25 mL of water.

A scheme of the used SDR for the production of CFO nanoparticles is reported in Fig. 1. The equipment mainly consists of a rotating disk of 15 cm in diameter over which two or more reagent streams may be injected. Injectors are of 1 mm in diameter and are placed at a distance of 1.5 cm from the disk surface. The flow rate of reagents as well as the position of the injectors

on the disk, intended as radial distance from the disk center can be fixed. Operation of the SDR requires additionally to fix the angular velocity of the disk.

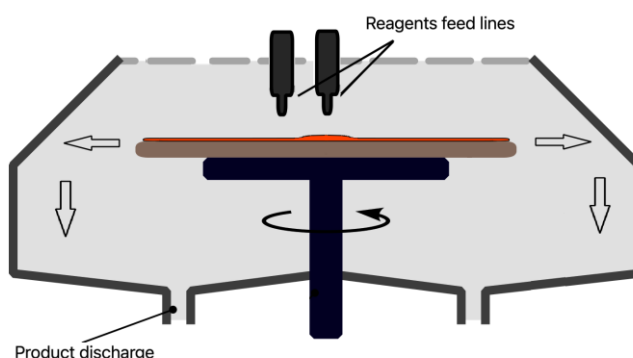


Fig 3.1 A scheme of the adopted spinning disk reactor.

The liquid composing the thin film will travel from the center towards the outer border of the disk and finally leave the surface due to centrifugal forces. Around the rotating disk a vessel collects the liquid precipitate which reaches the bottom of the reactor and exits continuously through the product discharged pipe [15]

In this work the precipitation process was performed at room temperature. On the surface of the rotating disk the metal ions solution and the sodium hydroxide solution were injected respectively at the center of the disk and at a radial distance of 3.5 cm from it. Two injectors of 1 mm in diameter were used for this purpose. The distance of the two inlet streams (r) was set equal to 3.5 cm, according to the optimal values found in a previous work [16]. The simultaneous injection of the two solutions was performed by means of two peristaltic pumps with a fixed flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$ and $25 \text{ mL}\cdot\text{min}^{-1}$ for the metal ions solution and NaOH solution, respectively. The rotational speed (ω) was fixed to $125 \text{ rad}\cdot\text{sec}^{-1}$.

After the precipitation reaction in the SDR a solid brown suspension was harvested from the bottom of the vessel and washed three times with a distilled water - ethanol mixture to remove any excess of alkaline or unreacted metal ions. Before washing, typical pH values of the suspension were equal to 12 ± 0.2 . After washing, neutrality was reached. Finally, the solid precipitate was separated by centrifuge and freeze dried overnight until a solid was obtained. The obtained powder was grinded and calcined at 450°C for 2 h, cooled to room temperature

and collected for analysis. The powdered samples of CFO nanoparticles were characterized and used for subsequent photocatalytic studies.

To validate the SDR approach as a process intensified technique to produce CFO nanoparticles, a STR consisting of a 250 mL capacity round bottom flask was employed at room temperature. The same reaction mixture adopted for the SDR was placed in the vessel and agitated by a 3-blade propeller impeller of 4 cm diameter placed about 2 cm from the bottom of the vessel. The NaOH solution was added to the reactor with a flow rate of 25 mL·min⁻¹ by means of an injector connected to a peristaltic pump positioned above the metal ions solution surface. All the STR experiments were carried out by adopting a mixing speed value equal to 1200 rpm.

After precipitation, the solid brown suspension was kept under constant stirring for 30 minutes to promote the dispersion of the particles and only then harvested for washing, calcination and characterization, by adopting the same procedures used with the SDR produced CFO nanoparticles.

3.4 Characterization

A wide-angle X-ray diffractometer, XRD, (D8 Discover, Bruker) was used to investigate the crystalline structures of the magnetic nanoparticles. The CuK-alpha radiation source and a Lynxeye XE detector, employed at 40 kV/40 mA. The diffractometer was fitted with the Bragg-Brentano geometry, the graphite monochromator and the diffracted beam, and operated at a scan rate of 2°/min and a step size of 0.7 ° 2θ. Each sample was dried and grinded to obtain a fine powder before each measurement.

The FT-IR spectra of the magnetic nanoparticles was measured adopting a Fourier transform infrared spectrometer (Spectrum 3, PerkinElmer) and using potassium bromide (KBr) as a background material. To prepare the sample, 1 mg of powder was mixed and grinded together with 199 mg of KBr. After this, the mixture powder was put into a mold and then compressed by a hydraulic pressure machine. The spectra of the obtained pellets were measured by adopting a wavenumber range between 650 cm⁻¹ to 4000 cm⁻¹.

Transmission electron microscopy (TEM) images and X-ray energy dispersive (EDX) elemental maps were acquired on an FEI Tecnai-Osiris instrument at 200 kV. Samples were

prepared by depositing one drop of the ethanol solution containing the nanoparticles on the surface of carbon-coated copper grids.

A scanning electron microscope, SEM, (Zeiss, MERLIN) was used to have a look at the morphological structure of the magnetic nanoparticles. Each sample was coated with a 5 nm layer of gold : palladium (80 : 20) alloy. The images were obtained at an acceleration voltage of 3 kV, resulting in magnification capabilities from 150,000 X to 200,000 X.

The EDX analysis and the determination of the atomic percentages of Cobalt ferrite nanoparticles was recorded by using X-Max 50mm² detector (Oxford Instruments) integrated into the SEM (MERLIN). Each sample was coated with a thin layer of carbon.

X-Ray Photoelectron Spectroscopy (XPS) measurements were carried out using a PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany). Analysis was performed using a monochromatic Al K α X-ray source of 24.8 W power with a beam size of 100 μ m. Samples were spread on FTO (Fluorine-doped Tin Oxide) glass before analysis.

A vibrating sample magnetometer, VSM, (Microsense model EZ-7) was employed to measure the saturated magnetization (Ms), and coercivity (Hc) of the Cobalt ferrite nanoparticles. The measurements were taken under a magnetic field strength of 10,000 Gauss at room temperature.

UV-vis absorption spectra in diffuse reflectance and transmittance were obtained using a PerkinElmer UV-Vis Spectrometer. The diffuse reflectance was collected by depositing the powders within quartz slides and the Kubelka-Munk function was applied to the raw data to eliminate scattering.

For Brunauer-Emmett-Teller (BET) analysis, nitrogen adsorption-desorption isotherms at 77 K were performed on a BELSORP mini (BEL Japan, Inc.) apparatus. Prior the measurements, samples were activated at 200 °C for 12 h under dynamic vacuum. The BET surface areas were estimated from the amount of N₂ adsorbed via the Brunauer-Emmett-Teller (BET) equation.

3.5 Photocatalytic Experiment

The CFO nanoparticles were tested for photodegradation of a methylene blue solution under UV and visible light generated by a 280 W Xe lamp provided with a 420 nm cutoff filter in the visible region. In a typical experiment, 7.5 mg of sample were added to the methylene blue solution (20 mL, 20 ppm) and stirred under dark conditions for 30 minutes to achieve absorption–desorption equilibrium by means of a propeller stirrer before starting the photocatalytic reaction. In a second step 10 mmol L⁻¹ of 30% H₂O₂ solution were added to the above solution. The concentration of the catalyst, of the organic dye as well as the H₂O₂ were optimized according to previous works reported in the literature [17]. At regular time intervals, 0.3 mL of the solution was sampled and centrifuged to remove the suspended solid particles. The clear supernatant was then used for UV-Vis spectra determination of methylene blue concentration at $\lambda = 664$ nm, by UV–vis spectrophotometry. The photocatalytic stability of CFO samples was performed for 4 subsequent cycles, by recovering the catalyst back from the bulk by means of a permanent magnet trap.

3.6 Results And Discussion

The XRD patterns of the CFO nanoparticles exiting the SDR (a) and the conventional STR (b) are reported both in Fig. 2. The patterns of both samples show major characteristic peaks at (1 1 1), (2 2 0), (3 1 1), (4 0 0), (5 1 1), and (4 4 0), corresponding to a cubic spinel structure [18]. The diffraction peaks of the CFO nanoparticles appear to perfectly match with the reference (JCPDS card no. 10–0325). However, the STR-derived sample shows some additional peaks if compared to standard data, probably due to the formation of included impurities such as hematite (Fe₂O₃) [19].

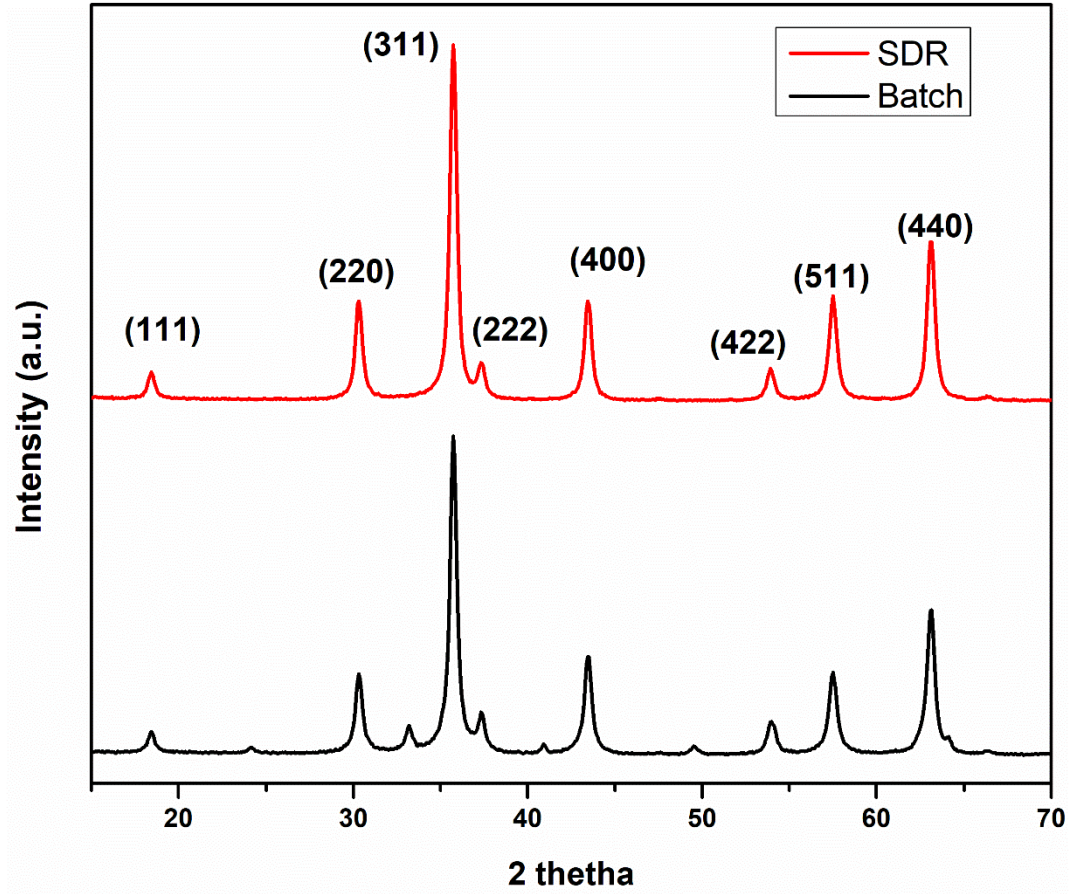


Fig 3.2 XRD Patterns of CoFe_2O_4 nanoparticles produced by SDR and batch (STR).

The crystallite size of CFO nanoparticle was calculated using the Debye-Scherrer equation [1]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad [1]$$

where D (nm) is the crystallite size, λ is the wavelength of $\text{Cu K}\alpha$ radiation, β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg angle [20]. The mean crystallite size for CFO nanoparticles was found to be 12.4 nm and 15.1 nm for the sample produced by SDR and STR, respectively.

To further investigate the surface composition and oxidation state of as-prepared CFO nanoparticles products, XPS experiments were carried out, as reported in Fig. 3 (a–d). Since XPS spectra for both samples produced by SDR and STR are very similar, in this work only the CFO produced by the SDR is shown. The XPS survey spectrum (Fig. 3a) exhibited characteristic peaks corresponding to the core levels of elements present in the CFO

nanoparticles. The survey scan covered a binding energy range from 0 to 1200 eV, allowing for the simultaneous detection of multiple elements without any impurities present in the sample. Peaks representing Cobalt (Co 2p), iron (Fe 2p), and oxygen (O 1s) were observed, confirming the expected chemical composition of the CFO nanoparticles.

The Co 2p core level spectrum displayed two prominent peaks at binding energies of 780.5 eV and 796.3 eV, corresponding to the Co 2p_{3/2} and Co 2p_{1/2} spin-orbit states, respectively. The observed binding energies are characteristic of Co²⁺ oxidation state [18]. Additionally, the appearance of satellite peaks at approximately 786.7 eV and 804.1 eV in the Co 2p region further supports the presence of strong electron correlation effects in the CFO nanoparticles [21]. The presence of well-resolved satellite peaks in the obtained spectra indicates a developed crystallinity and high purity of the CoFe₂O₄ nanoparticles. In the Fe 2p core level spectrum, two discernible peaks were observed at binding energies of 711 eV and 724 eV, corresponding to the Fe 2p_{3/2} and Fe 2p_{1/2} spin-orbit states, respectively. These binding energy values are consistent with Fe³⁺ oxidation state [22]. The observation of Fe³⁺ oxidation state in the Fe 2p spectrum confirms the expected chemical composition of CFO nanoparticles with spinel structure. The O 1s core level spectrum revealed three distinct peaks at binding energies of 529.7 eV and 532.2 eV. These peaks represent different oxygen species on the surface of the nanoparticles. The peak at 529.7 eV can be attributed to lattice oxygen, while the peaks at 532.2 eV are associated with surface hydroxyl group [23]. The presence of multiple oxygen peaks indicates the heterogeneous nature of the oxide surface, suggesting the potential involvement of oxygen vacancies, which can significantly influence the photocatalytic activity of the CFO nanoparticles.

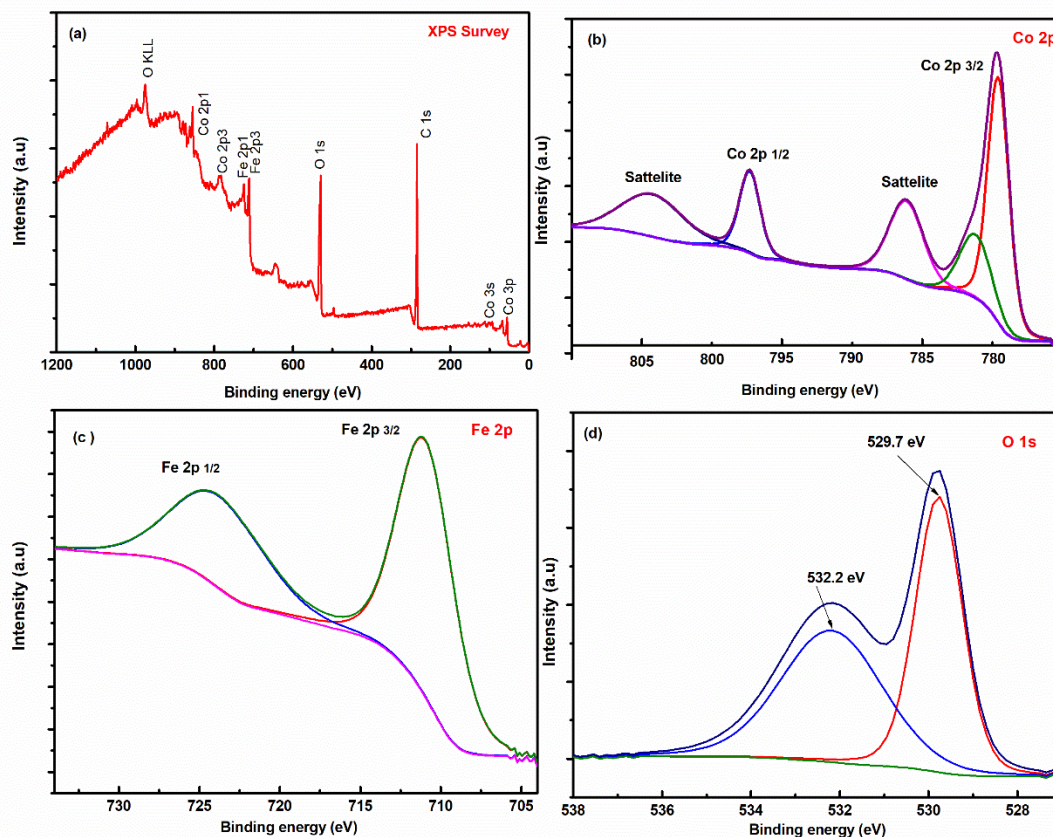


Fig 3. 3 XPS survey spectrum (a), Co 2p (b), Fe 2p (c) and O 1s (d) of CFO NPs.

FT-IR spectra analysis are used to explore the existed functional groups on the surface of the synthesized material. Figure 4 shows the Fourier-transform infrared (FTIR) spectra of CFO nanoparticles. Two distinct bands for metal-oxygen vibrations were observed in the range of 750–400 cm^{-1} for both the samples. The high-intensity band in the range of 750–500 cm^{-1} (ν_1) was attributed to the intrinsic stretching vibrations of the tetrahedral site-occupied metal-oxygen bond [$\text{M}^{2+}\text{tetra} \leftrightarrow \text{O}$]. The low-intensity band 450–400 cm^{-1} (ν_2) was due to the octahedral Fe^{3+} -oxygen stretching vibration [24]. The broad band centered at 3427 cm^{-1} and a low-intensity band centered at 1630 cm^{-1} were justified according to the stretching and bending mode of O–H bonds of physically adsorbed water molecules from humidity [25].

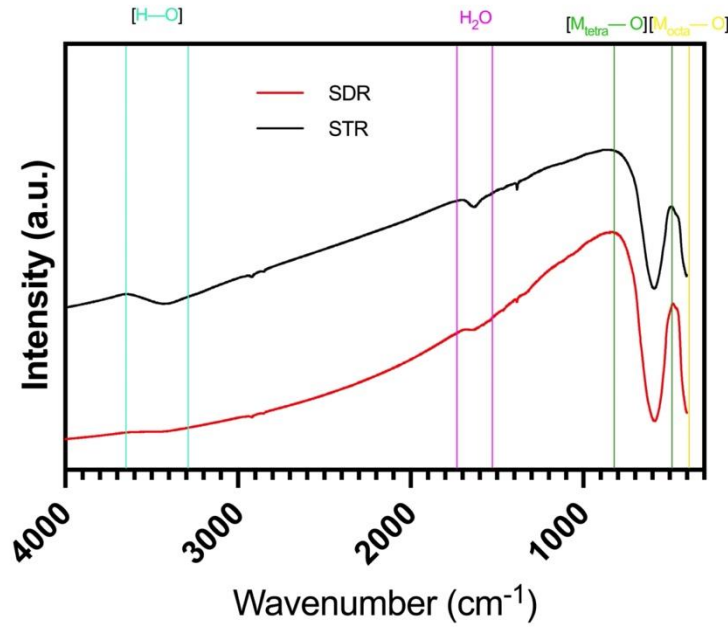
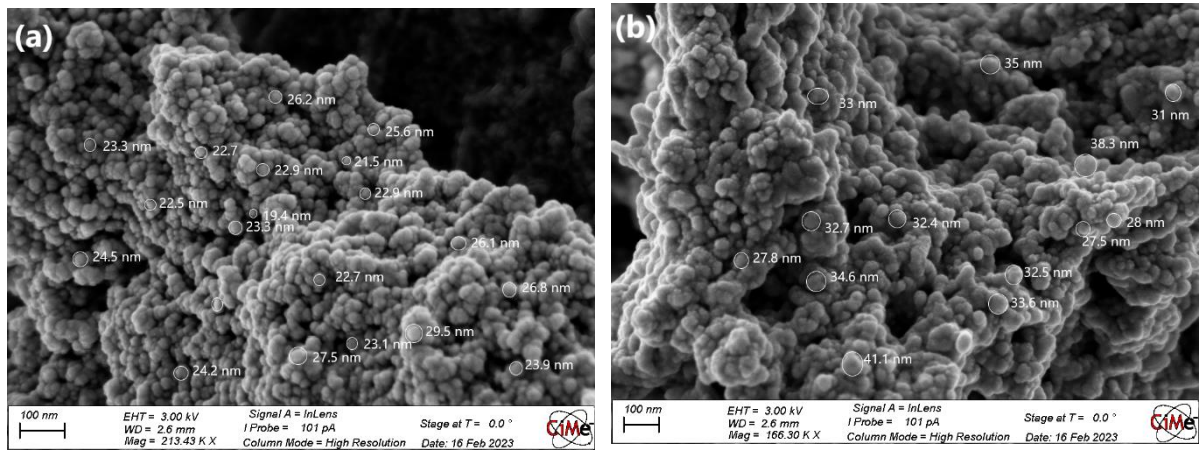


Fig 3. 4 FTIR spectrum of CFO nanoparticles.

The morphology of ferrite photocatalysts was characterized by scanning electron microscopy (SEM), and results are shown in Fig. 5. SEM micrographs showed agglomerated grains with a coral-like morphology. The particle size was observed to be around 23.5 ± 4.5 nm and 32.5 ± 14 nm for SDR and STR respectively. The STR particles are more agglomerated and bigger in



size than SDR. Along with that, the particle size distribution for SDR method is very uniform compared to the STR.

Fig 3. 5 SEM Images of CFO by (a) SDR (b) STR.

The EDX analysis was used to determine the atomic percentages corresponding to the Co : Fe mole ratio of the CFO magnetic nanoparticles. The results in Table 1 show that the EDX experimental Co : Fe mole ratios of CFO nanoparticles produced by STR and SDR are equal to 1 : 1.9 and 1 : 2 , respectively. The calculated synthesis values of Co : Fe mole ratios is 0.5; thus, the EDX experimental values correspond to the theoretical ones. Moreover, EDX spectra confirm that there are no other elements or impurities present in the sample. The peaks of C observed in the EDX spectrum were due to the coating at the time of SEM analysis for better visibility of the surface morphology. The 2D elemental mappings showed a uniform distribution of constituent elements in CFO, thus confirming the homogeneity of the photocatalyst, as shown in Figure 6.

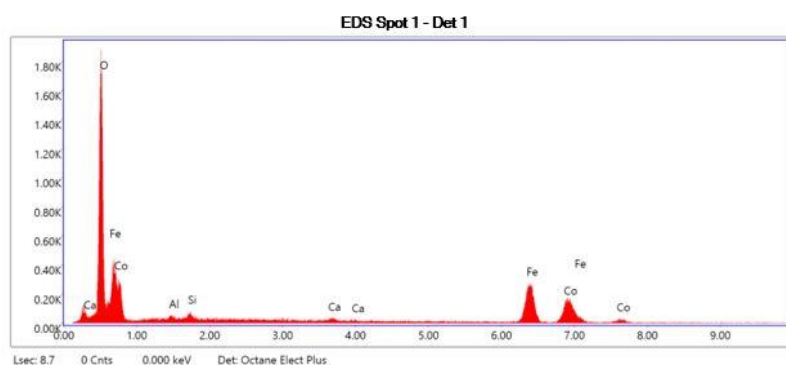


Fig 3. 6 EDS spectrum of CFO.

Table. 1. Atomic weight percentage of elements by EDS

SDR	STR	
Wt (%)	Wt (%)	Element
48.6	50.6	Fe
24.7	24.2	Co
26.5	25.1	O

The morphology, particles size and size distribution of ferrites was further investigated by transmission electron microscopy (TEM). The cubic crystallites can be observed from TEM

micrograph, which further supports the cubic shape estimated in XRD (Fig. 2). The obtained nanoparticles are polydisperse as could be seen from particle size distribution curves in Fig. 7 (a and b). This aspect can be observed by looking at the TEM images, with the particles produced by STR clearly form clusters.. The size distribution is estimated from several TEM images by counting at least 80 particles for each sample. The particles mean size was found to be equal to 23 ± 6 nm and 38.5 ± 25 nm for SDR and STR derived samples, respectively. The shape of the curve is, however, narrower for particles produced by means of the SDR compared to those produced by conventional stirred tank reactor. This indicates higher uniformity in the dimensions of the particles. The small variation in crystallite size among TEM and XRD analysis is because in XRD we estimate the spherical shape of crystals whereas, in TEM we directly visualize the crystals for analysis [26] .

The primary reason for this behavior may be due to the increased instabilities within the film on the disk surface that enhances micro mixing between the two reagents which aids in the production of uniformly high super saturation, causing nucleation of ferrite nanoparticles. The SDR does not increase supersaturation itself, as supersaturation and nucleation processes are independent of reactor geometry [27]. However, compared to the conventional STR, it does prevent high local supersaturation through effective mixing of the reagent streams flowing on the disc, thereby ensuring uniform supersaturation across the film layer. Within this near to uniform mixing environment more successful collisions between molecules can occur to form critical nucleus required for particle nucleation to take place, thus increasing nucleation rate in this way. An increase in nucleation rate means that supersaturation is consumed primarily by nucleation which contributes to the formation of reduced particle size [28]. In addition, the decrease in the residence time of the reactants on the disk surface leads to a reduction in the growth and agglomeration phase of the particles [29].

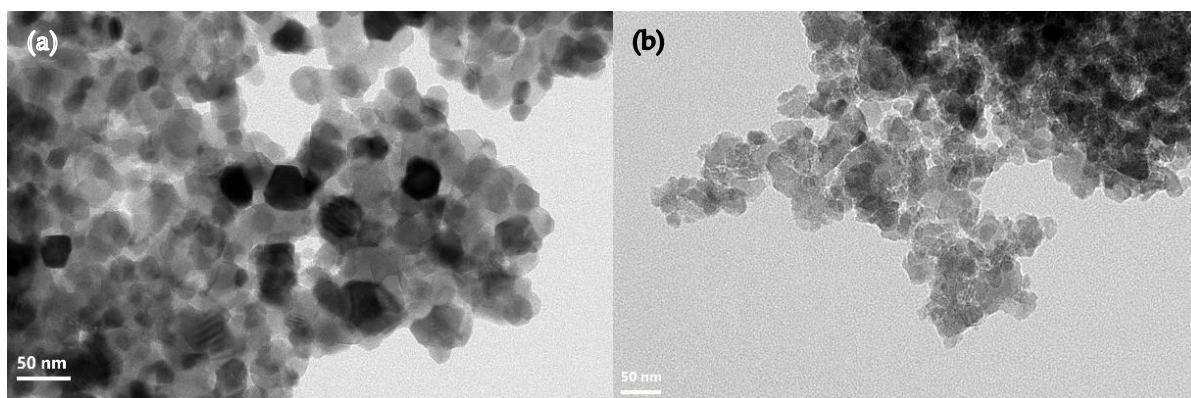


Fig 3.7 TEM image of CFO nanoparticles by SDR (a) and STR (b).

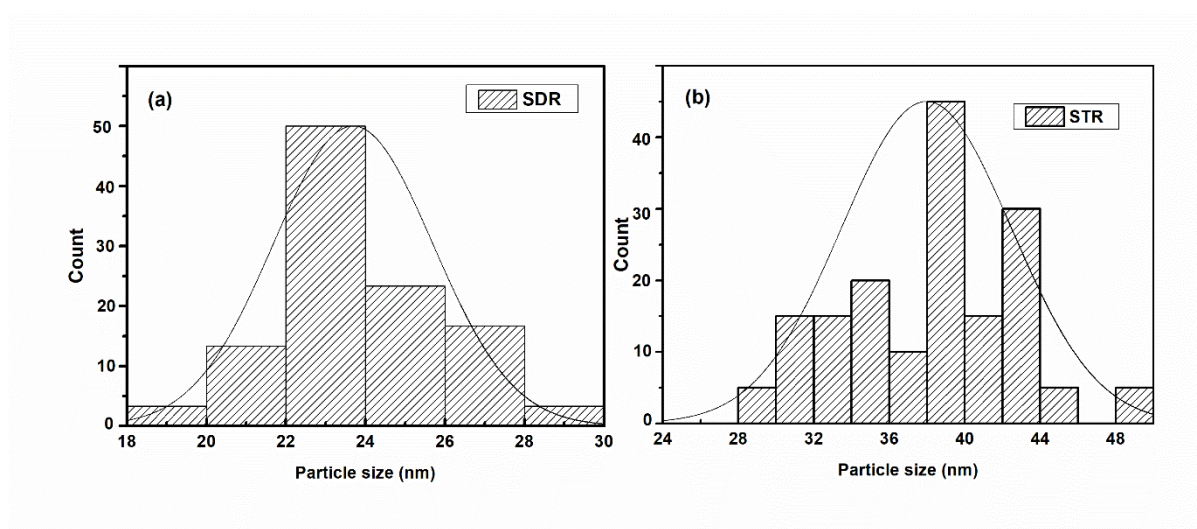


Fig 3.8 Particle size distribution charts of CFO nanoparticles for (a) SDR and (b) STR

Surface area properties

Since the photocatalytic activity of a catalyst depends, among others, on the size and surface area values of the photocatalyst, these parameters were measured by means of BET analysis. Figure 9 reports the obtained N₂ adsorption and desorption isotherms at 77 K of Cobalt ferrite nanocomposites produced by SDR and STR. The specific surface area (SSA), mean pore diameter, total pore volume of both Cobalt ferrite nanoparticles was measured, and the values are listed in Table 2.

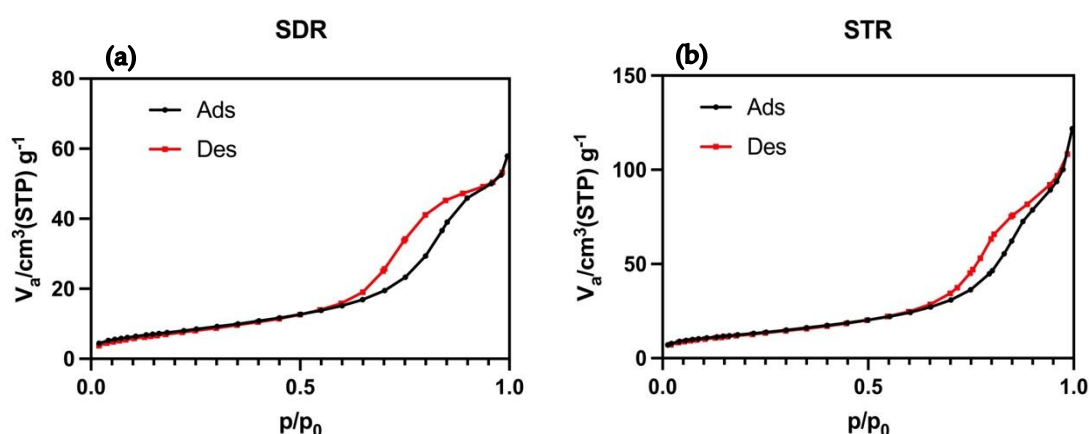


Fig 3.9 BET N₂ adsorption and desorption isotherms at 77 K for (a) SDR and (b) STR.

Table.2 BET surface area and porosity data for SDR and STR.

Sample	Surface area (m ² /g)	Mean pore diameter (nm)	Total pore volume (cm ³ g ⁻¹) ¹⁾
SDR	46.7	15.32	0.17
STR	29.0	11.94	0.08

From Table 2 it might be observed that the surface area of CFO nanoparticles obtained using SDR is higher (46.7 m²/g) compared to the STR, which is 29.0 m²/g. Additionally, the higher mean pore diameter of the CFO nanoparticles obtained by means of SDR will exhibit higher catalytic activity [30]. It is possible to observe that for both samples, the mean pore diameter is in the range of 0.4 to 50.0 nm, which is characteristic of micro- and a mesoporous materials [31] [32]. In this case, samples exhibit type IV N₂ adsorption-desorption isotherms with a hysteresis loop, confirming that they are mesoporous [28].

Magnetic characterization of the particles was performed by vibrating sample magnetometer (VSM) at room temperature (300 K) with maximum applied field up to 10 kOe. Figure 10 shows the M(H) loops of both samples at room temperature (300 K). From the graph, it is

possible to observe that both samples do not exhibit hysteresis with almost immeasurable remanence and coercivity, with values of coercivity (H_c) equal to 0.14 Oe and 0.01 Oe for the particles produced by STR and SDR, respectively. These values are a unique property of superparamagnetic materials [33]. Moreover, the saturation magnetization (M_s) values obtained at 10,000 Oe are equal to 25 emu/g and 21 emu/g for the particles produced by STR and SDR, respectively.

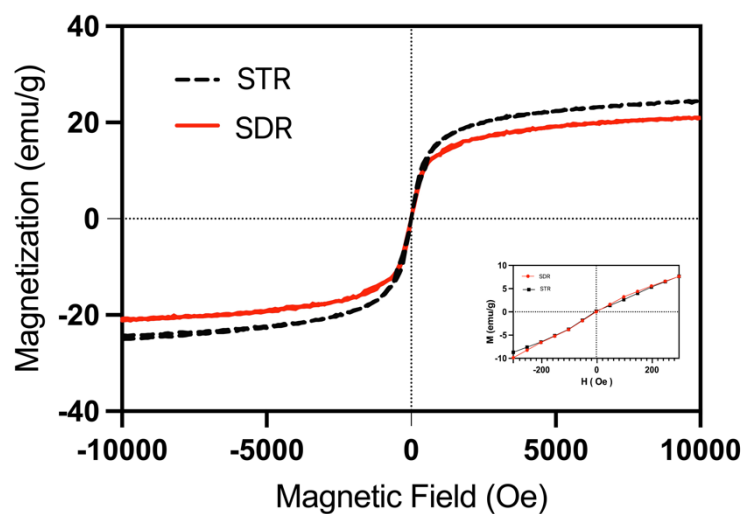


Fig 3.10 magnetic properties of the CFO nanoparticle for SDR and STR.

It is possible to observe that by decreasing the particle size, the saturated magnetization (M_s) has also decreased. This phenomenon can be justified by surface effects: as soon as the particle size decreases, their surface-to-volume ratio increases dramatically, leading to a larger proportion of atoms being located at the surface. The surface atoms may have different orientations compared to the atoms in the core of the particle leading to a lower net magnetization compared to larger particles where most atoms are in the core and have similar magnetic orientations [34] [35]. In both cases, the saturation magnetization (M_s) obtained at 10,000 Oe are much lower than bulk Co-ferrite (56 emu/g) [36].

Ultraviolet visible diffuse reflectance spectroscopy (UV-Vis DRS) analysis was performed to evaluate the optical properties of ferrite photocatalysts, and results have been reported in Figure 11.

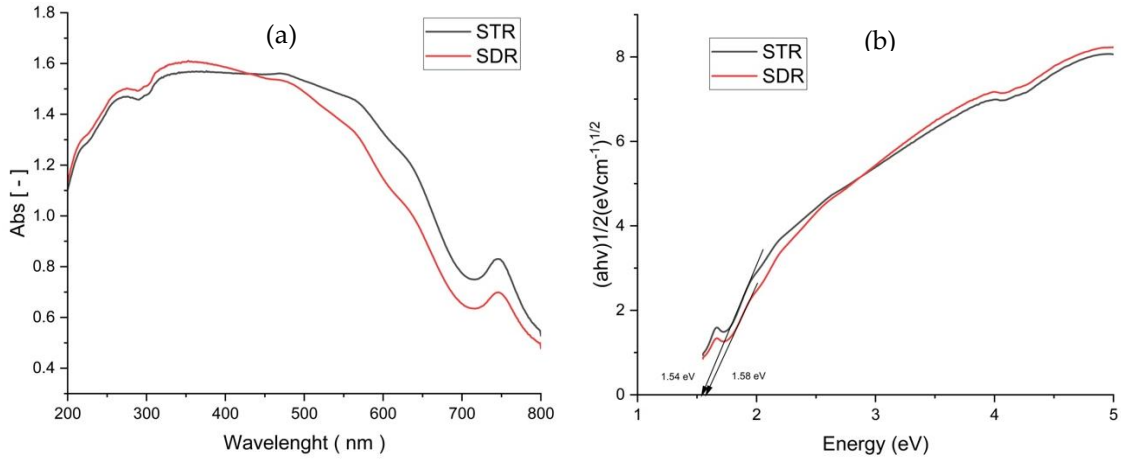


Fig 3.11 (a) UV-Vis absorption spectra (b) and calculated bandgaps of the CFO.

Cobalt ferrite exhibits a strong absorption band in the entire UV-Visible region. The optical direct band gap was calculated using equation [1] [37]:

$$(\alpha h\nu)^2 = B(h\nu - E_g) \quad [1]$$

where, α , ν , and B are absorption coefficient, light frequency, and the proportionality constant, respectively. The $(\alpha h\nu)^2$ versus $h\nu$ plots for ferrite photocatalysts have been shown in Figure 11 (b). The band gap calculated for CFO produced by SDR and STR was equal to 1.58 eV and 1.54 eV, respectively. The small difference in energy can be justified considering that energy band gap increases as particle size of the semiconductor nanomaterials decreases [36]. However, both values obtained correspond to those reported in the literature [38]. It is also clear from the absorbance and band gap graphs that the particles are excited by visible light. In order to evaluate the photocatalytic activity of the produced CFO nanoparticles, several tests on photodegradation of methylene blue (MB) under UV and visible light irradiation were carried out. The photocatalytic activity of the sample was also tested in absence of light irradiation (dark). For all the conditions, before each test the sample was kept under stirring for 30 minutes in the dark to minimize the effect of physical adsorption of the dye on the sample's surface. Each photocatalytic test was performed in triplicate. In the absence of photocatalyst, only 4% of dye degradation was observed with H_2O_2 and in the presence of UV-Vis light irradiation after 60 minutes of agitation. In the dark condition, less than 5 % of MB

dye was adsorbed on the surface of CFO NPs after 60 min of stirring. Therefore, it was evident that the contribution of adsorption in photocatalytic degradation of dye is minimal.

The photodegradation of the organic dye over CFO nanoparticles photocatalysts in presence of H_2O_2 is reported in Figure 12. It is evident that more than 98.7 % of MB dye was degraded within 120 minutes of irradiation over CFO photocatalysts under UV and visible light irradiation, while 88 % of the dye was removed during the same period of time in presence of

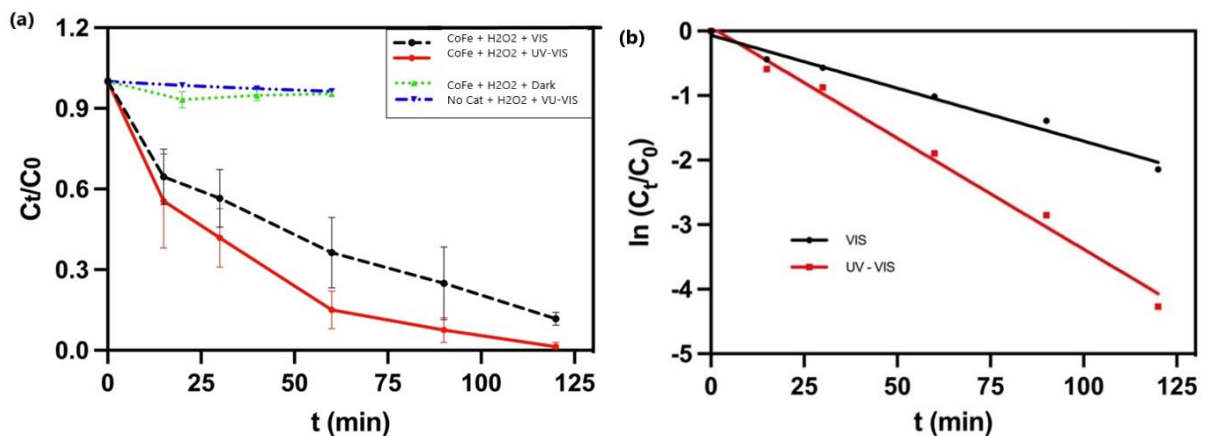


Fig 3.12 (a) Photocatalytic Degradation of MB (b) Kinetic linear model.

only visible light irradiation. This condition is due to the strong absorption band in the entire UV-Visible region (700 nm to 800 nm wavelength) as previously seen in Fig. 11 (a)

The photocatalytic degradation of MB follows a pseudo-first-order kinetic model equation [2]:
(43):

$$\ln(C_t/C_0) = -kt \quad [2]$$

$$t_{1/2} = 0.693/k \quad [3]$$

where C_0 and C_t are the MB concentration at time $t = 0$ and time ' t ', respectively, and $t_{1/2}$ is the half-life of the dye degradation. The slope of the $\ln(C_t/C_0)$ versus t plot is the apparent rate constant for the reaction (k). From Fig. 12 (b), the calculated k value was 2.18 min^{-1} and 1.23 min^{-1} for UV-Vis and visible light conditions, respectively. The kinetic rate of degradation for ferrite photocatalysts in this study was found like those reported in the literature [39].

Due to their magnetic behavior, the possibility of recover and recycle the photocatalyst by using a magnetic trap was investigated. From Fig. 3. 13, it can be seen that the MB still can be degraded up to 87 % and 85 % under UV and UV-Vis light irradiation after three cycles, which suggests that the CFO nanoparticles have a good photostability [40]. All the separations after photocatalytic reaction were taken out with the help of a permanent magnet [41].

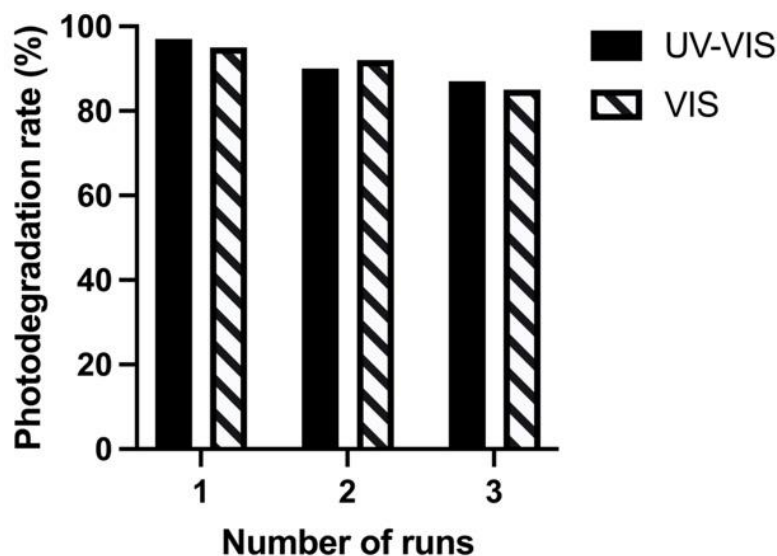


Fig 3.13 Recyclability test of CFO nanoparticles in UV-Vis and visible light.

3.7 Conclusion

The present study investigated the production and application of Cobalt ferrite nanoparticles synthesized by means of a SDR and a conventional STR using a co-precipitation method at room temperature, respectively. A comprehensive comparison was performed between the product outcome of the two reactor systems based on some key properties such as crystallinity, particle size, particle size distribution, surface area and magnetization efficiency. The CFO nanoparticles synthesized by means of the SDR method exhibits advantages including smaller mean particles size (approximately 23.5 ± 6 nm against 38.5 ± 25 nm for those obtained by means of the STR) and a narrower size distribution along with a substantially higher surface area ($46.7 \text{ m}^2/\text{g}$ compared to $29.0 \text{ m}^2/\text{g}$ for STR); thus indicating an enhanced catalytic potential. Despite slightly lower saturation magnetization levels, justified by finite size effects, the CFO nanoparticles synthesized by means of the SDR method also exhibited

encouraging catalytic attributes. Looking at photocatalytic activities, a remarkable performance in degrading methylene blue was observed. Under UV and visible light irradiation, degradation levels of 98.7% and 88% within 120 minutes were observed for the CFO produced by means of the SDR and the STR, respectively. Moreover, the observed photo activity is maintained on reuse of the material: and appears to be stable after three cycles, the nanoparticles provided up to 87% and 85% methylene blue degradation under UV and UV-Vis light irradiation, respectively. The observed performance of the developed material appears to qualify the produced CFO by means of the proposed production process as a promising material for pollutant degradation in wastewater streams.

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Chapter 4: Synthesis of Ag-decorated g-C₃N₄ and NiFe-LDH heterostructure photocatalyst using spinning disc reactor for process intensification

4.1 Abstract

The use of semiconductor materials in photocatalysis has drawn a lot of interest because of their potential to harness renewable solar energy to solve environmental and clean energy challenges. An important obstacle in practical applications is the development of a highly effective photocatalyst that operates efficiently under solar radiation. An optimal semiconductor photocatalyst should possess environmentally favourable characteristics, low cost, stability, and band edges that are well suited for the desired reaction and positioned appropriately to efficiently absorb visible light, thereby harnessing the primary component of the solar spectrum. A binary Z-scheme g-C₃N₄@NiFe-LDH heterostructure photocatalyst has been prepared in this study. Well-dispersed g-C₃N₄ nanosheets were loaded on the surface of a NiFe-LDH precursor using a unique method involving precipitation and a spinning disc reactor for the preparation of the catalyst. Next, the photocatalyst that was synthesized was decorated with Ag nanoparticles using a photoreduction process. The nanocomposites were thoroughly characterized using SEM, EDX, TEM, XRD, XPS and N₂ adsorption-desorption methods to determine their morphological structure, optical properties and surface area. Then it was tested for the photocatalytic degradation of RhB dye. The photocatalytic degradation tests demonstrated that the Ag-decorated g-C₃N₄@NiFe-LDH nanocomposites exhibited a maximum degradation efficiency of 99% for Rhodamine B dye within 240 min under visible light irradiation. This was accompanied by a corresponding pseudo-first-order reaction. The improved effectiveness of the photocatalysis may be mainly due to the fast transfer of charges at the Ag/LDH/ g-C₃N₄ interface and the surface plasmon resonance of the Ag nanoparticles. These factors boost the separation efficiency of the charge carriers produced by light and increase its absorption. The results of this research will provide novel perspectives for the fabrication and development of highly effective photocatalysts that can be powered by visible light.

Keywords: LDH, Z-scheme photocatalyst, Photocatalysis,

4.2 Introduction

An insufficient supply of energy and environmental management have always been a prominent concern worldwide [1]. Photocatalytic technology has become a prominent solution to utilize plentiful and sustainable solar energy, offering it an excellent solution to global environmental and energy concerns [2], [3]. In contrast, several methods are limited to the accumulation of harmful chemicals present in wastewater and are unable to fully break them down. These methods include physical adsorption, filtration, and solvent extraction procedures [4]. Photocatalytic technology, characterized by its cost-effectiveness and simplicity, has the potential to prevent secondary pollution [5]. Common photocatalysts, such as TiO_2 , Fe_2O_3 , CdS , and ZnO , can effectively degrade and oxidize organic pollutants and heavy metals. Additionally, they have potential uses in processes such as carbon dioxide reduction, water splitting and nitrogen fixation [6][7][8]. An essential obstacle that must be addressed to achieve the practical implementation of photocatalysis is the development of a highly efficient photocatalyst that effectively operates under solar radiation. An optimal semiconductor photocatalyst for practical applications should possess the following characteristics: environmental friendliness, affordability, stability, appropriate band edges for the desired reaction, along with precise positioning for absorbing visible light, which is the primary component of the solar spectrum [9][10]. For instance, Layered double hydroxides (LDHs), due to their unique layered structures, have garnered significant interest in the field of photocatalysis [11]. LDHs are clay-like substances composed of layers of metal hydroxides with positive charges that are interspersed with layers of anions. Photocatalysts have garnered considerable interest owing to their potential to degrade organic pollutants because of their distinctive characteristics, including adjustable composition, interlayer exchange, strong chemical stability, straightforward synthesis, and simple structural modification [12], [13]. LDH exhibit versatility in their chemical composition and structural morphology, including a large surface area, the ability to exchange interlayer anions, and the basic nature of surface hydroxyl groups. The characteristics of LDH make them a desirable option for semiconductor photocatalysts, especially in tasks such as photocatalytic water splitting and the breakdown of environmental contaminants [14], [15]. Although LDHs provide several

benefits, they encounter some obstacles, such as limited photocatalytic activity and rapid recombination of electron-hole pairs when exposed to visible light. These issues may be linked to their bandgap energy and low surface area [16], [17].

To address this difficulty, researchers have investigated many approaches, including the introduction of transition metal ions, use of semiconductor quantum dots as a protective layer, and their combination with other photocatalysts as a heterojunction. The photocatalytic performance of individual hydrotalcite materials falls short of anticipated outcomes. As a result of this motivation, researcher decided to create a composite photocatalyst by integrating LDH with other semiconductor materials with layered structure, such as metal-free polymeric graphitic carbon nitride and g-C₃N₄ (CN). CN has a suitable bandgap (2.70 eV) and can absorb light in the visible spectrum [18]–[20]. CN has gained recognition as a very stable and cost-effective photocatalyst with a broad light absorption spectrum, nontoxic properties, and easy functionalization [21], [22]. Its porous structure and high surface area provide a large active surface area for catalytic processes, which improves photocatalytic activity. Significant progress has been made in the utilization of CN-based catalysts for various applications, such as decontamination of polluted water [23], reduction of CO₂ by photoreaction [24], water splitting [25], and the production of solar fuel [26]. Despite its potential, the photocatalytic activity of g-C₃N₄ is hindered by its low surface area, poor light quantum utilization, and rapid recombination of photogenerated electron-hole pairs. To address these limitations, combining two distinct semiconductors, especially 2D layered structures that align properly in terms of band-edge potentials, has emerged as a highly promising strategy. This method aims to improve photocatalytic efficiency by preventing the recombination of photogenerated charge carriers. Therefore, creating a heterojunction photocatalyst is the optimal approach for boosting its photocatalytic capabilities, as stated by several study groups [27]–[30]. The advantages of layered composite photocatalysts encouraged us to create analogous layered composites by combining CN with other stacked semiconductor materials, such as LDHs, which have previously been documented by several researchers [31]–[34]. LDHs are good candidates for coupling with CN because of their layered structures, which are comparable to those of CN.

Furthermore, LDHs are characterized by their variable chemical composition, basicity of the

surface hydroxyl groups, and responsiveness to visible light. The integration of CN and LDHs with comparable layered structures is anticipated to combine their advantages, resulting in composites with improved photocatalytic capabilities [35], [36]. Alok et al. [37] used the co-precipitation approach to synthesise Zn-Al LDH with graphitic carbon nitride nanosheets in order to facilitate the photocatalytic breakdown of Phenol. The study showed that a photocatalyst consisting of 70% ZnAl LDH/ g-C₃N₄ exhibited the best efficiency among the other photocatalysts tested. A degradation efficiency of 79.35% was achieved over a period of 300 min. In addition, the surface area of the photocatalyst exceeded those of the other photocatalysts. Furthermore, a separate research team led by Yazdani et al. [38] successfully created a new type of photocatalyst film by synthesizing a graphitic carbon nitride g-C₃N₄-NiTi-layered double hydroxide heterojunction (g-C₃N₄-NiTi-LDH) using a simple hydrothermal synthesis method. The film was tested against methylene orange (MO) dye. The photocatalytic activity of the g-C₃N₄-NiTi-LDH film was superior to that of g-C₃N₄ and NiTi-LDH films. The g-C₃N₄-NiTi-LDH films attained a maximum MO degrading efficiency of 100% during a time frame of 240 minutes.

In addition, doping with metal nanoparticles is a technique used to increase the efficiency of heterojunction systems, such as Au, Pt, Ag, and Pd, in photocatalysis. Of all noble metals, silver (Ag) stands out as an appealing option owing to its affordability and impressive LSPR properties. The addition of Ag NPs to photocatalysts increases their capacity to absorb visible light, assists in the production of more reactive species and enhances the charge carriers' separation. These effects contribute to the increased performance of the photocatalyst in terms of its ability to initiate and drive photocatalytic reactions [39], [40]. The efficiency of catalysts in absorbing visible light has been shown to improve due to the local surface plasmon resonance (LSPR) phenomena associated with noble metals [41]. This study included the synthesis of a heterojunction nanocomposite consisting of NiFe-LDH/ g-C₃N₄ with the addition of Ag nanoparticles. This was achieved using a unique spinning disc reactor method that has capability of scale up and intensification. The developed catalyst was evaluated for its ability to degrade Rhodamine B dye via photocatalysis. Several methods including FT-IR, XRD, TEM, SEM, EDX, UV-vis DRS, XPS, BET, and PL were used for thoroughly characterizing the resulting materials. Furthermore, the kinetics of the reaction were thoroughly examined and the long-term stability of the photocatalyst was assessed using

cyclic testing.

4.3 Materials and methods

Ammonium fluoride (NH_4F , 98%), melamine (99%), sodium carbonate (Na_2CO_3 , 99.8%), sodium hydroxide (NaOH , 98%), and triethanolamine (TEOA, 99%) were acquired from Sigma–Aldrich. Merck provided CTAB, AgNO_3 , Fe (III) nitrate nanohydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%) and Ni (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%). Since all other reagents used in the study were of analytical grade, there was no need for further purification.

4.4 Synthesis of the materials

4.4.1 Graphitic Carbon nitride nanosheets (CN) Photocatalyst

Graphitic carbon nitride powder was synthesized using thermal polymerization. A ceramic crucible was used to hold 10.0 g of melamine, which was then placed in a muffle furnace and heated to a temperature of 550 °C at a rate of 4°C/min for a duration of 4 h. Subsequently, the collected samples were subjected to air cooling and grinding and designated as bulk g- C_3N_4 . The g- C_3N_4 nanosheets were prepared by adding bulk yellow g- C_3N_4 powder to a solution of 2 M Nitric acid, followed by calcination at 500 °C for 2 h at a heating rate of 5 °C/min. Ultimately, the product produced was g- C_3N_4 (CN) powder, which had a light-yellow color.

4.4.2 Synthesis of NiFe-LDH (NF)

A spinning disc reactor at ambient temperature was used for the synthesis of NiFe-LDH. The molar ratio of Ni/Fe used was 5.0. The metal precursors used in this study were iron (III) nitrate (Fe^{3+}) and nickel (II) nitrate (Ni^{2+}). A Fe^{3+} : Ni^{2+} molar ratio of 5:1 was dissolved in water (25 mL). The metal ion solution was combined with 25 ml of a 0.2 mM CTAB solution (0.1 g) in separate containers. Prior to the addition of the metal ion solution, the surfactant was dissolved in water and agitated for 15 min at room temperature to create micelles. Solution A, which consisted of a final combination solution of 50 mL, was agitated continuously at room temperature for an additional 10 min. Concurrently, a 3 M NaOH solution was created by dissolving 3 g of NaOH pellet in 25 ml of water, referred to as solution B.

A schematic of the spinning disc reactor (SDR) used for the synthesis of nano-sized NF particles is shown in Figure 1. The apparatus primarily comprises a 15 cm diameter revolving

disc onto which two or more reagent streams may be inserted. The injectors had a diameter of 1 mm and were positioned 1.5 cm apart from the disc surface. The flow rate of the reagents and radial distance of the injectors from the center of the disc may be set to a preset value. To operate SDR, it is necessary to stabilize the angular velocity of the disc. The liquid constituting the thin film migrates radially from the center to the periphery of the disc and ultimately disengages from the surface as a result of centrifugal forces. A vessel was positioned around the revolving disc to collect liquid that reached the bottom of the reactor. The liquid then leaves constantly through the discharged pipe. In this experiment, two solutions were injected simultaneously using two peristaltic pumps. The Solution A and Solution B were injected at constant flow rates of 100 mL/min and 30 mL/min, respectively.

The rotational speed (ω) in the experiment was set at a constant value of 125 rad/s (1200 rpm). Following precipitation in the SDR, a brown suspension was collected from the lower part of the vessel. The resultant mixture, which consisted of a brownish precipitate, was vigorously agitated for 30 min at ambient temperature. Subsequently, the combined solution was transferred to a 20 mL Teflon-lined autoclave and heated to 120 °C for 6 h. The obtained precipitate was filtered and repeatedly washed with distilled water and ethanol to remove any residual soluble ions until the pH of the wash liquid stabilized at 7. After washing the sediment, it was dried overnight in an oven at 80 °C. Subsequently, for further experimental use the sediment was ground to a fine powder.

4.4.3 Synthesis of g-C₃N₄/NiFe-LDH (CNNF)

The same conditions and methods used to prepare the NF were employed in this experiment. However, in this case, we introduced a suitable quantity of CN into the beaker containing solution A and then subjected it to ultrasonication for 1 h to achieve full dispersion of CN within solution A. Then the CN suspension was added to the salt solution before adding to SDR for reaction. Subsequently, the same protocol was implemented, mirroring that of NF. The slurry in this instance had a yellowish-brown color. Following washing with water and ethanol, the samples were dried and designated as CNNF.

4.4.4 Synthesis of Ag/ g-C₃N₄/NiFe-LDH (ACNNF):

Light deposition was used to deposit the surface of the CNNF with Ag nanoparticles. CNNFs

(0.4 g) were added to a mixture of 200 ml of deionized water and methanol. The mixture was then agitated for 30 min. Subsequently, 1 ml of AgNO_3 (1 M) was added. The resulting solution was exposed to a 500-watt Xenon lamp for 30 min. The brown solution was repeatedly rinsed with deionized water and then placed in an oven at 50 °C to obtain the ternary product ACNNF.

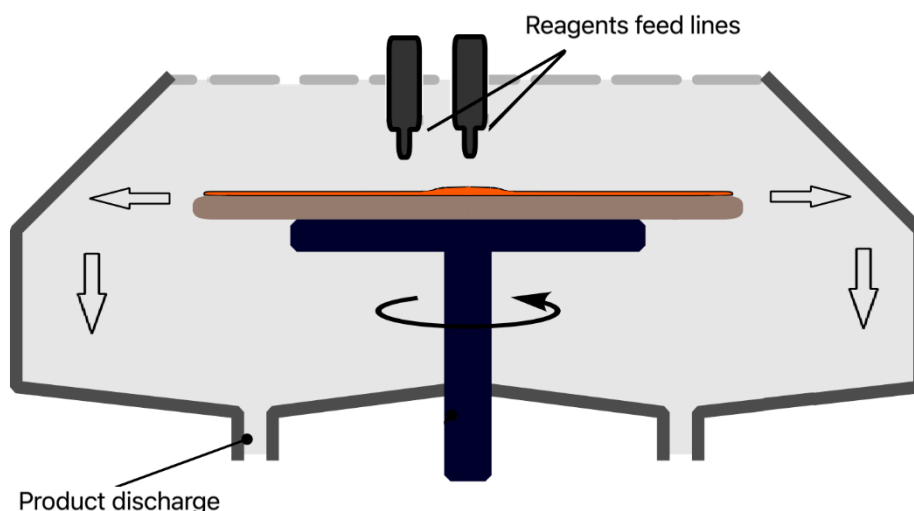


Fig 4. 1 Schematic diagram of Scanning disc reactor

Fig 4. 2 Schematic diagram of Scanning disc reactor

4.5 Characterization

The sample morphology was investigated using TEM (model JEM-2100F, JEOL) and field emission SEM (model JWSM-7001F from JEOL). The equipment was operated at 200 kV. For TEM analysis, the samples were dispersed in ethanol and drop-cast on a 400 mesh Cu TEM grid coated with holey carbon. The elemental composition was assessed using energy-dispersive X-ray spectroscopy (EDX) integrated with a TEM system. XRD was employed to analyse the crystal structure using a Bruker D8 diffractometer with $\text{Cu K}\alpha$ radiation having a wavelength of 1.54 Å. The surface area, pore volume, and pore size of the samples were characterized using nitrogen (N_2) adsorption-desorption isotherms with a Brunauer-Emmett-Teller (BET) analysis on an ASAP 2020 Micrometrics analyzer, a device for automated

micropore and chemisorption physisorption analysis. The pore size distributions were calculated from the adsorption isotherms using the Barrett-Joyner-Halenda (BJH) method. Prior to the measurements, the samples were degassed at 100 °C. The surface chemical states were examined by X-ray photoelectron spectroscopy (XPS) using a Thermo Fisher ESCALAB 250Xi spectrometer. The spectrometer was equipped with a monochromic Al-K α X-ray source and had a pass energy of 1486.6 eV. Using ultraviolet photoelectron spectroscopy (UPS) with an excitation energy of 21.22 eV, the work functions were verified using the same instrument. The UV-vis diffuse reflectance spectra (DRS) were obtained using a Cary 4000 UV-vis spectrophotometer, with BaSO₄ serving as the reflectance reference.

4.6 Photocatalytic activity

Additionally, a lab-made photochemical reactor was used to investigate the photocatalytic degradation performance of the synthesized nanocomposites and other reference materials. For the standard experiment, to a solution containing 50 mL of RhB, 50 mg of the catalyst was added. The mixture was stirred in the dark. Prior to addition of the visible light, a state of adsorption-desorption equilibrium may be attained during a duration of 40 min. Subsequently, photocatalytic degradation experiments were carried out at 25 °C using xenon lamps with a power output of 500 W and a wavelength range of more than 420 nm. During each interval of the experiment, approximately three mL of the reaction solution was collected by filtering out the powdered nanoparticles. The filtrate was analysed using ultraviolet spectrophotometry. The relative change in the concentration (C_t/C_0) was estimated by measuring the absorbance of the sampled solutions. The absorbance was measured at a maximum absorption wavelength of 464 nm. The term " C_0 " refers to the concentration of the reactant before it is exposed to light, whereas " C_t " represents the concentration of the reactant after a certain amount of time " t " has passed after illumination.

4.7 Results and discussion

4.7.1 Morphology and structural analysis

Figure 2 shows the X-ray diffraction (XRD) patterns of the samples. The image clearly shows that all samples exhibit two distinct diffraction peaks (at 27.6 and 13.2°) corresponding to

graphitic carbon nitride, except for the NF sample, which consists of bare NiFe LDH. The peak at 27.6° exhibits a distinct arrangement of layers in the conjugated aromatic system (plane 002), whereas the peak at 13.2° corresponds to the repeating structural unit (100), as shown by JCPDS card no. 87-1526. The diffraction peaks for the uncoated LDH were detected at 11.7° , 23.5° , 34.4° , 38.8° , and 60.1° , which corresponding to the (003), (006), (009), (012), and (110) planes, respectively, based on the reference (JCPDS card no. 38-0715). By observing the composite samples (fig 2c and 2d), it is evident that the diffraction peaks of both the materials coexist. Furthermore, it is evident that the CN peak at 27.4° has undergone shift to 27.2° . Additionally, in the sample with Ag doping, the distinctive peaks exhibit a little decrease in intensity, perhaps attributed to alterations in the anions that are incorporated inside the LDH layer. In addition, the absence of a discernible peak for Ag indicated that the Ag concentration was insufficient.

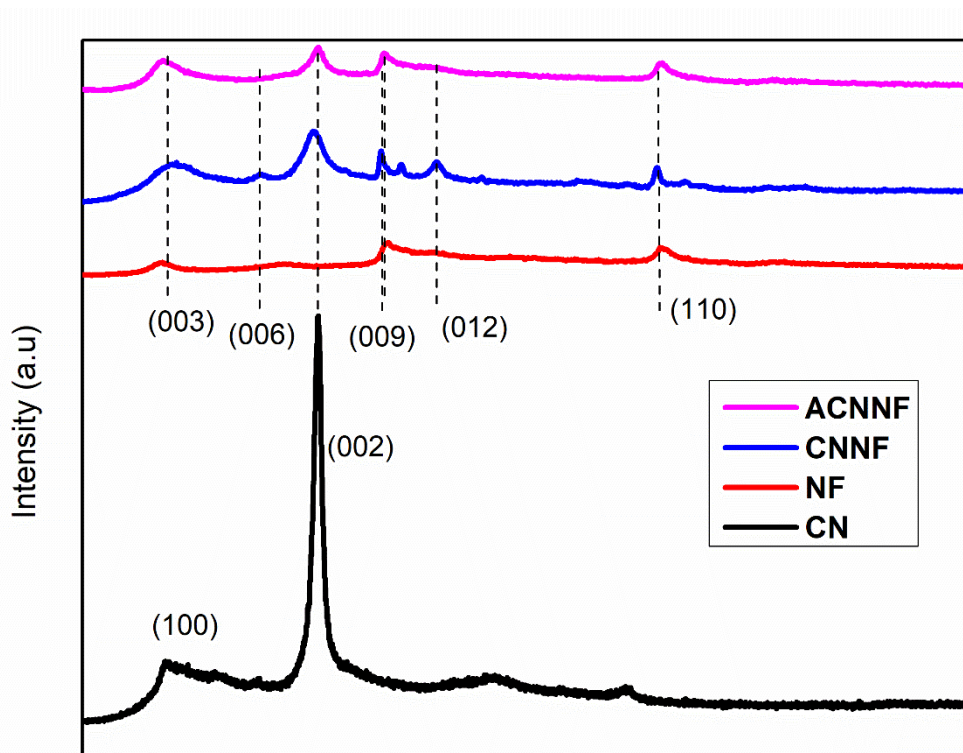


Fig 4.3 XRD pattern of the Samples

Fig 4.4 XRD pattern of the Samples

The surface morphologies of the samples were examined by SEM. SEM analysis of the CN, LDH, and composite photocatalyst samples provided useful information about their morphological features and the influence of Ag doping on the material. CN analysis, as shown

in Fig. 3a, reveals a 2D sheet-like structure with an uneven orientation in the SEM image. This indicated that the CN nanosheets were successfully separated from their bulk form by ultrasonic exfoliation. This discovery is consistent with prior research that has shown the creation of CN nanosheets using ultrasonication [42]. The 2D planar structure of CN provides an advantage by promoting the effective separation of charge carriers created by light, hence improving the ability of the material to catalyse chemical reactions using light energy. The scanning electron microscope (SEM) image of the Ni-Al LDH (Fig. 3b) displays a structure with a three-dimensional flower-like shape, consisting of self-assembled nanoflakes. The distinctive three-dimensional configuration provides a significant surface area for photocatalytic reactions, consequently enhancing the presence of reactive sites and facilitating enhanced catalytic efficiency. Additional examination of the composite photocatalyst (Fig. 3c) shows that CN nanoparticles surround the LDH surface, indicating the formation of a heterojunction between the two substances. The heterojunction structure is essential for promoting effective charge separation and reducing the chances of electron-hole recombination, thus enhancing the photocatalytic efficacy of the composite photocatalyst. Also, for the distribution of Ag nanoparticles in the samples, Element mapping images of ACNNF sample can be seen in Supplementary materials S1. In summary, SEM analysis provides convincing evidence of the unique morphological features of the CN, LDH, and composite photocatalyst samples. The samples were subjected to elemental analysis using energy-dispersive X-ray spectroscopy (EDX) in conjunction with SEM. The results are shown in Figure 5 (a,b,c,d). The energy peaks of CN, LDH, CNNF, and ACNNF were analysed. The results clearly demonstrate that each sample exhibited a distinct spatial distribution of all related elements, including C, N, Ni, O, Fe and Ag shown in supplementary Fig S1. This confirmed the development of each sample.

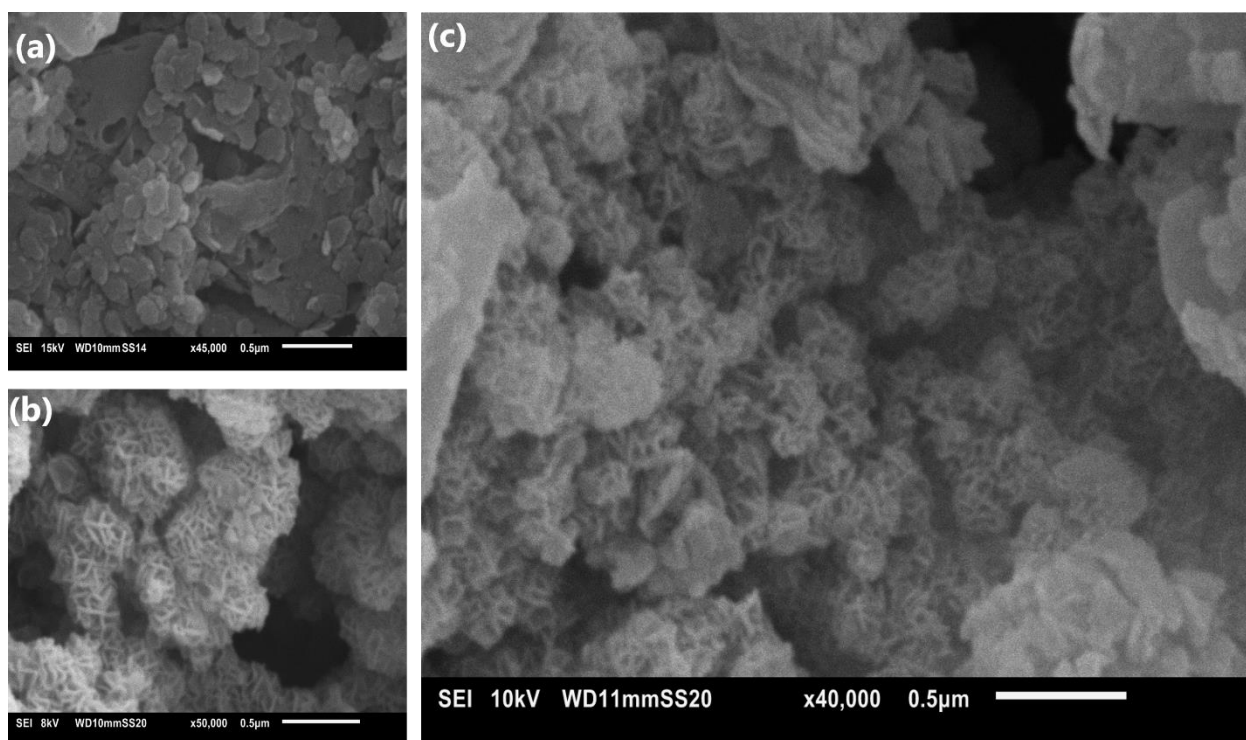


Fig 4.5 SEM images (a) CN (b) NF (c) CNNF

Figure 4 shows the TEM images of the samples. Figure 4a shows the TEM images of CN nanosheets. Whereas, Fig 4b shows TEM image of heterostructure of CN and LDH. Initially, the nanosheets were stacked in a spherical shape at the centre. Subsequently, the remaining nanosheets developed uniformly and scattered around the core structure. The NiFe-LDH nanosheets near the centre of the curd exhibited the highest density (Figure 4b). It is advantageous to enhance the specific surface area of the catalyst by creating voids through stacking of sheet-like structures. Furthermore, as seen in Figure 4c, the nanosheets are arranged in a stacked configuration which are next to the particulates, forming an intertwined planar structure that facilitates efficient transmission and rapid separation of the photogenerated carriers. Also, Ag nanoparticles can be seen in Fig 4c that is distributed uniformly throughout the samples. This can also be confirmed from the EDX mapping images in the supplementary section S1. For further investigating about the pore structure and specific surface area of the material, N₂ adsorption-desorption technique was used.

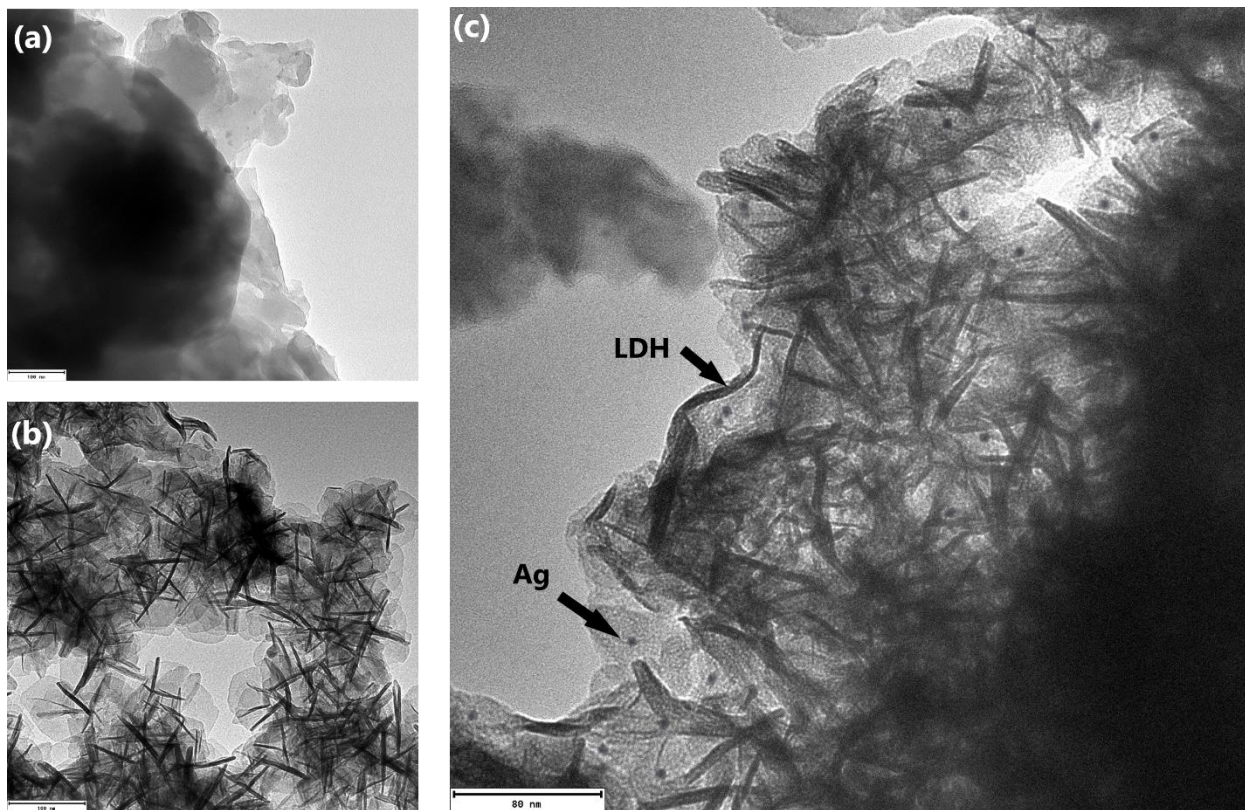


Fig 4. 6 TEM images (a) CN (b) CNNF (c) ACNNF

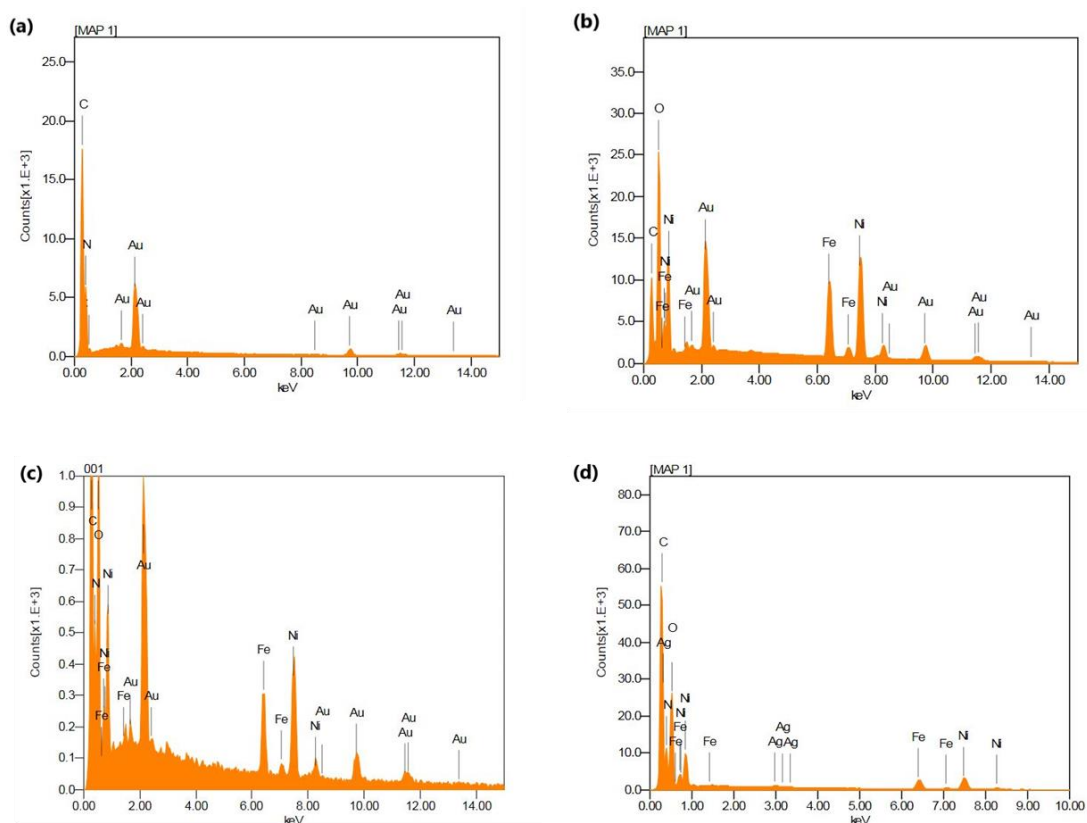


Fig 4. 7 EDX of (a) CN (b) NF (c) CNNF (d) ACNNF

BET analysis can be used to quantify the specific surface area of pure CN, NiFe-LDH and CN/LDH nanocomposites by nitrogen adsorption–desorption studies. Figure 5 presents the N₂ adsorption-desorption isotherms and the associated pore-size distribution curves (shown in the inset), providing detailed insight into the porosity of the sample. Additionally, Figure 5 depicts a characteristic physisorption isotherm displaying a Type IV hysteresis loop within the relative pressure range of $P/P_0 = 0.2\text{--}1.0$, indicative of mesoporous materials. As shown in Figure 5, all the samples exhibit a type IV isotherm, which indicates the presence of a mesoporous structure. The Brunauer Emmett-Teller (BET) specific surface area of g-C₃N₄ and LDH is 13.4 and 16.7 m²/g, respectively. The specific surface area of CNNF increased to 56.4 m²/g in comparison to pure g-C₃N₄, as shown in Table S1. ACNNF's surface area was 89.5 m²/g, which is much higher than that of the individual components.

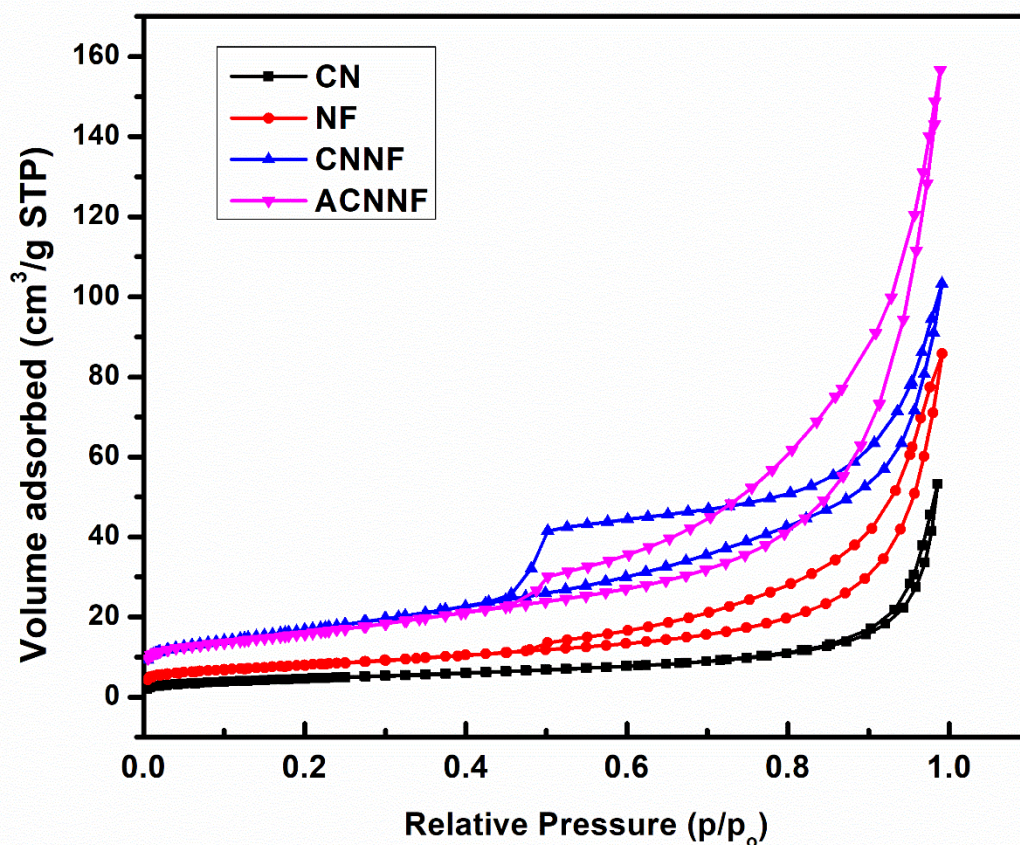


Fig 4. 8 N₂ adsorption-desorption isotherms, BET Graph of Samples

4.7.2 XPS Spectroscopy

The chemical composition and status of the elements inside the ACNNF were determined using XPS, as shown in Figure 7. Upon acquiring the CN and ACNNF spectra, the findings were compared. The study verified that CN is composed only of carbon (C) and nitrogen (N) components, but the ACNNF composite surface exhibited signals from carbon (C), nitrogen (N), nickel (Ni), aluminium (Al), and silver (Ag) (Fig. 7a). This indicates the presence of CN, LDH, and Ag. The analysis of the C 1s spectra (Fig. 7b) revealed two distinct peaks at 284.1 eV and 287 eV. These peaks may be accredited to the presence of CN on the surface and the bonding of nitrogen atoms in aromatic rings (N-C=N) with carbon atoms exhibiting sp²-

hybridization, respectively [43]. The peaks at 398.2 eV, 399.6 eV, and 401.5 eV are generated by deconvolution of the N 1s peak (Fig. 7c). The triazine unit, which consists of nitrogen atoms with sp² hybridization, is indicated by a prominent peak at 398.2 eV, indicating the existence of several functional groups containing nitrogen on the surface of g-C₃N₄. These particular functional groups may consist of amino (-NH₂), imine (=NH), and amine (-NH-) groups. Hydrogen atoms carrying free amino groups (C-N=H) are associated with a less intense peak at 401.5 eV [44]. The Ni 2p spectra (Fig. 7d) exhibits peaks at 855.43 eV and 873.2 eV. This suggests that the Ni(OH)₂ group is present in LDH. Furthermore, the presence of oxidised Aluminium, potentially in the form of aluminium hydroxides, is suggested by the Fe peaks at 712.1 eV and 725.0 eV [45]. The peaks seen at 373.0 eV and 367.1 eV in the Ag 3d spectrum correspond to Ag 3d_{3/2} and 3d_{5/2}, respectively. This confirms the presence of metallic silver and suggests the presence of silver nanoparticles or metallic silver in the composite material (Fig. 7f) [46]. In summary, these findings confirm the effectiveness of ACNNF.

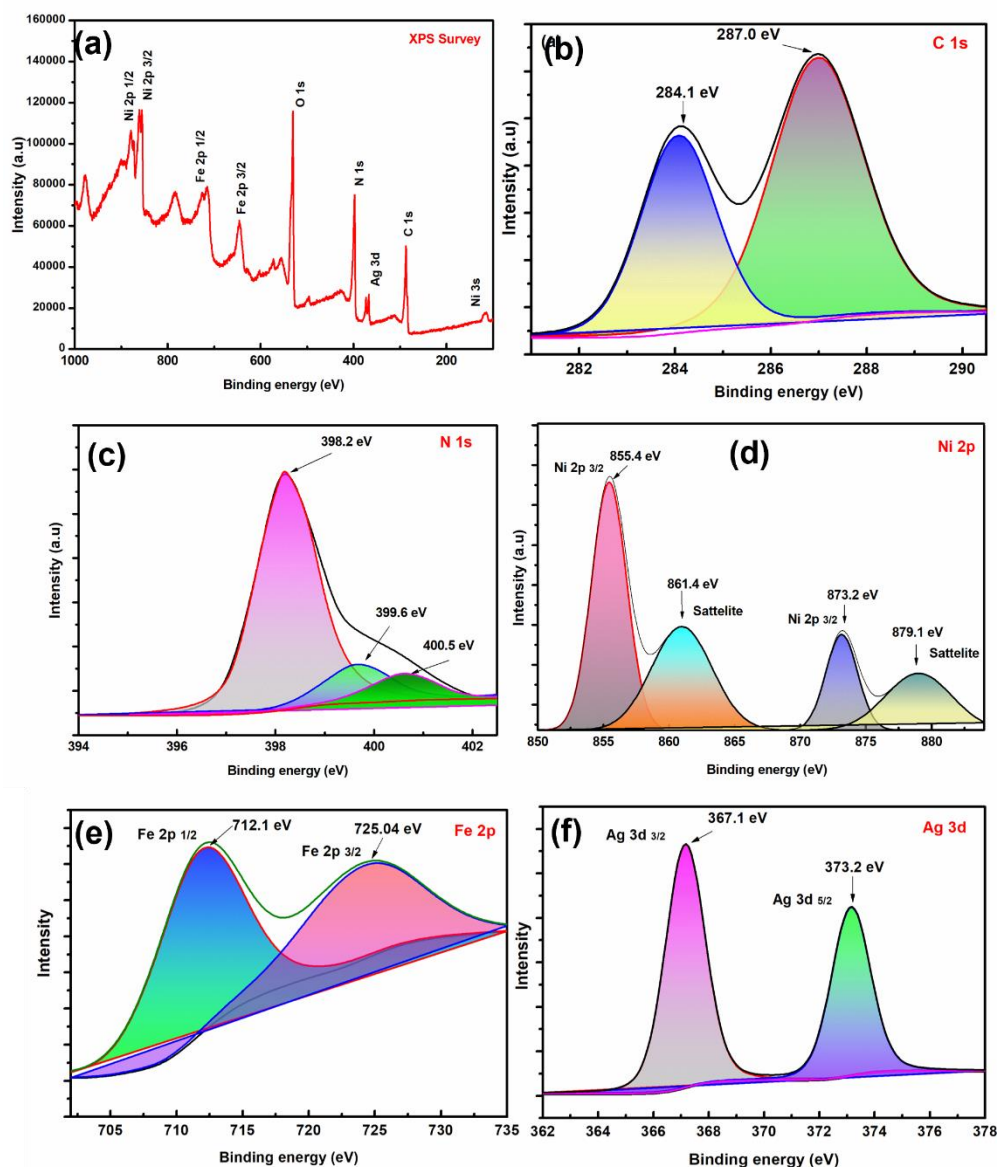


Fig 4. 9 XPS spectra of samples (a) Survey plot (b) C (c) N (d) Ni (e) Fe (f) Ag

PL spectroscopy analysis is crucial for understanding the mechanisms of the charge separation and light generated recombination. The PL spectra of the pure CN, NF, CNNF, and ACNNF composites in the wavelength range of 360–700 nm is presented in Fig. 8. This behaviour can be explained by the recombination of photoexcited electrons and holes, resulting in band-band photoluminescence. Moreover, the intensity of the emission band was reduced for CNNF compared with that of pure CN and LDH. The intensity decrease of ACNNF was the largest, which suggests the establishment of a heterojunction between CN

and LDH. The arrangement, together with the ideal concentration of CN, may significantly impact the separation of photo-induced charges and the reduction of their combination. In summary, this research indicates that ACNNF has the capability to capture the visible solar spectrum and inhibit the recombination of charges, thereby causing increase in the photocatalytic productivity.

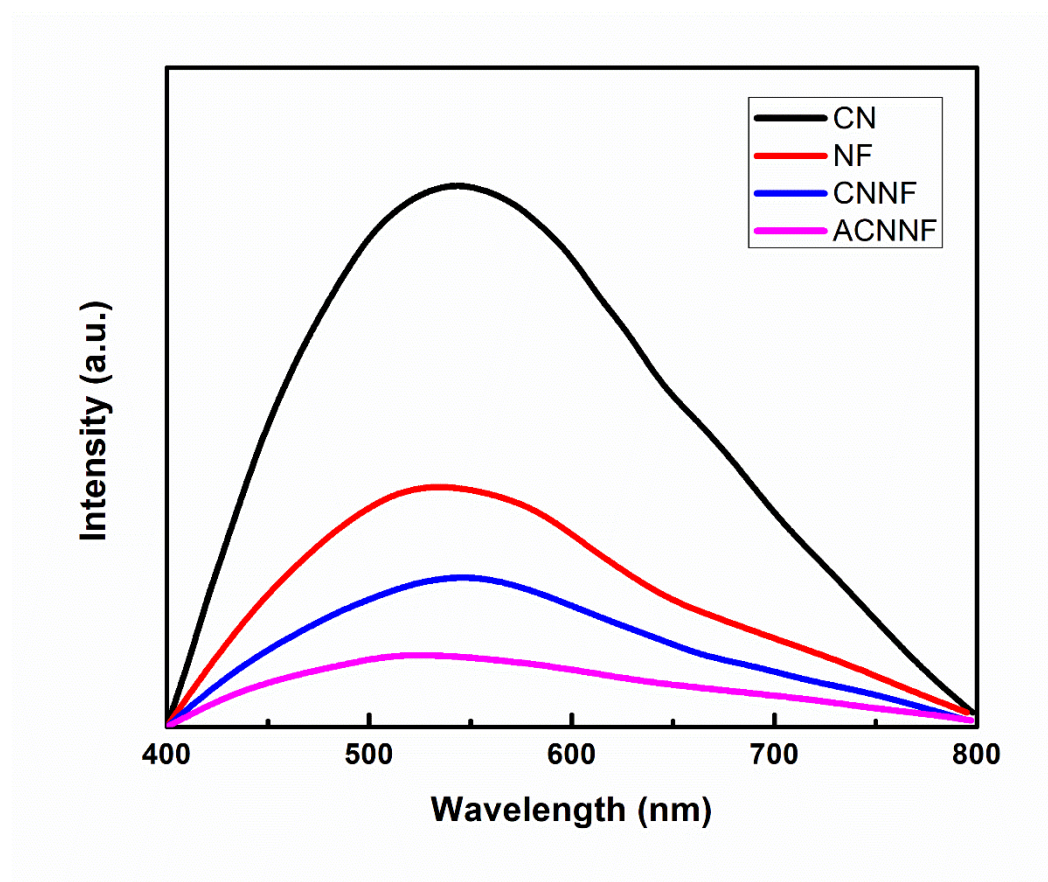


Fig 4. 10 Photoluminescence spectroscopy of Samples

UV-Vis Diffuse Reflectance Spectroscopy (DRS) was used to evaluate the light absorption capacity of the ACNNF composite. The DRS spectra (Fig. 9) exhibit clearly defined absorption peaks at certain wavelengths. An absorption peak was detected in the UV band (200–300 nm) of pure graphitic carbon nitride (CN). This peak corresponds to ligand-metal charge transfer (LMCT) transitions involving the 2p orbital of oxygen and 3d orbital of Ni^{2+} inside the layered

double hydroxide (LDH) layer. Additionally, this may be attributed to Ni^{2+} d–d transitions occurring within the LDH. The absorption edge of pure CN at a wavelength of 460 nm corresponds to a bandgap energy of 2.68 eV. Two distinct pairs of absorption bands were detected in the pure LDH spectra, with peak wavelengths of 375 nm and 420 nm, and approximately 650 nm and 740 nm, respectively. The incorporation of Ag nanoparticles onto CNNF greatly improved the effectiveness of light absorption throughout the entire range of wavelengths being studied. This development may be attributed to the distinctive attributes of Ag NPs, that is, the surface plasmon resonance (SPR) effect. This improvement provides proof of the deposition of Ag on the CNNF nanocomposites, resulting in amplified production of photoexcited charges. Consequently, the exceptional light-absorbing capacity of ACNNF is expected to improve photocatalytic performance [40].

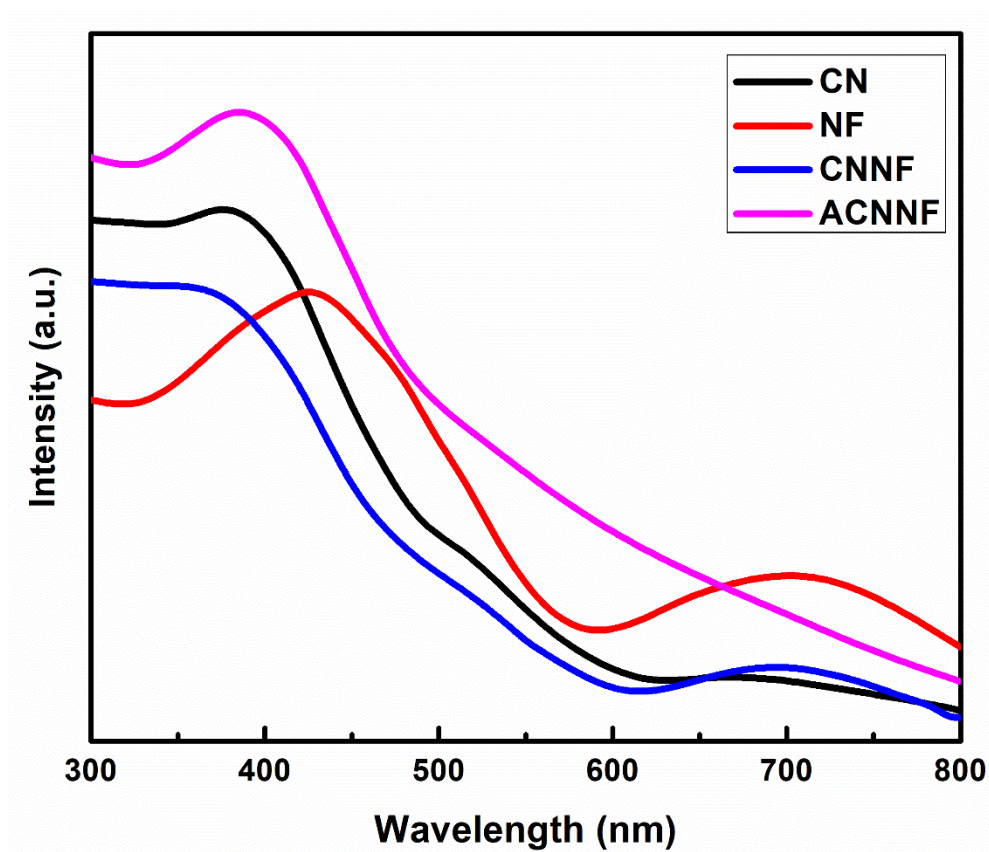


Fig 4.11 The UV-Vis diffuse reflectance spectra of Samples

4.8 Photocatalytic degradation

Negligible changes in the concentration of the RhB dye were observed in the absence of a catalyst or sunlight irradiation for approximately 40 min. This suggests that the self-degradation of the RhB dye was minimal. The adsorption of contaminants onto the catalyst surface is the first step in the photocatalytic degradation. The photocatalytic efficiencies of pure g-C₃N₄, NiFe-LDH, and nanocomposites with Ag deposition were assessed by comparing the outcomes of RhB elimination under both dark and visible-light exposure. Initially, the dye solution was examined in the absence of a catalyst, and the degradation of the dye was insignificant. Consequently, it was determined that degradation was induced by the combined presence of the photocatalyst and light. The RhB dye adsorption test was carried out in the absence of light to attain adsorption equilibrium. The rate of adsorption increased from 6.3% to 23.3% for CN and ACNNF, respectively.

The adsorption rates of NF and CNNF were 12% and 14.7%, respectively. Previous studies have shown that both g-C₃N₄ and NiFe-LDH exhibit low adsorption capacities [47] [48]. Figure 9 demonstrates that there was no noticeable deterioration of RhB when photocatalyst was not present, indicating its stability and lack of a photolytic reaction. The degradation efficiency of RhB under visible-light irradiation was found to be only 39% after 240 min using pure NiFe-LDH. In contrast, pure CN achieved a significantly higher degradation rate (78%) under the same conditions. Furthermore, it was found that combining g-C₃N₄ with NiFe-LDH to create a heterojunction resulted in a beneficial synergistic effect. However, the photocatalytic performance of the CNNF nanocomposite was suboptimal because the heterojunctions were not fully developed, and the interfacial effects were limited.

The addition of Ag notably improved the photocatalytic degradation of RhB, with the ACNNF nanocomposite exhibiting exceptionally high efficiency, achieving up to 99% degradation. It was observed that g-C₃N₄ sheets distributed on the surface of the NiFe-LDH flower-like nanocomposite could potentially create p-n heterojunctions that enhance the internal electric field. This heterojunction formation between g-C₃N₄ and NiFe-LDH promotes the effective separation and movement of photogenerated electron-hole pairs, substantially boosting the photocatalytic performance of the composites.

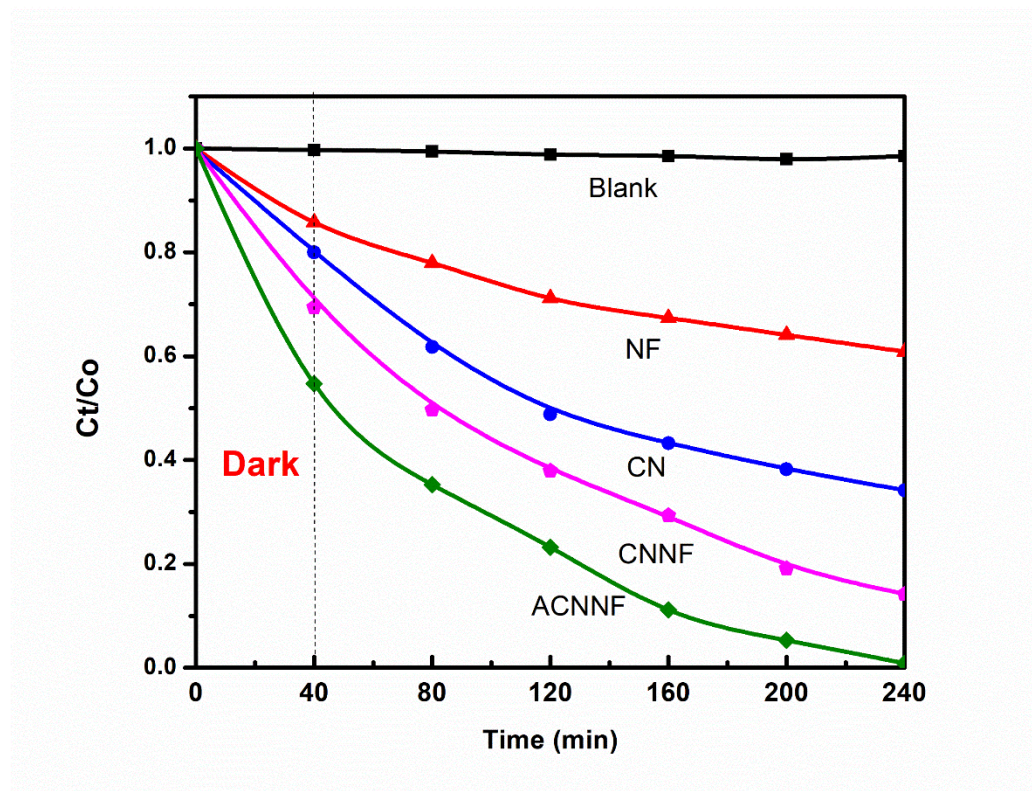


Fig 4. 12 Photocatalytic degradation of RhB under visible light

To evaluate the degradation characteristics of RhB and to determine the kinetic reaction rate, the Langmuir-Hinshelwood (L-H) model was applied. The analysis of photocatalytic kinetics often involves the application of pseudo-first-order kinetics, typically described by a specific formula [41]:

$$-\ln (C_t/C_0) = k_{at}$$

where the initial concentration of RhB is denoted by C_0 , measured in mg/L, C_t indicates the concentration of RhB at a given time which is also measured in mg/L and k_a (per h) represents the pseudo-first-order reaction's rate constant.

As illustrated in Figure 11, the strong correlation coefficients ($R^2 > 1$) confirmed that the photocatalytic degradation of RhB followed pseudo-first-order kinetics. The reaction rate constants of the pure g-C₃N₄ and NiFeLDH catalysts were approximately 0.341/h and 0.132/h, respectively. The ACNNF nanocomposite exhibited significantly higher reaction rates (0.92/h) than the pure g-C₃N₄ and NiFe-LDH catalysts, showing increases of approximately 2.7 times and 7.2 times, respectively. Consequently, the development and design of this new Ag-doped g-C₃N₄@NiFe-LDH photocatalyst is highly significant and feasible for application in environmental remediation. Moreover, it is crucial for photocatalysts to possess a specific regeneration capacity to effectively degrade pollutants in actual applications. The stability of the photocatalysts was assessed by cyclic degradation experiments. Fig. S3 depicts the ACNNF nanocomposite exhibited superior photocatalytic activity. This demonstrates that the photocatalyst met the fundamental criteria for industrial wastewater treatment. However,

there was a progressive decrease in the subsequent degradation tests because of catalyst loss during recovery operations.

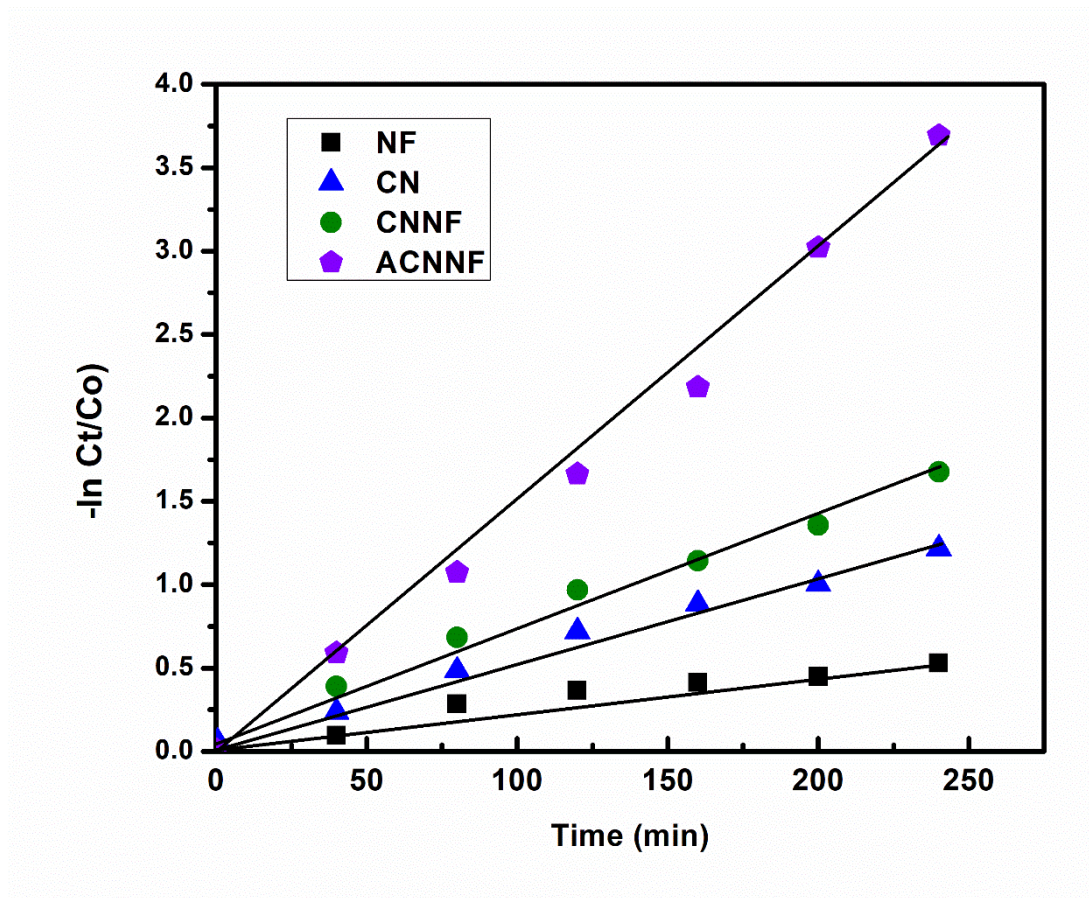


Fig 4. 13 Pseudo first order Kinetics fitting curves

4.9 Photocatalytic mechanism

Free-radical trapping experiments were performed to understand the RhB degradation process. For this study, three types of substances were chosen as quenchers to eliminate specific types of radicals. Isopropanol (IPA) was used to scavenge the hydroxyl radicals ($\cdot\text{OH}$), ethylenediaminetetraacetic acid (EDTA) was used to scavenge holes (h^+), and 1,4-benzoquinone (BQ) was used to scavenge hydroxyl radicals ($\cdot\text{OH}$). These choices are based on previous studies [46, 47]. Figure 8a shows that the photocatalytic degradation efficiency of RhB slightly decreased to 75% upon the addition of a specific amount of IPA under constant experimental conditions. This suggests that the hydroxyl radicals ($\cdot\text{OH}$) was not the primary

reactive species in the degradation of RhB. Conversely, the introduction of ethylenediaminetetraacetic acid (EDTA) or benzoquinone (BQ) significantly hindered the reaction, indicating the substantial roles of holes (h^+) and superoxide radicals ($\cdot O_2^-$) during the photocatalytic reaction. Notably, inhibition by BQ exceeded 74%. These findings indicate

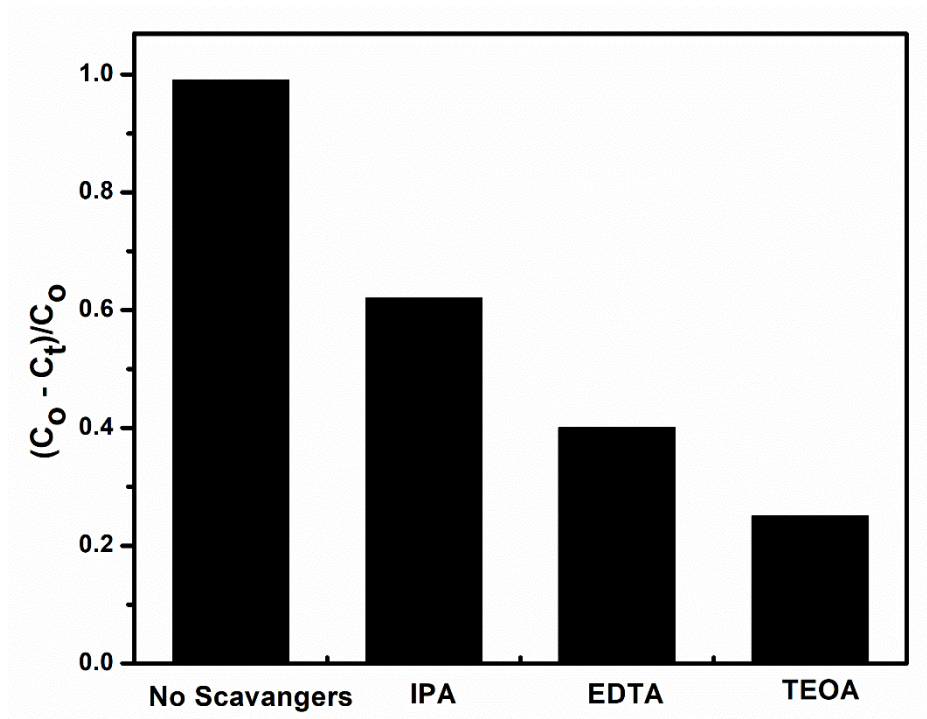


Fig 4. 14 Effect of different Scavengers study on degradation of RhB dye

that both h^+ and $\cdot O_2^-$ are crucial active species that effectively degrade RhB in photocatalytic systems by targeting the pollutants.

A hypothesis was formulated based on the mechanism depicted in Figure 13 to provide a comprehensive explanation of the increased productivity of the photocatalyst. To examine this mechanism, calculations were conducted on the valence bands (VB) of LDH and CN using the following equation [36]:

$$E_g = E_{VB} + E_{CB},$$

The Valance bond potential is denoted as E_{VB} , whereas Conduction band CB potential as E_{CB} , and the band-gap energy as E_g . The VB and CB positions of LDH and CN were determined using VB XPS, as illustrated in supplementary figures Fig. S2. The relevant bandgap values were determined using Talc's relationship, as shown in Fig. S3. The

measurements were used to calculate the absolute bandgap, as well as the locations of the semiconductor VB and conduction band (CB).

The bandgaps of CN, NF, CNNF, and ACNNF were calculated to be 2.70, 2.31, 2.20, and 2.14, respectively. LDH had a VB edge at 1.61 eV, whereas CN had a VB edge at 1.37 eV, as determined by the VB-XPS data. The location of the CB in pure LDH with an energy gap of 2.31 eV was found to be -0.70 eV. The energy gap (E_g) for CN (2.70 eV) led to a CB position of -1.31 eV. Visible solar light stimulates pure CN and LDH, which causes electrons to move from the VB, thereby creating holes in the band to the CB. The photoexcited electrons can move from the CB of CN to the CB of LDH. Simultaneously, the holes in the VB of the LDH can move towards the VB of CN. This ultimately leads to the separation of the charges involved. Indeed, it can be observed that the CB location of LDH is at -0.70 eV, which is lower or less negative than the CN edge at -1.31 eV.

In contrast, the VB of CN was more positively charged than that of LDH, 1.61 eV and 1.36 eV, respectively. Therefore, the described band structure precludes the recombination of photogenerated charges in both CN and LDH. Additionally, the CB electrons of the LDH were directed towards the surface of the catalyst. In addition, the holes in the VB of CN can initiate and promote the oxidation of TEOA ($\text{TEOA}/\text{TEOA}^+ = 0.61\text{V}$), thereby facilitating the overall process. Ultimately, the ACNNF catalyst demonstrates a shift towards longer wavelengths in its optical absorption of light when compared to pure LDH, hence enhancing its ability to capture photons.

4.10 Conclusions

In this study, g-C₃N₄@NiFe-LDH heterostructure photocatalysts were effectively synthesized using a spinning disc reactor. Photocatalysis studies showed that the Ag-doped composite exhibited exceptional photocatalytic activity, leading to the almost complete destruction of RhB. Furthermore, the photocatalytic degradation efficiency of the composite exceeded 80% even after four cycles. In addition, a thorough analysis of the potential photocatalytic degradation mechanism was conducted, and a Z-scheme heterojunction structure was proposed between g-C₃N₄ and NiFe-LDH. The separation and transfer of photogenerated carriers is enhanced by this structure since it is capable of generating an internal electric field.

This improvement in carrier dynamics considerably enhances the photocatalytic activity of the material, making it more efficient for its application. Following are the factors attributable to the enhanced photocatalytic performance: (1) The incorporation of Ag-doped defects modifies the band structure of Ag and reduces the band gap, thereby enhancing the efficiency of electron and hole separation and transmission. (2) The flower-shaped structure exhibited several active sites that effectively used the reflection and scattering of sunlight to increase the efficiency of light utilization and boost the photocatalytic activity. (3) The combination of Ag-doped CN/NiFe-LDH with the surface plasmon resonance (SPR) effect created a Z-scheme heterojunction that significantly enhanced the degradation of contaminants. This study presents a straightforward and efficient method for designing a new type of photocatalyst based on g-C₃N₄ heterojunction. This photocatalyst has potential for use in environmental remediation.

4.11 References

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Chapter 5: Silver Decorated Graphitic Carbon Nitride (gC₃N₄) /NiAl Layered Double Hydroxide Nanocomposite Photocatalyst for Enhanced Hydrogen Generation via Water Splitting

5.1 Abstract

In recent years the hydrogen generation by means of photocatalysis has increased in interest due to new encouraging results. To optimize the photocatalytic efficiency some difficulties are encountered in finding the ideal semiconductor material. In this work, a Ag-decorated NiAl-LDH/gC₃N₄(CN) nanocomposite produced by means of a hydrothermal method and photo-deposition is proposed. The developed catalysts exhibit remarkable visible light-induced hydrogen production performance, resulting in 2650 $\mu\text{mol.h}^{-1}\text{g}^{-1}$ H₂ yield. This value appears to be higher than those reported by adopting more common NiAl-LDH catalysts. In detail, it was found that adding 3.0 wt% Ag to the Ag/CN/LDH nanocomposite highest photocatalytic performances were achieved, resulting in H₂ yield values significantly higher if compared to those obtained by adopting pure CN/LDH composites, LDH or pure g-C₃N₄. The Ag/CN/LDH nanocomposites exhibits a remarkable photostability in successive runs, therefore no significant reduction of the performances as a function of time was observed. The findings suggests that the developed material qualifies as very interesting to achieve effective visible-light-sensitive photocatalysts for H₂ generation, in a cheap, sustainable and renewable manner.

Keywords:

Graphitic carbon nitride nanosheets, NiAl LDH, Ag Photo deposition, H₂ generation, Photocatalytic water splitting.

5.2 Introduction

In recent years a sensible increase in energy demand was observed, connecting to increased industrial emissions in the environment and raising much concern for the ecosystem on earth. Parallel to this, the depletion of natural energy resources is a serious threat to all industrial sectors.

In this framework, the need to develop clean and cheap energy sources that addresses actual challenges are require [1]. Hydrogen (H_2) has been identified as a possible choice of such energy vector, since it features high specific enthalpy of combustion values and the combustion results carbon-less and thus clean. Currently, around 95% of H_2 is generated by means of natural gas reforming. This highly energy-intensive process leads to significant global greenhouse gas emissions [2]. Photocatalytic water splitting by using visible light is gaining interest as one of the most promising routes to produce hydrogen fuel [3][4]. However, the solar energy conversion efficiency values of actual available photocatalysts remains too low for industrial interest. Some progresses to increase efficiency values were registered by adopting combined light-induced charges materials, such as those exhibiting photoexcited electron-hole pairs [5]. Developing suitable photocatalysts is therefore key to achieve efficient solar driven production of hydrogen.

In practice, the photocatalyst should be formed on earth-abundant, non-toxic elements[6][7]. Graphitic carbon nitride ($g-C_3N_4$), has recently drawn interest of research worldwide owing to the high thermal, chemical and mechanical stability exhibited by this material, connected to cheap production processes, a non-toxic nature and an enhanced visible light activation [8]. However, the $g-C_3N_4$ activity for water splitting applications appears to require more improvement. Recent research have explored different possible strategies, such as the formation of heterojunctions with different photocatalysts, doping with transition metal ions, or surface modification with functional groups [9]. Researchers agrees that reducing the thickness of $g-C_3N_4$ by exfoliation broadens band gap values, enhancing valence effects and conduction band edges thus improving redox capabilities [10][11]. Parallel to this the doping of $g-C_3N_4$ with transition metal ions leads to increased photocatalytic activity values due to the introduction of new active sites for redox reactions, structural modification of the band gap and enhanced mitigation of charge recombination [12]. Heterojunction formation between $g-C_3N_4$ and other photocatalyst such as TiO_2 or ZnO were observed to be capable of

improving the performance of photocatalyst as a result of the development of type-II heterostructure configuration that promotes the isolation of photogenerated charges [13][14]. Moreover, surface modification of g-C₃N₄ with -OH, -COOH, or -NH₂ increases water solubility, stability and interaction with the electrolytes, leading to improved photocatalytic performances [15]. All the findings increases the productivity of g-C₃N₄ up to a point where reduced specific surface area values, inefficient light harvesting methods and swift recombination of charge carriers limits further progresses. It is commonly suggested that interface engineering is required to overcome these constraints [16].

The layered structure of semiconductors owing to their two-dimensional interlayer spaces and high layer charge density leads to the characteristic of efficient electron transport required for advanced oxidation processes. In this framework, layered double hydroxides (LDHs) are particularly efficient and suitable as photocatalysts since they exhibit the appropriate conduction band and valence band positions for activation by visible light spectrum [17]. LDHs are mostly clay like materials, chemically represented by $[M^{II-x}M^{IIIx}(OH)_2]^{z+}(An)^{z/n} \cdot yH_2O$, where divalent and trivalent cations are indicated by M^{II} and M^{III}, respectively, and An are anions between the layers [18]. A unique feature of LDH is the even distribution of divalent and trivalent cations among all hydroxide layers, avoiding cluster formations. This fact leads to an efficient structure with a capability to easily tune their chemical composition by stabilization of different di- and trivalent cations provided by transition metals in the brucite layer octahedral lattice. Finally, LDHs are easy to synthesize. [19]. A main drawback of pure LDHs are low surface area and weak adsorption capability, reducing sensibly their potential efficiency [20]. To overcome this limitation, it is possible to perform a heterojunction construction with other appropriate materials to enhance the LDHs photocatalytic activity by raising the active surface values and adsorption capabilities [21]. Different LDH nanocomposites by adopting a heterojunction method for their synthesis to tackle photocatalytic water splitting and solar fuel production purposes have been successfully studied, such as CoAl LDH/gC₃N₄ [22], P doped ZnAl LDH [23], CdS/NiAl LDH [24], gC₃N₄/NiFe-LDH [25], ZnTi-LDH/gC₃N₄ [26] and FeWO₄/NiAl-LDH [27].

Asif et al. [28] developed a simple co-precipitation method to synthesize the composite of graphene oxide (GO) and Co-Al LDH, obtaining a photocatalyst with enhanced

photogenerated yield of methylene blue (MB) degradation assisted by visible light illumination. The best sample achieved a considerable value of MB dye degradation of 71%. Nayak et al. [24] developed another photoactive material by grafting bismuth oxycarbonate (BOC) onto NiFe-LDH on g-C₃N₄ support. The resulting architecture promotes electron transfer for surface reactions. In this case, water splitting occurs at the junction of Bi₂O₂CO₃ grafted NiFe-LDH and gC₃N₄ nanosheets, aided by the additional exchange of charges at the interface, capable of amplifying the oxygen and hydrogen evolution reaction rates. Samuei et al. [29] investigate the effects of cobalt doping to develop CoNiTi-LDH with improved photocatalytic properties for redox reactions associated with water splitting. The authors synthesized CoNiTi-LDH and performed various characterization studies to understand the structure and properties of their material. They found that CoNiTi-LDH had a reduced plate area and a boosted degree of order, leading to an abridged band-gap and improved photocatalytic yield compared to NiTi-LDH. CoNiTi-LDH exhibited a photooxidation yield of 366 $\mu\text{mol g}^{-1} \text{h}^{-1}$, twice the value (166 $\mu\text{mol g}^{-1} \text{h}^{-1}$) observed for NiTi-LDH; . Megala et al. [25] prepared a material by performing a 2D/2D heterojunction combining gC₃N₄/NiAl-LDH nanocomposites and verified a production performance of H₂ production adopting visible-light- sources. The authors found that the composite catalyst was highly efficient and measured an output of 2170 $\mu\text{mol h}^{-1} \text{g}^{-1}$ of H₂. These excellent performances may be justified by the accomplishment of the 2D/2D heterojunction, which demonstrated effective separation of charges under light irradiation and to improved electronic conductivity in the composite catalyst [30]. The two-dimensional LDHs and the g-C₃N₄ leads to active sites that significantly reduce the required distance for transporting electrons and holes, thus improving redox reactions. The morphology and composition of LDHs combined to the heterojunction construction with g-C₃N₄ and the possibility to fine tune their band gap by the adjustment of MII and MIII additions, leading to interesting active surface area values and enhanced adsorption capabilities qualify these materials as best candidates for visible light photocatalytic processes [2]. Indeed, LDHs can be easily designed with specific inter layer spacing and number of layers to promote efficient photo induced charge transfer across the interface of heterojunction, promoting at the end specific electron-hole separations and obtain higher surface area of the 2D LDHs and gC₃N₄ and increased adsorption capabilities on the

catalyst surface [30]. Also, to promote mitigation of charge recombination due to reduced transfer distance of charge carriers within g-C₃N₄ and LDHs [31].

Progressing to develop these materials further, it was noticed that the noble metal nanoparticles (NPs) such as Pt, Pd, Au, and Ag, when added to the photocatalyst, have some effect on their optical characteristics, in particular promoting a local surface plasmon resonance (LSPR) effect [29], [32], [33]. Among noble metals, silver (Ag) is a particularly attractive due to be cost-effective if compared to other noble metals and lead to sensible LSPR characteristics. Incorporating Ag NPs into the photocatalyst matrix has been observed to be profitable in enhancing photocatalytic activity, due to a better visible light absorption ability, to promote carrier separation, and to facilitate the generation of more active species [34], [35].

The work presented here was focused on a simple and viable route to produce a heterojunction photocatalyst of gC₃N₄/NiAl (CN/LDH) with Ag nanoparticles for the photocatalytic generation of H₂ is presented. The obtained results shows high efficiency of the optimized nanocomposite to obtain a sustainable H₂ production. In particular, the H₂ production of Ag deposited LDH/CN composite catalyst with 70 wt% of gC₃N₄ were 100 and 1000 folds greater hydrogen production rates when compared to pristine gC₃N₄ and NiAl-LDH, respectively. The obtained results appears to qualify the developed material in this work as an exciting and sustainable catalyst for the production of H₂ via photocatalysis aided by a visible light source.

5.3 Materials and methods

5.3.1 Chemicals and reagents

Melamine (99.0% pure), Nickel Nitrate Hexahydrate (99.0% pure), Ammonium Fluoride (99.0% pure), Aluminum Nitrate Nanohydrate (99.0% pure), Silver Nitrate and urea were procured from Sigma-Aldrich.

5.3.2 Synthesis of Graphitic Carbon nitride (g-C₃N₄) nanosheets (CN) photocatalyst

The powder of bulk graphitic carbon nitride was prepared by adopting a thermal polymerization method. Briefly, 10.0 g melamine was added to a ceramic crucible, transferred to a box furnace equipped with ramping capability. At 4°C/min, the powder was heated to 550 °C for four hours. After natural cooling, the obtained sample was ground and labeled as bulk g-C₃N₄. The nanosheet synthesis was achieved by adding bulk g-C₃N₄ powder to a 2M nitric acid solution and subjecting it to calcination for 2h at 500 °C at a 5 °C/min rate. The final sample was a pale yellow powder of g-C₃N₄ (CN).

5.3.3 Synthesis of NiAl LDH and CN/LDH composite photocatalyst

A spinning disc reactor at ambient temperature was used for the synthesis of NiAl-LDH. The molar ratio of Ni/Al used was 5.0. The metal precursors used in this study were iron (III) nitrate (Al³⁺) and nickel (II) nitrate (Ni²⁺). A Al³⁺: Ni²⁺ molar ratio of 5:1 was dissolved in water (25 mL). The metal ion solution was combined with 25 ml of a 0.2 mM CTAB solution (0.1 g) in separate containers. Prior to the addition of the metal ion solution, the surfactant was dissolved in water and agitated for 15 min at room temperature to create micelles. Solution A, which consisted of a final combination solution of 50 mL, was agitated continuously at room temperature for an additional 10 min. Concurrently, a 3 M NaOH solution was created by dissolving 3 g of NaOH pellet in 25 ml of water, referred to as solution B.

A schematic of the spinning disc reactor (SDR) used for the synthesis of nano-sized NiAl particles is shown in Figure 4.1. The apparatus primarily comprises a 15 cm diameter revolving disc onto which two or more reagent streams may be inserted. The injectors had a diameter of 1 mm and were positioned 1.5 cm apart from the disc surface. The flow rate of the reagents and radial distance of the injectors from the center of the disc may be set to a preset value. To operate SDR, it is necessary to stabilize the angular velocity of the disc. The liquid constituting the thin film migrates radially from the center to the periphery of the disc and ultimately disengages from the surface as a result of centrifugal forces. A vessel was

positioned around the revolving disc to collect liquid that reached the bottom of the reactor. The liquid then leaves constantly through the discharged pipe. In this experiment, two solutions were injected simultaneously using two peristaltic pumps. The Solution A and Solution B were injected at constant flow rates of 100 mL/min and 30 mL/min, respectively.

The rotational speed (ω) in the experiment was set at a constant value of 125 rad/s (1200 rpm). Following precipitation in the SDR, a brown suspension was collected from the lower part of the vessel. The resultant mixture, which consisted of a brownish precipitate, was vigorously agitated for 30 min at ambient temperature. Subsequently, the combined solution was transferred to a 20 mL Teflon-lined autoclave and heated to 120 °C for 6 h. The obtained precipitate was filtered and repeatedly washed with distilled water and ethanol to remove any residual soluble ions until the pH of the wash liquid stabilized at 7. After washing the sediment, it was dried overnight in an oven at 80 °C. Subsequently, for further experimental use the sediment was ground to a fine powder.

5.3.4 Synthesis of g-C₃N₄/NiAl-LDH (CN/LDH)

The same conditions and methods used to prepare the NiAl were employed in this experiment. However, in this case, we introduced a suitable quantity of CN into the beaker containing solution A and then subjected it to ultrasonication for 1 h to achieve full dispersion of CN within solution A. Then the CN suspension was added to the salt solution before adding to SDR for reaction. Subsequently, the same protocol was implemented, mirroring that of NF. The slurry in this instance had a yellowish-brown colour. Following washing with water and ethanol, the samples were dried and designated as CN/LDH

5.3.5 Ag deposition on CN/NiAl LDH nanocomposite photocatalyst

A photoreduction technique was adopted for Ag nanoparticles (NPs) deposition on the produced CN/LDH. Methanol was employed as a hole scavenger to obtain the Ag/CN/LDH composite photocatalyst. The composite CN/LDH was dissolved in methanol/water solution (1:4 vol. ratio), where 100 mg was added to 50 mL solution prepared by ultra-sonication, and an amount of silver nitrate corresponding to 3.0 wt% Ag deposition was added. The obtained solution was then irradiated for 60 min under magnetic stirring conditions using a 250W

Xenon lamp. Finally, the Ag/CN/LDH nanocomposites were obtained after centrifugation of the suspension, followed by distilled water washing and oven drying at 80 °C for 12h.

5.4 Characterization

X-ray diffractograms were obtained by using a Bruker D8 Advance providing a CuK radiation ($\lambda = 1.5406 \text{ \AA}$) for the examination of crystallographic features and phase composition of the synthesized materials. Measurement were performed within 2θ range from 10° to 80° and of 5° s^{-1} scan rate. To identify and examine the functional groups in prepared catalysts Fourier transform infrared (FTIR) spectroscopic analysis was utilized using the KBr pellet approach on a Bruker Tensor 27 Fourier transform infrared spectrometer (FTIR). UV-visible diffuse reflectance spectra was performed to measure the optical absorption of the samples on a Perkin Elmer Lambda 25 diffuse reflection spectrometer. The results for X-ray photoelectron spectroscopy (XPS) were acquired from X-ray photoelectron spectrometer (Thermo Scientific K-Alpha). The prepared catalysts' photoluminescence (PL) spectra were procured from a JASCO-FP-8200 Fluorescence spectrometer. Scanning electron microscopy (SEM) was adopted to get insight on surface morphology (instrument FE-SEM, JEOL JSM 7001F).

5.5 Photocatalytic H₂ production

The hydrogen production by means of water splitting was performed in a sealed quartz reactor (180 mL) under controlled light illumination conditions (300 mW/cm^2). According to the adopted protocol in this work, 15 mg of sample was added to a solution of 45mL deionized water and 5 mL of the hole scavenger substance, that is triethanolamine (TEOA), starting the light driven water dissociation. The reactor was provided with a Quartz Tungsten Halogen lamp. The top pf the reactor is sealed by means of a rubber septum. Before each experiment, the reactor was purged with nitrogen to eliminate residual gases. The experiment was carried out by irradiation of the given solution for 5 hr. Every 1h the amount of produced H₂ gas was measured. Parallel to this, a sample of the formed H₂ gas (1.0 mL) was withdrawn with a gas-tight micro syringe and was analyzed with the aid of GC-14C, Shimadzu gas chromatograph exhibiting a TCD detector, using as a molecular sieve 5 column and carrier gas nitrogen.

5.6 Results and discussion

5.6.1 Crystallinity

The crystallinity of the photocatalyst was measured through X-ray diffraction (Fig 1). As evident, every material containing pure LDH exhibits two distinct peaks for carbon nitride appearing at 13.2° and 27.6° , analogous to (002) and (100) diffraction planes, respectively. The sharp peak observable at $\sim 27.6^\circ$ for (002) plane represents the typical interplanar conjugated aromatic rings stacking. Moreover, the extremely small diffraction peak at $\sim 13.2^\circ$ for (100) plane indicates repeating units [13], [36]. On contrary, pure LDH exhibits sharp and distinct XRD peaks at 11.71° and 35.13° corresponding to (003) and (006) planes. Relatively weak peaks can be seen at 23.43° , 39.55° and 46.90° which are associated to (012), (015) and (018) diffraction planes, respectively. Finally, peak appearances may be observed at 61.02° , and 62.42° reflecting (110) and (113) crystallographic planes separately. All these planes are well describing a hexagonal NiAl-LDH (JCPDF 22-0452) [37]. Coexistent or peaks found in both LDH and CN are evident from CN/LDH patterns, which suggests that the hybrid composite is fully developed. The Ag/CN/LDH composite photocatalyst XRD patterns exhibits peaks associated with CN and LDH, with a remarkable intensification of the LDH peaks as its content increases in the sample. Moreover, it might be observed that the peak at 27.6° resulted slightly shifted, justified by a firm coordination between all the materials in the composite catalyst Ag/CN/LDH. A solid peak for Ag is absent from the pattern, hidden due to its high disparity and low loading. However, in this work, other analytical techniques were employed to verify the presence of Ag in the produced Ag/CN/LDH composite.

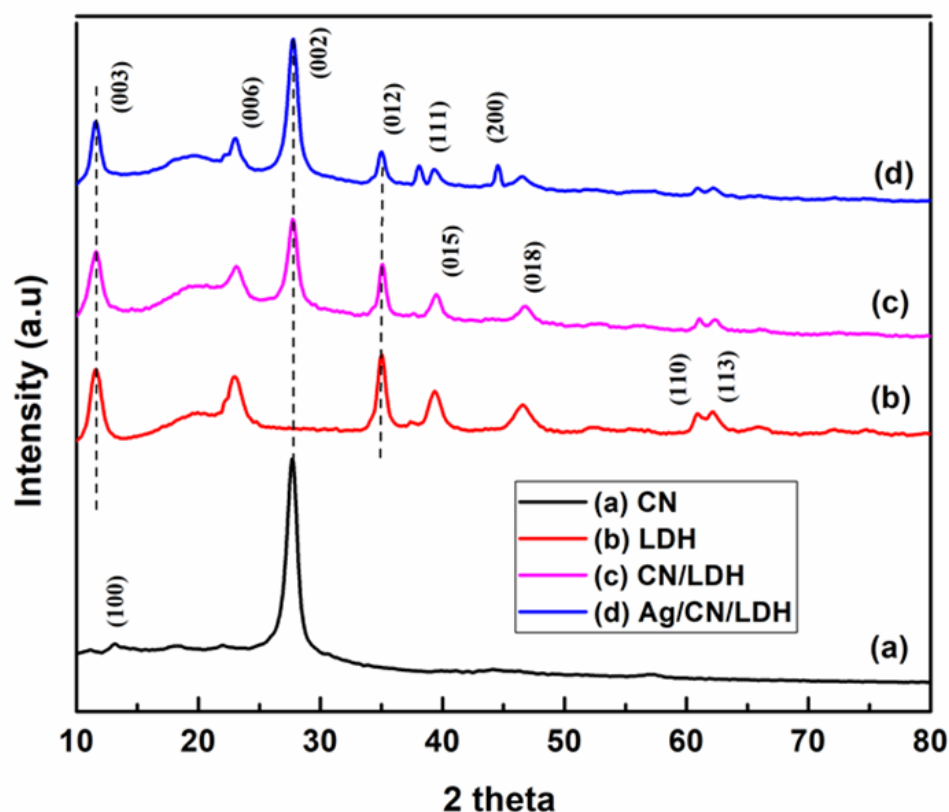


Fig 5. 1 XRD analysis for CN, LDH, CN/LDH, and Ag/CN/LDH samples.

5.6.2 Fourier transform infrared spectroscopy (FTIR) analysis

The investigation and analysis of various functional groups in the prepared samples was performed by means of FTIR spectra measurements, as reported in Fig. 2. The g-C₃N₄ vibrational analysis revealed a distinct and sharp band at 805 cm⁻¹ indicating a s-triazine ring system in breathing mode. The observed 3200-3400 cm⁻¹ wide band indicates the presence of N-H components in stretching vibrational modes. These components are connected with amino groups which are not condensed. Moreover, in the stretching mode, some bands in the 1200–1650 cm⁻¹ range indicate aromatic C–N heterocycles [38]. The broad peak between 1630 cm⁻¹ and 3490 cm⁻¹ implies asymmetric and symmetric stretching vibrations of (Ni/Al-OH) and interlayer water molecules bending vibrations, respectively [25]. The antisymmetric nature of interlayer carbonate anions in their v₃ mode is detected at 1370 cm⁻¹, while the peak observed at 2150 cm⁻¹ is associated with the CO₂ presence in the LDH lattice. The bands that appear at wavenumbers less than 800 cm⁻¹ can be justified by lattice vibrations of metal-oxygen-metal (Ni-O-Al) and metal-oxygen (Ni-O and Al-O) LDH cation layers. Furthermore,

the spectra for nanocomposites and pure gC_3N_4 have a peak at 1630 cm^{-1} is ascribed to stretching mode aromatic C-N, and at 807 cm^{-1} , the spectra can be attributed to S-thiazine ring system's six-membered ring's bending vibrations, which are all out of plane [39].

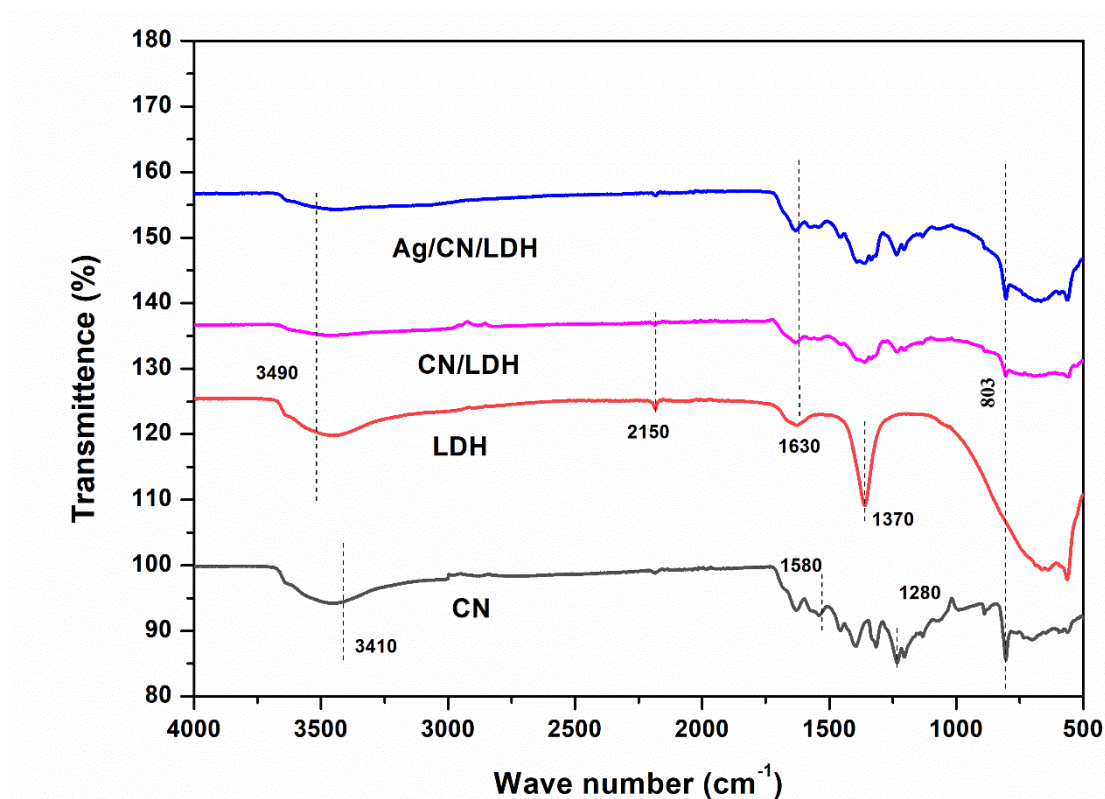


Fig 5. 2 FTIR spectra of CN, LDH, and its nanocomposite with Ag deposited.

5.6.3 Morphological investigation

The surface morphological examination of the samples was performed by scanning electron microscopy (SEM) and Transmission electron spectroscopy (TEM). The SEM images for pure CN and CN/LDH are reported in Fig. 3. It is possible to observe by the image obtained from CN (Fig. 3a) the presence of a two-dimensional sheet-like assembly with random arrangement, confirming that the ultrasonic exfoliation of bulk carbon nitride created the obtained CN nanosheets. This finding is consistent with previous studies on CN, which reported the same exfoliation into nanosheets by means of ultra-sonication [38]. The 2D sheet-like structure of CN can mitigate a charge recombination, leading to enhanced photocatalytic activity. The CN/NiAl LDH (Fig. 3b) sample revealed hierarchical 3D flower-like morphology composed from self-accumulated nanoflakes. The LDH's 3D structure provide a moderate surface area for photocatalytic reactions and improve active sites availability. The SEM and TEM images of the CN/LDH composite photocatalyst shown in Fig 3.b and Fig. 3c respectively

that the CN sheets were wrapped over the LDH surface, providing a proof of a heterojunction between these two materials. The heterojunction structure promotes charge separation, reducing the possibility of a recombination of the charges, thus increasing the light-induced performances of the composite catalyst. Finally, the TEM image of Ag/CN/LDH (Fig. 3d) exhibits the uniform distribution of Ag nanoparticles over the surface of the prepared catalyst. The distribution of the Ag nanoparticles was homo-geneous and act as a co-catalyst, promoting efficient resistance to charge recombination and elevated photocatalytic performance of the composite.

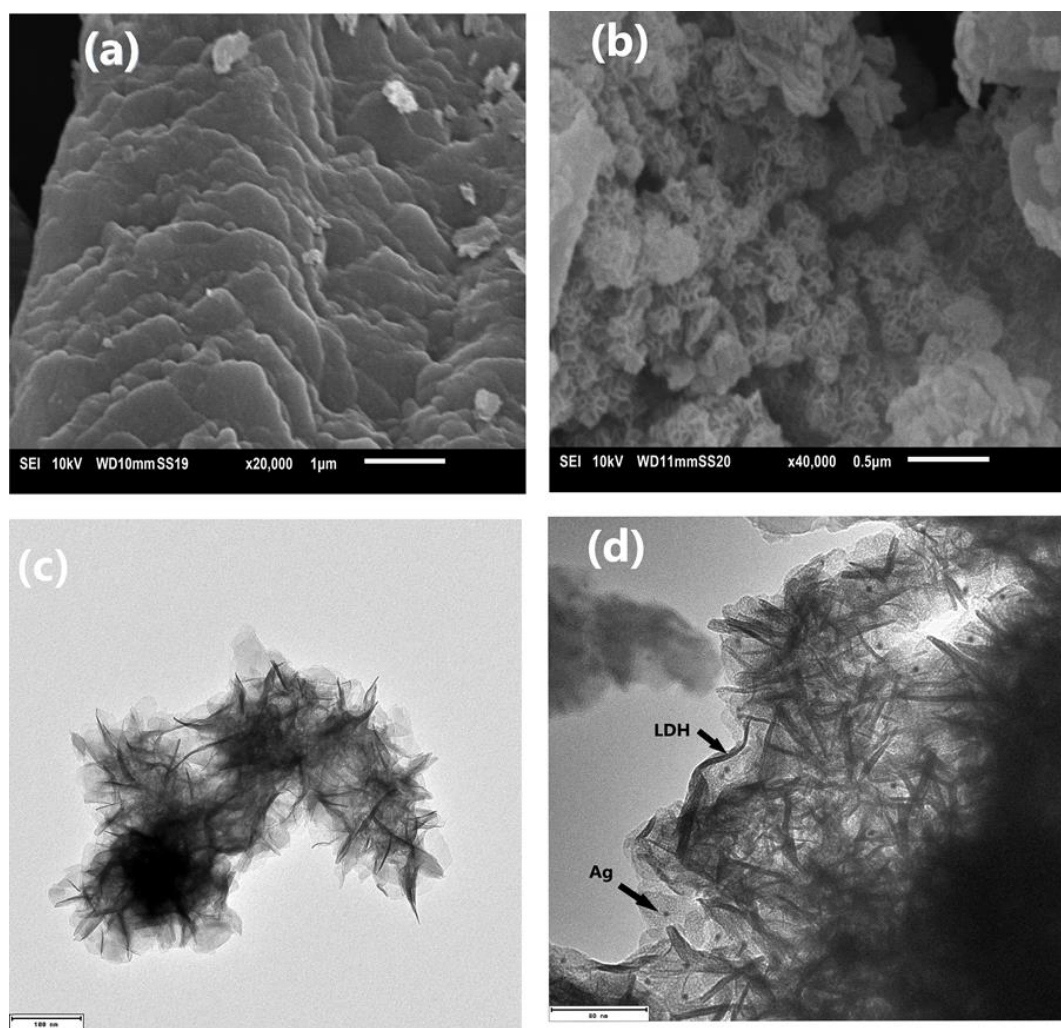


Fig 5. 3 SEM images (a), (b) and TEM images (c), (d) of samples, (a) g-C3N4 (b) CN/LDH, (c) CN/LDH (d) Ag/CN/LDH

5.6.4 Optical properties

To assess the light harvesting ability of Ag/CN/LDH composite, UV-Vis Diffuse Reflectance Spectroscopy (DRS) was employed. The obtained DRS spectrum (Fig. 4) revealed distinct absorption peaks at specific wavelengths. For pure graphitic carbon nitride (CN), an absorption peak was observed in the ultraviolet region between 200 nm and 300 nm. This peak can be associated with ligand-metal charge transfer (LMCT) transitions among 2p orbital of oxygen and 3d orbital of Ni^{2+} inside layered double hydroxide (LDH) layer, as well as Ni^{2+} 's d-d transitions within the LDH. The adsorption edge of pure CN at 460 nm corresponds to a band-gap of 2.68 eV. In the spectrum of pure LDH, two sets of dual absorption bands were observed, centered on 375 nm and 420 nm, and approximately 650 nm and 740 nm, respectively. At 420 nm and 650 nm absorption bands were identified as spin-forbidden shifts between the 1T_{2g} (D) and 3A_{2g} (F) energy levels and the 1E_g (D) and 3A_{2g} (F) energy levels, respectively [29, 30]. The introduction of Ag nanoparticles (NPs) onto CN/LDH significantly enhanced light absorption efficiency across the entire wavelength range under investigation. The unique characteristic of Ag NPs known as surface Plasmon resonance (SPR) effect can be credited for this development. This improvement is an evidence of Ag deposition on CN/LDH nanocomposites, leading to exaggerated formation of photoexcited charges. As a result, the excellent capability of Ag/CN/LDH to absorb light should enhance photocatalytic performances.

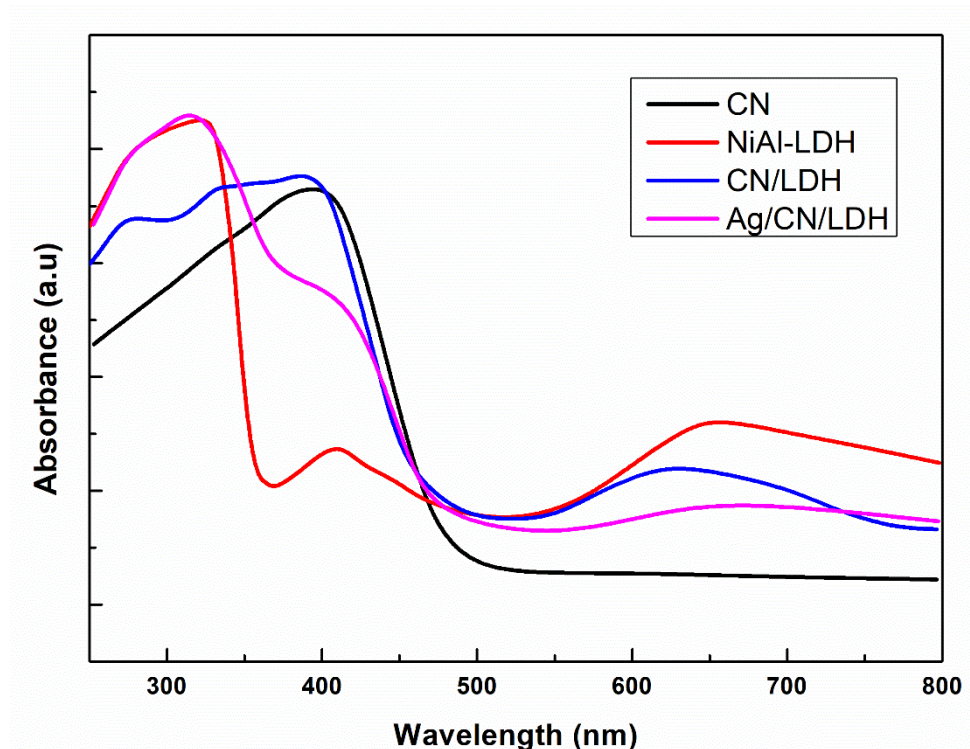


Fig 5. 4 UV –vis diffuse reflectance spectra of pure CN, pure LDH, CN/LDH composite, and Ag/CN/LDH composite samples.

The PL spectroscopy analysis is essential to understand the light-induced charges separation and recombination phenomena. Fig. 5 reports the PL spectra for pure gC_3N_4 , and CN/LDH and Ag/CN/LDH composite within wavelength range of 360 nm to 700 nm. A peak can be noticed at 460 nm, which is associated to pure CN. This behavior can be explained by recombination of photoexcited electrons and holes, which induces band-band photoluminescence. Furthermore, the emission band intensity decreased for the CN/LDH relative to pure CN and LDH. Ag/CN/LDH exhibits the highest value of intensity reduction, indicating the formation of CN and LDH heterojunction. This formation, together with optimal CN weight percent, can have a substantial effect on the segregation of photo-induced charges and mitigation of their recombination. Overall, the performed analysis suggests the ability of Ag/CN/LDH to harvest visible solar spectrum and depress the recombination of charges leading to boosted photocatalytic productivity.

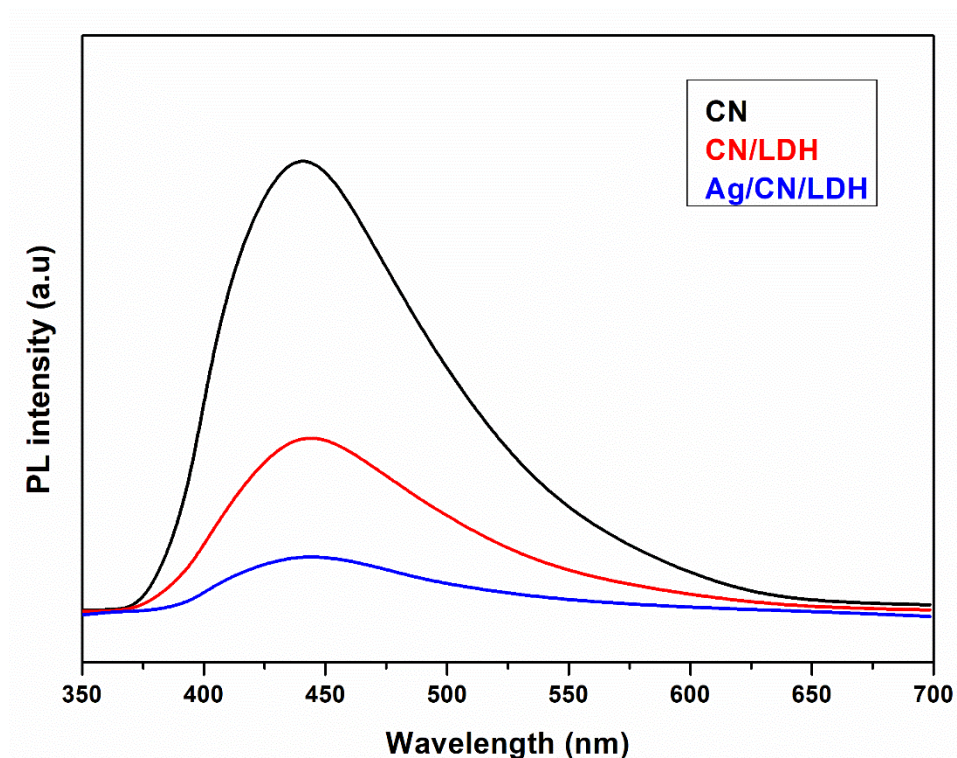


Fig 5. 5 Photoluminescence spectroscopy of CN, CN/LDH and Ag/CN/LDH

5.6.5 X-ray photoelectron spectroscopy (XPS) analysis

The status of elements inside the Ag/CN/LDH and their chemical composition was measured by means of X-ray photoelectron spectroscopy (XPS), as reported in fig 6. After obtaining the CN and Ag/CN/LDH spectra, it was possible to compare the results and the analysis confirmed that CN consists of only C and N elements, whereas Ag/CN/LDH composite surface includes signals from C, N, Ni, Al, and Ag elements (Fig. 6a). suggesting that CN, LDH and Ag are all present. The deconvolution of C 1s spectrum (Fig. 6b) indicated bands at 284.7 eV and 288.3 eV, which can be justified by adsorbed surface sites of carbon nitride and N in aromatic rings (N-C=N) bonded to carbon atoms with sp^2 -hybridization, respectively [4]. Peaks at 398.5 eV, 399.8 eV, and 401.2 eV are obtained by deconvolution the N 1s peak (Fig 6c). The triazine unit (C-N=C) N atoms with sp^2 hybridization are represented by main peak at 398.5 eV, and the other two peaks show presence of various functional groups comprising nitrogen on g-C₃N₄ surface. The specific functional groups could include amino (-NH₂), imine (=NH), and amine (-NH-). The less intensive peak at 401.2 eV corresponds to hydrogen atom containing free amino groups (C-N=H). Furthermore, at 404.5 eV a peak observed is related to π excitations [40]. The spectrum for Ni 2p (Fig. 6d) shows bands at 856.43 eV and 873.7 eV, indicating the LDH contains Ni(OH)₂ group. Additionally, the Al peaks at 67.5 eV and

74.5 eV indicated oxidized aluminum is present, possibly as aluminum oxides or hydroxides. At 368.1 eV and 374.0 eV peaks in the Ag 3d spectrum are associated to Ag 3d_{5/2} and 3d_{3/2}, confirming the existence of metallic silver, suggesting the presence of silver nanoparticles or metallic silver in the composite (Fig. 6f) [41]. Summarizing, these results appears to validate the successful synthesis of Ag/CN/LDH.

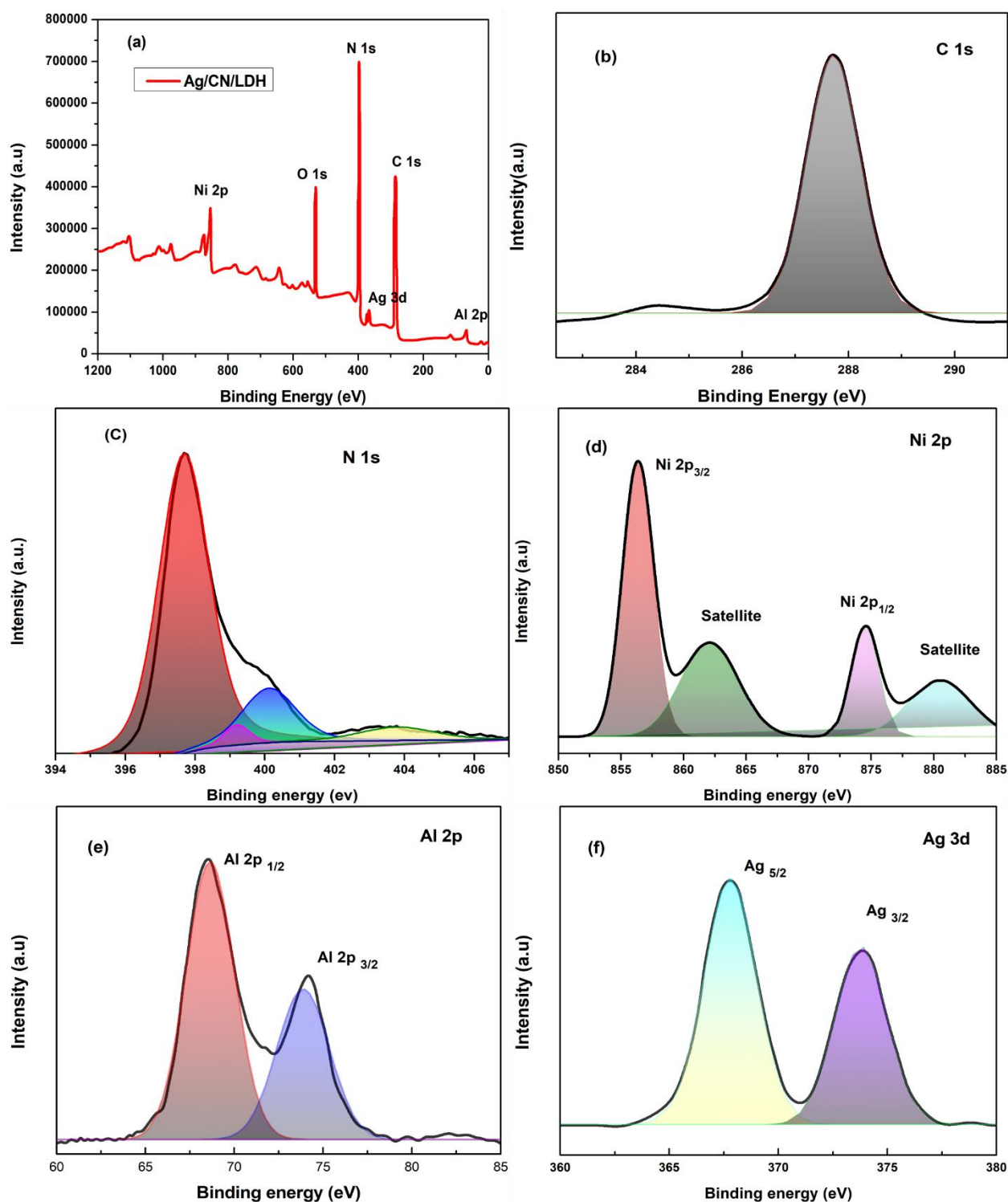


Fig 5. 6 XPS spectra of the Ag/CN/LDH (a) Survey spectrum, (b) C 1s, (c) N 1s, (d) Ni 2p, (e) Al 2p, and (f) Ag 3d.

5.7 Photocatalytic Hydrogen (H₂) production

The productivity of the prepared photocatalyst in terms of H₂ yield from water splitting was measured in the presence of hole scavenger 10 % triethanolamine (TEOA) under visible solar

illumination. The obtained results exhibits an exceptional photocatalytic activity of LDH/CN and Ag/CN/LDH nanocomposites for hydrogen production under the employed 250W Xe lamp simulated light irradiation used during the experiments. As it is possible to observe from Fig. 7, pure LDH give rise to a H₂ production of 35 $\mu\text{mol.h}^{-1}\text{g}^{-1}$; this value is in line to those reported in literature [42]. The same applies to pure CN, with a H₂ evolution rate of about 15 $\mu\text{mol.h}^{-1}\text{g}^{-1}$ [22]. On contrary, the coupling of LDH with CN resulted in a significant gain in the catalyst performance, with H₂ yields of 1750 $\mu\text{mol.h}^{-1}\text{g}^{-1}$, that is a 100 fold higher magnitude. This sensible improvement in the activity can be justified by the enhanced separation of charges and transfer efficiencies because of LDH and CN coupling, which promotes the use of photo-induced charges in favor to the hydrogen production.

Better results were obtained with the deposition of Ag on the CN/LDH composite, yielding 2650 $\mu\text{mol.h}^{-1}\text{g}^{-1}$ of H₂. The photoluminescence (PL) studies further support this improved photocatalytic activity of LDH/CN and Ag/CN/LDH photocatalyst. The reduced PL intensity observed for the composite photocatalyst indicates an appreciably decreased recombination rate of the photogenerated electron-hole pairs, thus boosting performances accordingly. Overall, the results of this study provide promising evidence for the development of a cheap and highly efficient photocatalyst for clean energy production, with CN/LDH and Ag/CN/LDH composites as promising candidates and that will require further investigation and optimization.

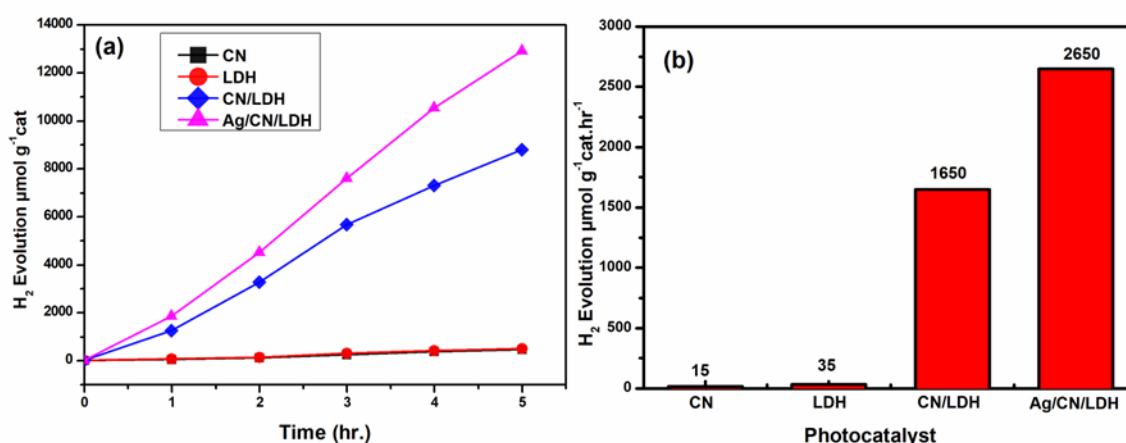


Fig 5. 7 H₂ production rate of photocatalysts (a) under continuous irradiation of a Xenon lamp for 5 hr. (b) H₂ production per hour (average)

5.8 Photocatalytic H₂ evaluation mechanistic overview

To fully describe the boosted productivity of photocatalyst, the mechanism in Fig. 10 was hypothesized. To investigate this mechanism, LDH and CN valence band (VB) calculations were performed with the help of equation [35]:

$$E_g = E_{VB} + E_{CB},$$

Where VB potential is E_{VB} , CB potential is E_{CB} , and the band-gap energy is E_g , respectively. The positions of VB and CB for LDH and CN were evaluated from VB-XPS as shown in Fig. 8, and the estimation of values for relevant band-gap was made using Tauc's relation (Fig. 9). The absolute band-gap, semiconductor CB, and VB positions were calculated on the basis of these measurements.

In this case, LDH had the VB edge at 1.61 eV and CN at 1.37 eV, respectively and according to the results obtained from VB-XPS. From E_g of pure LDH (2.31 eV) the position of CB was at -0.70 eV. The E_g for CN (2.68 eV) resulted to a CB position equal to -1.31 eV.

The incidence of visible-solar light excites the pure CN and LDH, transporting electrons toward the CB and leaving holes in VB. These photo-excited electrons have the freedom to travel from CB of CN to that of LDH, and simultaneously the holes in the VB of LDH are free to migrate towards the valence band of CN, resulting at the end in a segregation of the involved charges. In fact, it is possible to observe that the LDH conduction band position (-0.70 eV) is lower than or less negative than the CN edge (-1.31 eV). On the contrary, the CN valence band (1.61 eV) compared to the LDH (1.36 eV) is more positive. As a consequence, the given band structure prevents photogenerated charges from recombining in both CN and LDH, and CB electrons of LDH are driven towards the catalyst surface where the reactions for the hydrogen production occurs. Furthermore, holes assembled in the VB of CN can trigger and induce TEOA ($TEOA/TEOA^+ = 0.61V$) oxidation, assisting the overall mechanisms. Finally the Ag/CN/LDH catalyst exhibit a redshifted optical absorption of light if compared to pure LDH, amplifying photon harvesting capabilities.

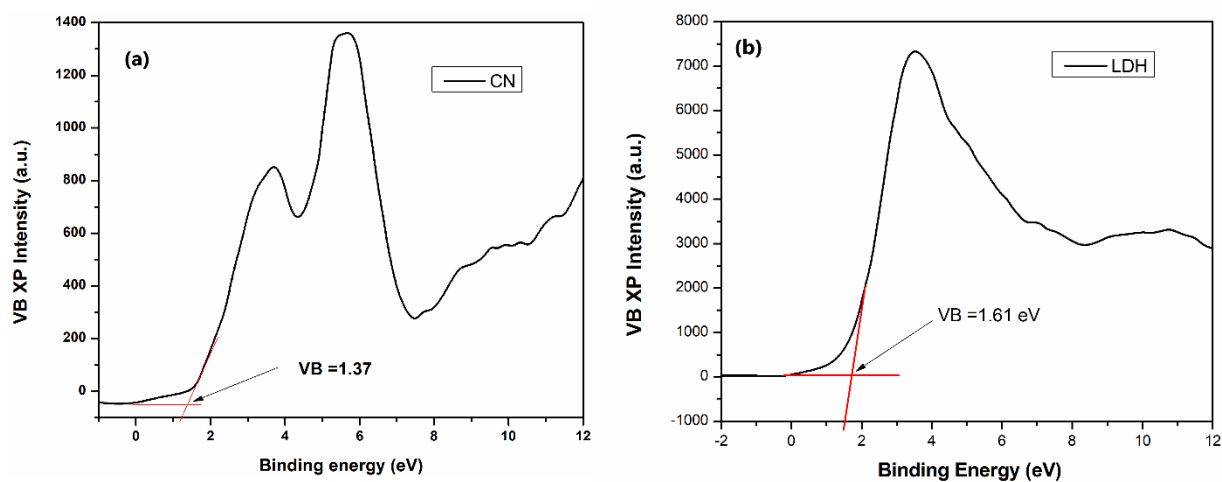


Fig 5. 8 VB XPS spectra of (a) CN and (b) LDH

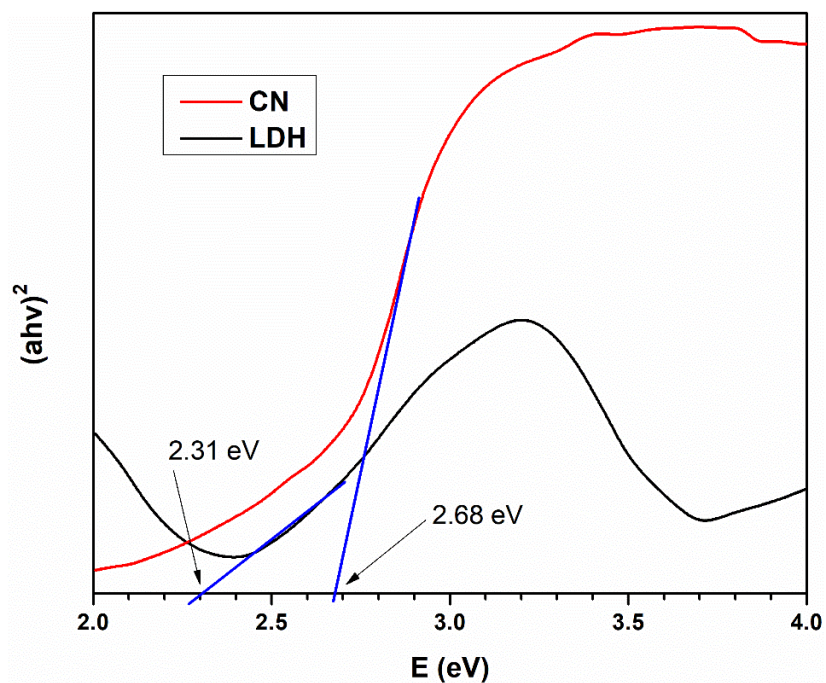


Fig 5. 9 Band gap of CN and LDH using Tauc's relationship.

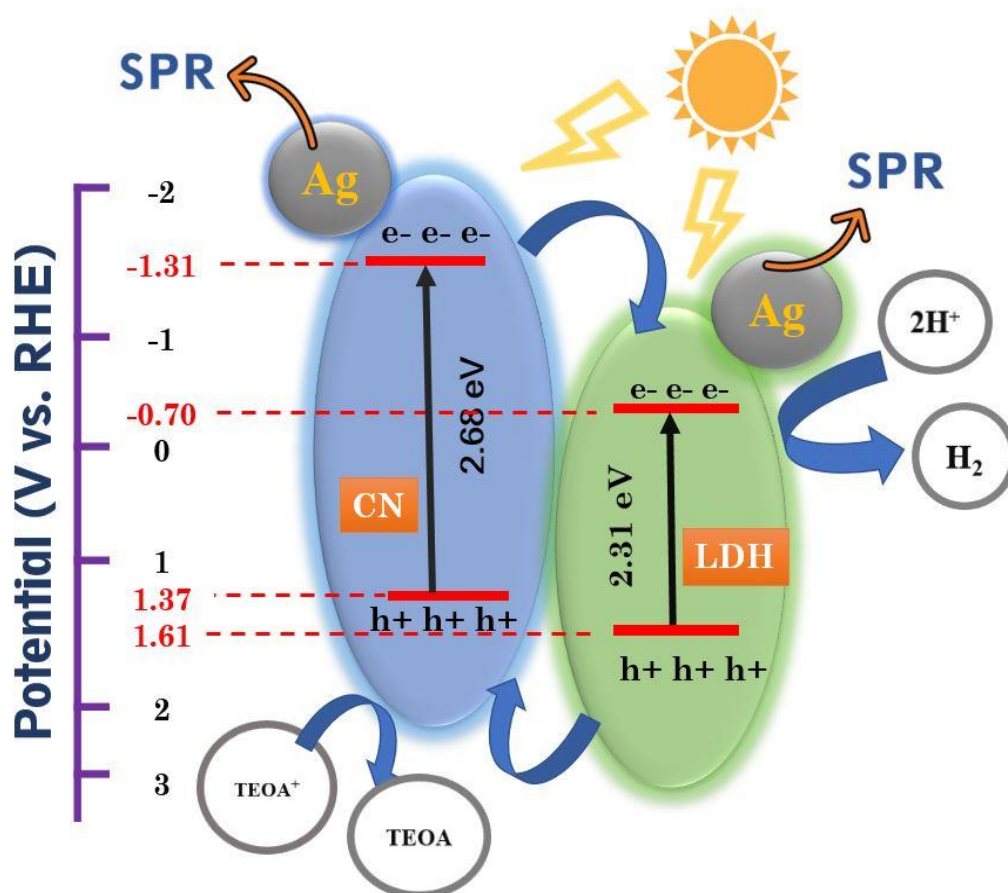


Fig 5. 10 Proposed mechanism of H_2 generation via photocatalytic water splitting employing Ag/CN/LDH nanocomposite photocatalyst.

5.9 Conclusions:

Ag deposited CN/LDH nanocomposite as a visible light activated catalyst for H_2 production from water splitting was prepared by adopting in-situ hydrothermal methods followed by photo-deposition. The performances and effectiveness of prepared samples were evaluated towards H_2 production via water splitting in the presence of a visible solar irradiation source. The photocatalytic performances of Ag/CN/LDH with 3.0 wt. % of Ag exhibits highest values of H_2 generation, up to a 100 fold greater magnitude of yield if compared to the pure counterparts. The proposed mechanism to describe the observed performances of the Ag/CN/LDH is based on a charge carrier separation and migration, together with a redshifted optical absorption and quenched PL spectrum if compared to pristine LDH, CN or CN/LDH sample. The results obtained in this work qualifies the developed photocatalyst as an efficient and sustainable way for hydrogen production.

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Data Availability Statement: The authors are pleased to provide the published data upon email request

Conflicts of Interest: The authors declare no conflict of interest

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Chapter 6: Conclusions

In this thesis the synthesis, characterization and application of bimetallic nanomaterials focusing on their use in environmental remediation and energy conversion was deeply explored. The research addressed critical challenges in the development of nanomaterials for catalysis, pollutant degradation and energy applications by integrating advanced synthesis techniques and process intensification strategies. This approach allowed for the creation of high-performance nanomaterials with enhanced properties that are tailored for specific applications.

The work presented in this thesis has led to several key findings, each contributing to a better understanding and an advancement in nanomaterials production. These findings range on multiple areas, including the synthesis of bimetallic oxides and Layered Double Hydroxides (LDHs), the integration of composite catalysts, the effects of noble metal doping, and the performance of these materials in both environmental and energy-related applications.

6.1 Synthesis of Bimetallic Oxides and Layered Double Hydroxides (LDHs)

The primary objective of this thesis was to develop advanced bimetallic oxide nanomaterials and LDH-based composites. Bimetallic nanomaterials offer unique advantages due to their ability to combine the distinct properties of two metals, leading to synergistic effects that enhance their performance in catalytic and environmental applications. By employing synthesis methods such as co-precipitation, hydrothermal techniques, and Spinning Disc Reactor (SDR) technology, this research successfully developed Fe-Ni-Al bimetallic oxides and LDH materials with controlled size, shape, and surface morphology.

The use of process intensification techniques, particularly SDR technology, was a significant contribution to the field. SDRs enable rapid and controlled mixing of chemical precursors on a rotating disc, which promotes uniform nucleation and growth of nanoparticles. This method proved to be effective for synthesizing bimetallic nanomaterials with high surface area, uniform particle size, and enhanced catalytic properties. The ability to finely control the reaction conditions using SDRs resulted in nanomaterials that exhibit improved reproducibility and scalability, addressing one of the major challenges in nanomaterials synthesis.

One of the most significant outcomes of this research was the successful transformation of LDHs into mixed metal oxides through thermal decomposition (calcination). Calcination at controlled temperatures resulted in the formation of highly active metal oxides with large surface areas and uniform metal site distribution. These mixed metal oxides demonstrated superior catalytic activity in various processes, including carbon dioxide reforming, hydrocarbon cracking, and oxidative dehydrogenation. The presence of multiple oxidation states within these oxides facilitated redox reactions, further enhancing their catalytic performance.

6.2 Integration with Composite Catalysts

Another key aspect of this thesis was the integration of bimetallic oxides and LDH-based nanomaterials with composite catalysts such as graphitic carbon nitride ($\text{g-C}_3\text{N}_4$). $\text{g-C}_3\text{N}_4$ has gained attention in recent years due to its high photocatalytic activity, excellent chemical stability, and ability to form heterostructures with other nanomaterials. This thesis explored the synergistic effects of combining $\text{g-C}_3\text{N}_4$ with bimetallic oxides to enhance photocatalytic processes, particularly for pollutant degradation and energy conversion applications.

Furthermore, the integration of $\text{g-C}_3\text{N}_4$ with bimetallic oxides led to improved stability and durability of the photocatalysts. This is particularly important for practical applications, where long-term stability and resistance to deactivation are essential for the sustainable use of nanomaterials. The research demonstrated that the hybrid nanomaterials could maintain their catalytic activity over multiple cycles of pollutant degradation, highlighting their potential for real-world environmental remediation applications.

6.3 Noble Metal Doping to Enhance Catalytic Performance

The third major area of investigation in this thesis was the doping of bimetallic oxides and LDH-based composites with noble metals such as silver (Ag) and gold (Au). Noble metal doping is a well-established strategy for enhancing the catalytic properties of nanomaterials, as it introduces new active sites and improves electron transfer processes. The incorporation of Ag and Au nanoparticles onto the surface of the bimetallic oxides resulted in significant improvements in catalytic performance, particularly in reactions such as the hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and pollutant degradation.

The research showed that noble metal doping enhanced the catalytic activity of the bimetallic oxides by facilitating electron transfer and creating additional active sites for chemical reactions. This was particularly evident in electrochemical applications, such as fuel cells and water splitting, where the presence of noble metals improved the efficiency of key reactions. For example, Ag and Au-doped bimetallic oxides demonstrated increased activity in the ORR, which is a critical reaction in proton-exchange membrane fuel cells (PEMFCs). The improved electron transfer capabilities of the noble metal-doped materials resulted in lower overpotentials and higher current densities, leading to enhanced fuel cell performance.

In addition to their enhanced electrochemical performance, the noble metal-doped nanomaterials also exhibited improved photocatalytic activity for pollutant degradation. The presence of noble metals increased the absorption of visible light and promoted the generation of reactive oxygen species (ROS), which are essential for breaking down organic pollutants in water. This research demonstrated that noble metal doping is an effective strategy for improving the photocatalytic performance of nanomaterials, making them more efficient and versatile for environmental applications.

6.4 Applications in Environmental Remediation

One of the primary motivations behind this research was to develop nanomaterials that could be used for environmental remediation, particularly for the degradation of organic pollutants in water. The synthesized bimetallic oxides, LDHs, and noble metal-doped composites were tested for their ability to degrade a range of pollutants, including dyes, pharmaceuticals, and chlorinated hydrocarbons. The results demonstrated that these nanomaterials were highly effective in catalyzing the degradation of pollutants, often achieving complete degradation within a short period.

The photocatalytic degradation of organic pollutants was a key focus of this research. The hybrid nanomaterials, particularly those doped with noble metals, exhibited superior photocatalytic performance compared to traditional catalysts. This was due to their enhanced light absorption, charge separation, and generation of reactive oxygen species. The materials were tested under various conditions, including different light sources and pollutant concentrations, and consistently showed high degradation efficiency.

The research also explored the potential for these nanomaterials to be used in real-world water treatment systems. The stability and reusability of the catalysts were evaluated over multiple cycles of pollutant degradation, and the results indicated that the materials maintained their catalytic activity with minimal loss in performance. This is a crucial finding, as it demonstrates the potential for these nanomaterials to be used in sustainable water treatment systems that require long-term operational stability.

6.5 Applications in Energy Conversion

In addition to their environmental applications, the synthesized nanomaterials were also tested for their performance in energy conversion processes, particularly in fuel cells and supercapacitors. Bimetallic oxides and LDH-based nanomaterials are known for their excellent electrochemical properties, making them ideal candidates for use in energy storage and conversion devices.

The research demonstrated that the noble metal-doped bimetallic oxides exhibited enhanced performance in key electrochemical reactions, such as the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR). These reactions are critical for the operation of fuel cells, which convert chemical energy into electrical energy. The noble metal doping improved the efficiency of these reactions by reducing the overpotential and increasing the electron transfer rate, resulting in higher power output and improved overall performance of the fuel cells.

The materials were also tested as electrodes in supercapacitors, where they demonstrated high specific capacitance, excellent cycling stability, and fast charge-discharge capabilities. These properties are essential for the development of high-performance energy storage devices that can be used in portable electronics, electric vehicles, and renewable energy systems. The research highlighted the potential for these nanomaterials to be used in next-generation energy storage and conversion technologies, where efficiency, stability, and scalability are key considerations.

6.6 Future works

While this research already has provided some significant contributions to the field of bimetallic nanomaterials, several areas require further investigation to fully realize the potential of these materials in practical applications. The following are some suggestions of future work for further research and development:

1. **Scale-Up and Industrial Application:** One of the major challenges in the field of nanomaterials is the ability to scale up the synthesis processes for industrial applications. While this research demonstrated the effectiveness of SDR technology and other synthesis methods for producing nanomaterials with consistent properties, further work is needed to optimize these processes for large-scale production. Future research should focus on identifying the key factors that influence scalability, such as precursor concentration, reaction temperature, and reaction time, to ensure that the nanomaterials can be produced at an industrial scale without compromising their performance.
2. **Long-Term Stability and Reusability:** Although the synthesized nanomaterials demonstrated excellent catalytic performance in laboratory settings, their long-term stability and reusability in real-world applications require further investigation. Issues such as nanoparticle aggregation, catalyst deactivation, and leaching of noble metals need to be addressed to ensure the sustainable use of these materials in environmental and energy systems. Future research should focus on developing strategies to improve the stability and durability of the nanomaterials, such as coating or encapsulating the nanoparticles to prevent degradation.
3. **Broader Applications:** While this research primarily focused on environmental remediation and energy conversion, bimetallic nanomaterials hold potential for a wide range of other applications, including biomedical applications, electronics, and agriculture. For example, bimetallic nanoparticles could be used in drug delivery systems, where their unique properties could enhance the efficacy and targeting of therapeutics. Additionally, these materials could be explored for use in flexible electronics and sensors, where their electrical conductivity and mechanical strength could enable the development of advanced devices. Expanding the scope of research

to explore these applications could yield new insights and opportunities for innovation.

4. **Green Synthesis Techniques:** As sustainability becomes an increasingly important consideration in nanomaterials research, future work should focus on developing green synthesis techniques that minimize the use of toxic chemicals and reduce the environmental impact of nanomaterials production. This could involve the use of natural reducing agents, such as plant extracts or microorganisms, to synthesize nanoparticles in a more environmentally friendly manner. Additionally, solvent-free synthesis methods and the use of renewable energy sources for material production could further reduce the ecological footprint of nanomaterials.
5. **Exploring New Combinations of Metals:** While this research focused on specific combinations of metals, such as Fe, Ni, Al, Ag, and Au, future work could explore the use of other metal combinations to further enhance the properties of the nanomaterials. For example, incorporating transition metals, rare earth elements, or non-metallic elements into the nanomaterial structure could lead to the development of materials with new and improved catalytic, electronic, or optical properties. This could open up new possibilities for the use of nanomaterials in a wider range of applications.

6.7 Final Remarks

In conclusion, this thesis has contributed to the advancement of bimetallic nanomaterials and their applications in catalysis, environmental remediation and energy conversion. Using process intensification techniques and advanced synthesis methods, high-performance nanomaterials with enhanced properties were developed. The integration of composite catalysts and noble metal doping further improved the catalytic efficiency and stability of these materials, making them suitable for practical applications.

The findings of this research have significant implications for the design and development of next-generation nanomaterials that can be used to address global challenges such as pollution, climate change, and energy sustainability. As the field of nanomaterials continues to evolve, the insights gained from this research will serve as a foundation for future work aimed at

creating more efficient, sustainable, and scalable technologies for environmental protection and renewable energy production.