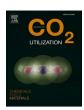
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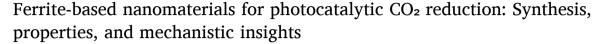
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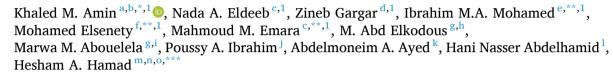
# Journal of CO<sub>2</sub> Utilization

journal homepage: www.elsevier.com/locate/jcou



# Review Article





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## ARTICLE INFO

# Keywords: Magnetic ferrites CO<sub>2</sub> conversion Physicochemical properties Air purification Solar fuels

#### ABSTRACT

The scientific community has shown increasing interest in the use of magnetic nanoparticles, particularly ferrite-based nanomaterials, for the photocatalytic reduction of carbon dioxide (CO<sub>2</sub>). Compared to other nanomaterials, they could provide a range of advantageous characteristics, including high performance, low cost, low toxicity, and distinctive magnetic properties that facilitate separation using external magnetic fields. This review offers a comprehensive and updated assessment of ferrite-based magnetic nanomaterials for photocatalytic CO<sub>2</sub> reduction. It uniquely integrates recent advancements in synthesis, properties, and mechanistic insights, highlighting emerging materials to bridge fundamental science with practical challenges for sustainable CO<sub>2</sub> conversion and solar fuel generation. It presents a thorough overview of their synthesis, characterization, and photocatalytic properties, surveying techniques like dimensional tuning, co-catalyst loading, doping, coupling with plasmonic materials, oxygen vacancies, charge separation methods, morphological optimization, porosity enhancement, heterojunction formation, and Z-scheme implementation. By bridging the gap between fundamental science and applied challenges, this review identifies emerging design principles and future directions for developing highly efficient, magnetically recoverable photocatalysts aimed at mitigating CO<sub>2</sub> emissions through solar-driven chemical transformation.

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Received 15 April 2025; Received in revised form 26 June 2025; Accepted 12 July 2025 Available online 22 July 2025

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#### 1. Introduction

Environmental pollution and the energy crisis are amongst the most significant contemporary global challenges [1–3]. Both the generation of power and its use have substantial repercussions for the natural environment. Among several methods, photocatalytic technology is one of the viable approaches that offers several advantages, including the low cost of the process, as well as operation under ambient pressure and temperature [4,5]. However, based on the relevant literature and a number reviews, the main technical barriers that limit the utilization of photocatalysts include the following: (i) first and foremost, the quantified energy bandgap structure implies the absorption of a quantified amount from the solar spectrum, which leads to low energy utilization; (ii) the e<sup>-</sup>/h<sup>+</sup> rapid recombination via heat generation or luminescence; and (iii) difficulty in the direct recovery and isolation of photoactive materials after catalysis [6,7]. All these constraints hamper economic characteristics and the long-term sustainability of heterogeneous photocatalyst materials. Consequently, the chemical fabrication of an appropriate photocatalyst that is active in solar power generation is critical to achieving acceptable photocatalytic efficiency results. Therefore, the chemical design of high-performance, easily separated photocatalysts is a priority in photocatalysis technology.

Among several materials that can be used as photocatalysts, titanium dioxide ( $\text{TiO}_2$ ) is the most extensively studied, owing to its powerful oxidation power, chemical and biological inertness, low cost, and high stability across a broad pH range [8,9].  $\text{TiO}_2$  is considered a pioneering and well-studied photocatalyst due to its high reactivity, eco-friendliness, and sufficient stability, as well as a bandgap of  $3.03\,\text{eV}$  (rutile), and  $3.18\,\text{eV}$  (anatase). While the bandgap of  $\text{TiO}_2$  is appropriate for photocatalysis compared to other metal oxides e.g., ZnO, CdS, and WO<sub>3</sub> [10–13],  $\text{TiO}_2$  faces significant limitations:  $\text{TiO}_2$  can only absorb a small portion of the visible region of sunlight and is difficult to separate and recover after a photocatalytic reaction [14,15].

To address these fundamental limitations, particularly the challenges of visible light utilization and catalyst recovery, magnetic photocatalysts have emerged as a promising solution. Magnetic photocatalysts were first developed by Hiroshi et al. in 1994, who prepared magnetic photocatalysts via the deposition of TiO<sub>2</sub> over a magnetite substrate [16]. Magnetic materials have gained increasing priority in several disciplines, such as catalysis [17,18], biomedicine/biotechnology [19-22], and water treatment [23-25]. Magnetic photocatalysts offer alternative solutions to the issues of visible light response and catalyst recovery challenges. The integration of magnetic properties into photocatalysts has been developed to take advantage of both high activity and the easy reusing of semiconductor photocatalysts. Magnetic nanoparticles (MNPs) have emerged as promising candidates for the photocatalytic reduction of carbon dioxide (CO2) and photocatalytic degradation of hazardous compounds due to their unique advantages, including high performance, low cost, low toxicity, and distinctive magnetic properties. Several thorough reviews have already been published that focus on magnetic photocatalysts [7,26-28]. However, few evaluations have concentrated on the adaptable qualities and logical construction of magnetic-based photocatalysts.

Recently, photocatalytic CO<sub>2</sub> reduction has gained significant attention due to its dual role in addressing both energy shortages and greenhouse gas mitigation [29]. Compared to other nanomaterials like TiO<sub>2</sub>, which often suffer from challenges such as rapid electron-hole recombination and difficult post-reaction separation, ferrite-based magnetic nanomaterials offer significant advantages due to their tunable magnetic properties, narrow bandgaps, and structural versatility [30]. Despite their promise, a systematic and focused evaluation of their synthesis strategies, structure-activity relationships, and mechanistic roles in photocatalytic CO<sub>2</sub> reduction is still lacking. Most prior reviews have only broadly addressed materials properties including heteroatom-doped/hierarchical porous carbon materials [31], transition metal nitrides [32], porous aromatic frameworks [33], covalent

heptazine framework [34], MXene@MOF [35] as well as ferrites [36] without studying deeply into the nuanced role of ferrites in photocatalytic applications.

This review aims to fill this critical gap by providing a contemporary and comprehensive analysis of ferrite-based magnetic nanomaterials, emphasizing their synthesis, structural modification, and photocatalytic mechanisms with a focus on their application in heterogeneous photocatalysis for environmental remediation and sustainable energy conversion. The review will elucidate the key features required by the research community to gain a comprehensive understanding of the behaviors shown by magnetic materials in the context of generation of solar fuels through CO2 reduction, and provide insights into the design and development of MNP-based photocatalysts with enhanced performance for environmental remediation and sustainable energy production. Particular emphasis is placed on performance-enhancing techniques such as bandgap engineering, charge carrier optimization, and hierarchical morphology regulation. The photocatalytic activity of MNPs can be further enhanced through dimensional tuning, co-catalyst loading, doping, and coupling with plasmonic materials, the utilization of oxygen vacancies, charge separation approaches, morphological considerations, porosity optimization, heterojunction formation, and the implementation of the Z-scheme. These techniques can be used to tailor the physicochemical characteristics of MNPs, such as their bandgap energy, surface area, and charge separation efficiency, in order to achieve optimal photocatalytic performance. This review provides an integrated overview of the synthesis, characterization, and photocatalytic characteristics of ferrite-based magnetic nanomaterials, and offers a comprehensive examination of several techniques employed to promote photocatalysis for air purification and energy conversion applications. By integrating current advancements and addressing key knowledge gaps, this review provides valuable insights into the design of next-generation magnetic photocatalysts with enhanced activity, selectivity, and reusability. We believe that the information presented will inform future advancements in practical and scalable photocatalytic devices, facilitating clean energy generation and environmental remediation and helping to address the difficulties associated with the widespread use of magnetic-based photocatalysts in the production of renewable and sustainable energy.

# 2. Magnetic photocatalysts

The most extensively used iron oxide-based materials are magnetite (Fe<sub>3</sub>O<sub>4</sub>), maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>), and MFe<sub>2</sub>O<sub>4</sub> (where M stands for divalent metallic cations, e.g., Cu, Zn, and Co). Magnetic photocatalysis has received extensive attention due to its paramagnetic/ferrimagnetism, moderate environmental impact, low-toxicity, high-adsorption capacity, and stability [37]. A primary advantage is their simple recovery for liquid phase reactions, eliminating the need for complex centrifugation or filtration, which contributes to increased durability by preventing agglomeration. Unfortunately, some drawbacks have been raised by implementing magnetic photocatalysts, such as photocatalytic performance and their stability as the contact between the utilized photocatalysts and magnetic particles causes the photogenerated electron-hole recombination and the photo-dissolution of the magnetic particles [14]. Magnetic photocatalysts can be simply recovered for liquid phase reactions [28]. One of the main advantages of magnetic separation is the conformity removal of the enforced catalyst from the liquid phase without complex centrifugation, filtration, or other impractical approaches for recycling, leading to expected durability increasing due to their agglomeration-avoiding properties [38,39].

To circumvent such limitations of the low photocatalytic activities, several approaches have been implemented by research and overcome the technical issues. In addition, many attempts have been made to modify the structural, optical, electrical, and photoelectrochemical properties, which resulted in improvement in the photocatalytic activity of iron oxide-based nanomaterials such as doping [40]. Another strategy

for improving photocatalytic activity is the coupling of magnetic materials with semiconductor photocatalysts, which seems to be one of the most adequate solutions. The validity of the separation of non-magnetic materials can be accomplished using magnetically-separable materials in the hybrid photocatalytic framework [41–43].

Bibliometric analysis is a crucial statistical tool for mapping the top of the line in certain areas of research and identifying critical data for a variety of reasons, including identifying potential research topics and corroborating findings. The technique involves tools for identifying and analyzing indexed keywords based on the number of citations, revealing general trends through keyword analysis, and identifying and clustering knowledge gaps in recent publications. The network and density visualization (Fig. 1) demonstrate a bibliometric mapping analysis employing the most recent 5000 results up to the year 2025, as documented in Scopus. The Data were collected using the keywords "ferrites", "magnetic materials", and "magnetite". This map visually represents the interconnectedness of research themes, highlighting prominent areas of investigation and emerging trends within the field of magnetic materials. It reveals clusters of related works and identifies key research directions, thereby providing a foundational context for the current review by illustrating the historical and contemporary landscape of ferrite research.

#### 3. Fundamentals of ferrite-based magnetic photocatalysts

The increased appeal of transition metal oxides, endowed with magnetic properties, can be readily elucidated in light of their promising

conductivity, catalytic performance, magnetic characteristics, electronic properties, and photo response [44]. Of the several types of magnetic nanoparticles, ferrites are a particularly noteworthy category of magnetic materials that have found broad application in numerous fields. As the magnetic response is strongly dependent on porosity, surface area, and the size of the prepared particles, the synthesis of particles with different sizes could allow for the tailoring of the particles to specific applications [6,45].

Ferrites represent a category of ceramic materials that are produced through the process of combining and heating iron (III) oxide (Fe<sub>2</sub>O<sub>3</sub>, often known as rust) with one or more metallic elements, including, but not limited to, manganese (Mn), strontium (Sr), barium (Ba), zinc (Zn) and nickel (Ni). Most of the reported ferrites have the chemical formula  $M^{2+}Fe_2^{+3}O_4^{2-}$ ; wherein M is indicative of divalent metal ions, including  $Ni^{2+}$ ,  $Mn^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ , and others. Combining two or more types of M<sup>2+</sup> ions, or a monovalent ion with a trivalent metal ion, results in the creation of mixed ferrites that can be modified and tailored to specific applications. Ferrites are ferrimagnetic oxides that possess both high magnetic and high electrical resistivity. The saturation magnetization of ferrites is less than half that of ferromagnetic alloys; nevertheless, they possess advantages like withstanding high frequencies, greater heat resistance, lower prices, and higher corrosion resistance. In recent studies, some ferrites have been reported as electrophotocatalyst, including NiCo nanoferrites [46]. Ferrite-based electrophotocatalysts have exhibited inherent limitations that include low conductivity, a limited redox-active surface area, and inefficient charge-transfer kinetics. These issues could be addressed through the following

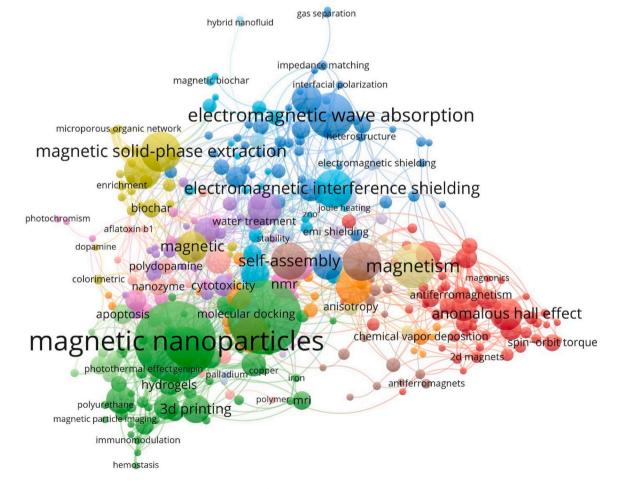


Fig. 1. Bibliometric mapping: network visualization and density visualization of research themes related to ferrites, magnetic materials, and magnetite, based on recent Scopus data. The map illustrates the interconnectedness of research areas, highlighting prominent topics and emerging trends within the field of magnetic materials.

approaches: doping, heterostructure engineering, integration with conductive frameworks, and defect modulation strategies to enhance charge carrier dynamics.

# 4. Synthesis strategies of ferrite nanoparticles

The development of diverse techniques for the synthesis of ferrite nanoparticles has been the subject of substantial research over the last decade. To create ferrite nanoparticles of the optimal size, shape, stability, and biocompatibility, various synthetic approaches have been employed. The synthesis process is governed by two factors: practicability and cost-effectiveness. The magnetic iron oxide photocatalysts' inherent colloidal characteristic makes the synthesis process time-consuming. Advanced chemical-based synthetic approaches including co-precipitation [47,48], microemulsion[48,49], thermal decomposition, microwave [50,51], hydrothermal (solvothermal) [52,53], sonochemical [53,54], and biosynthesis approaches [55,56] have been followed for the synthesis of ferrite-based magnetic photocatalysts (Fig. 2).

# 4.1. Co-precipitation

Hydrolytic coprecipitation, which utilizes the Massart process, is a method for designing MNPs on a large scale that has been recognized in the scientific community [57]. The coprecipitation is carried out  ${\rm Fe^{2+}/Fe^{3+}}$  salt solution with a high pH value, at either ambient or elevated temperatures. The rapid growth of monomers has exceeded the critical supersaturation, followed by slower growth, resulting in the synthesis of small particle sizes in the nanoscale range. Thereafter, the nuclei develop at the same speed, resulting in monodisperse NPs [58]. Even though this rapid approach has extraordinary shape and phase homogeneity control, it has poor size control [59]. Experimental characteristics, such as the practiced temperature, pH, and salts employed,  ${\rm Fe^{2+}/Fe^{3+}}$  ratio, as well as the nature of the base, have a significant consequence on the size and form of the designed NPs. However, the pH parameter is one that affects the size of MNPs [60]. The repulsion among initial MNPs adds smaller magnetite NPs as the pH of the reaction rises.

Overall, this method makes use of low-cost ingredients and moderate reaction conditions, and it may be used to directly synthesize nanoparticles in water. Topel *et al.* and Bhandari *et al.* developed polyethyleneimine (PEI)-coated Fe<sub>3</sub>O<sub>4</sub> NPs with a measured diameter of approximately 10 nm that were covalently coupled with fluorophores using a modified coprecipitation process [61,62]. Shape-controlled iron oxide nanoparticles can also be made using the coprecipitation approach. Shen *et al.* have recently studied the production of Fe<sub>3</sub>O<sub>4</sub> NPs with improved saturation magnetization in different forms, including nanocubes, nanoneedles, and nanospheres using a coprecipitation approach, and by changing the proportion of surfactant. The morphology of the prepared materials can be controlled via the amount of surfactant (sodium dodecyl sulfate), according to the results from transmission electron microscopy (TEM) [63].

# 4.2. Hydrothermal

The hydrothermal process is defined as the development of ferrite nanoparticles in an aqueous environment under conditions of elevated pressure and temperature, which are meticulously calibrated to ensure optimal functionality [64]. This approach uses a sealed container or autoclave to perform a chemical reaction at a certain temperature and high vapor pressure. The procedure is known as hydrothermal synthesis when water is used, with the reaction solvent and another solvent being referred to as solvothermal synthesis. The production of crystalline ferrite nanoparticles of uniform size can be achieved through the execution of reactions in aqueous solutions at elevated temperatures and pressures [65]. Various studies have been published on using hydrothermal synthesis to produce iron oxide MNPs, either with or without the use of stabilizing surfactants [66,67]. A surfactant-free hydrothermal approach was developed to create iron oxide NPs with nano-sized holes. The produced samples were calcined in air and nitrogen, yielding MNPs with cavities ranging from 7 to 15 nm and 5-12 nm in diameter, respectively [68]. The shape and crystallinity of the produced MNPs were determined by the correct solvent mixture, time, pressure, and temperature. When compared to the microemulsion method, this method can produce better NPs. However, because this procedure

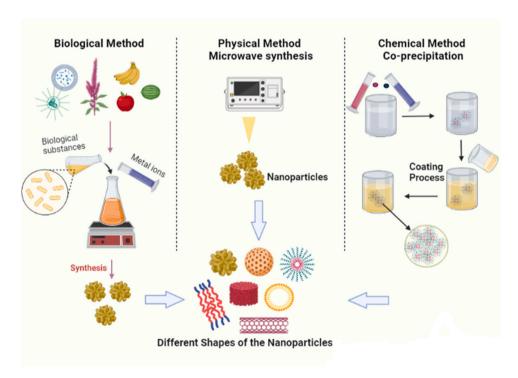


Fig. 2. Diverse fabrication strategies for spinel ferrite-based nanomaterials, illustrating biological, physical, and chemical methods. The figure was created with BioRender.com.

necessitates high pressure and requires more power, it must be carried out with extreme caution and with specialized equipment. In comparison to sol-gel and other approaches, the hydrothermal process is favored because it produces NPs of the desired shape, size, crystallinity, and composition consistency [69]. However, as the reaction requires high temperatures and pressures and the use of special reactors, the strategy is not as energy-efficient if compared with other simple fabrication methodologies.

# 4.3. Microemulsion

Based on thermodynamics, microemulsion is a stable isotropic dispersion of two immiscible phases (like water and oil) in the presence of surfactants or co-surfactants. The monolayer could be formed at the interface layer between the two phases of water and oil [70]. The fundamental disadvantage of hydrolytic methods is their inability to obtain a homogeneous size in the synthesized ferrite NPs. As a result, amphiphilic molecules (surfactants) were used to improve reaction conditions by creating nanoreactors in which the coprecipitation process could take place in constrained environments, either as micelles or reverse micelles. The aqueous phase microemulsions (water-in-oil, w/o) were distributed as micro-droplets (typically less than 50 nm in diameter) in the continuous hydrocarbon phase, which was enclosed by the utilized surfactant molecules. The contents of the utilized surfactant affect the reverse micelle size [71]. The microdroplets in bi-identical microemulsions (w/o) carrying the appropriate reactants would then collide, consolidate, and break, eventually forming precipitate in the micelles [72]. However, by adding a solvent to the microemulsions (like ethanol or acetone), the precipitate could be easily removed via centrifuging or filtration. Microemulsions could be employed in this situation. The w/o microemulsion technique was utilized to design ferrite NPs through the use of several types of surfactants to evaluate the shape, size, homogeneity, and crystallinity of the produced MNPs. The oil phase was n-heptane, with traditional one-chain surfactants and new Gemini surfactants, whereas the co-surfactant phase was n-hexanol. The displayed results reveal that the film flexibility of reverse micelles and the lifetime of a surfactant in the formed micelle have a substantial impact on nanocrystalline nucleation and growth. Furthermore, the temperature of the samples had a major effect on crystal defects, with the hydrophobic chain length having a significant impact on the lattice defect in response to temperature changes [73]. Consequently, the microemulsion approach has a significant impact on the design of MNPs with limited size distribution and homogeneous magnetic characteristics, given the increased size control. However, when compared to the coprecipitation process, the microemulsion route produces MNPs with poorer yields and lower crystallinity. However, it has been demonstrated that heating the reverse micelle improves the crystallinity of ferrite. Scaling up is also problematic because of the sensitivity of the preparation environments, the necessity for significant volumes of non-aqueous solvent, and the difficulty of removing the utilized surfactants [74].

# 4.4. Thermal decomposition

Thermal decomposition has been employed to produce high-quality ferrite MNPs [75] [71,76]. The procedure entails the decomposition of metal components in boiling organic solvents in the presence of surfactants, thereby yielding stable MNPs with well-defined magnetic characteristics [77]. The key reason for the success of this method can be attributed to the rapid burst nucleation followed by crystallization. The process can be further optimized by controlling associated factors, such as the type of precursor and surfactant, their relative ratios, solvent, reaction temperature, and reaction duration [70]. Earlier studies have described the thermal decomposition method for synthesizing MNPs with a limited size distribution in the range of 3–50 nm and form control, exhibiting spherical or cubic morphology [78,79]. Hufschmid *et al.* 

studied the chemical production of iron oxide NPs from the degradation of various precursors for their capacity to create NPs with specific size and phase purity requirements [75]. In contrast, the creation of harmful organic–soluble solvents is a danger factor associated with this approach, which decelerates its practice in the biomedical sector [50]. For producing magnetic particles of smaller sizes, the thermal composition is more recommended than coprecipitation.

# 4.5. Microwave-assisted technology

The microwave-assisted methodology has gained interest due to its merits of quick volumetric heating, higher rate of reaction, reduced reaction time, and increased familiar yield [80]. Microwaves can be employed as another source of heat, either on their own or in combination with other synthesis methods. This method has been classified as a non-hydrolytic approach because the microwave-assisted technique is frequently paired with thermal breakdown. It can also be used to speed up hydrolytic processes such as hydrothermal and sol-gel. Microwave-assisted polyol methodology was used to produce spinel-structured MIFe<sub>2</sub>O<sub>4</sub> (M is Mn or Co) NPs with diameters smaller than 10 nm [81]. The small particle sizes are most likely the consequence of the microwave synthesis's rapid and homogenous reactions. They discovered that by altering the water ratio to ethylene glycol (EG) during microwave heating, they could control the reaction temperature and crystal quality. Gonzalez-Moragas et al. recently reported on the production of aqueous-dispersible iron oxide NPs using a microwave-aided methodology. They used multimode equipment to raise the volume of the reaction from 4.5 up to 50 mL, resulting in a significant reduction in the compulsory cost, energy, and duration of producing high quantities of MNPs [51]. The fundamental benefit of introducing microwaves into the reaction system is the ability to obtain an exceptionally fast kinetic crystallization. However, other approaches, including thermal decay, co-precipitation, and so on, require processes for improving crystallinity due to long reaction periods, which account for industrial or commercial usage.

#### 4.6. Sonochemical method

This approach utilizes the acoustic cavitation phenomenon for synthesis due to the constant production, expansion, and abrupt collapse of bubbles in solutions. When the solution container is placed in an ultrasonic reactor with a high cooling rate, high pressure, and a high temperature, NPs are created by the collapse of bubbles accompanied by severe shockwaves and micro-jets [82]. As the bubbles have already been formed, they have effectively accumulated ultrasonic energy and a vacuum emboldens the diffusion of solute vapor into their volumes, resulting in the development of bubbles. This growth may continue until the bubble reaches its maximum size and collapses, releasing the stored energy [83]. It has been established that the substantial cooling rates of collapsed bubbles yield amorphous or, in other words, low-crystalline NPs. Conversely, non-volatile precursors have the capacity to yield nanostructured products [84]. Abbas et al. used a sonochemical approach to make homogenous ferromagnetic magnetite nanocubes in the absence of surfactants [85]. To enhance the crystallinity of the magnetic nanocubes, a 600 °C annealing process was employed. However, the presence of a thin non-magnetic dead layer on the surface resulted in a reduction of the saturation magnetization with increasing annealing temperature. the presence of a thin non-magnetic dead layer on the surface resulted in a reduction of the saturation magnetization with increasing annealing temperature. Bang et al. introduced the use of carbon templates to produce nanoscale particles from hollow iron oxides [86]. The assembled NPs were crystalline hematite with extremely weak ferromagnetism and were thermodynamically-stable.

Notwithstanding the necessity for the ultrasound irradiation mechanism, the sonochemistry methodology significantly reduces the anticipated reaction time by enhancing mixing through a non-invasive

energy mechanism. The process under investigation yields NPs that exhibit a restricted, homogeneous size distribution. Additionally, these NPs demonstrate high crystallinity and adequate dispersity.

#### 4.7. Biosynthesis

The green source preparation of NPs via the biosynthesis method has gained wide attention [87]. The process involves the implementation of various techniques aimed at the elimination of hazardous compounds, thereby ensuring environmental safety. Plants are currently being studied for their ability to biosynthesize metal NPs, which can be synthe sized utilizing plant tissue [88], extract [89–91], exudates [92], fungi [93], and enzymes [94]. It is critical to address effective procedures for the synthesis of NPs for further biomedical uses [95]. In addition, utilizing plants could sometimes be more advantageous than other biological procedures, as it eliminates the time-consuming of maintaining microbial cultures [96]. The application of F. oxysporum and Verticillium sp. with an aqueous solution of ferricyanide [Fe(CN)<sub>6</sub>]<sup>3+</sup> and ferrocyanide [Fe(CN)<sub>6</sub>]<sup>4+</sup> has been demonstrated to produce magnetite NPs with proper stoichiometr. F. oxysporum has been observed to yield quasi-spherical magnetite NPs with a particle size ranging from 20 to 50 nm, while the Cubo octahedral magnetite NPs were produced by verticillium sp. and revealed a size in the range of 100-400 nm [97]. Lagenaria siceraria leaves generated cubic and well-stable biomagnetic Fe<sub>3</sub>O<sub>4</sub> NPs (BMNPs) with a size of 30–100 nm using a hot water extract. The antioxidant behavior and biocidal activity against Escherichia coli and Staphylococcus aureus were enhanced [98]. The aqueous extract of the Lantana camera was used to make a less costly and environmentally friendly design of iron oxide NPs [105]. The photosynthesized NPs were proven to be pure and crystalline, with a particle size of 10-20 nm. Moreover, Sandhya and Kalaiselvam used an alcohol extract of Borassus flabellifer L. seed peels to synthesize hexagonal facets 35 nm Fe<sub>3</sub>O<sub>4</sub> NPs [98]. For the construction of magnetite NPs, the biosynthesis method has several advantages: it is non-toxic, cost-effective, and ecologically friendly methodology. However, the state of reaction and the size of the magnetite NPs can be regulated in a single-vessel reaction under low conditions.

# 4.8. Comparative overview of synthesis strategies

The method of synthesizing ferrite-based magnetic nanoparticles used in photocatalytic  $CO_2$  reduction greatly influences their properties and performance. Different techniques offer varying degrees of control over size, crystallinity, and surface characteristics. It is therefore essential to select an appropriate synthesis approach, bearing in mind that each method offers specific advantages and limitations with regard to control over nanostructure, scalability, cost and environmental impact (Table 1). There are trade-offs in terms of scalability, cost, and environmental impact.

The choice of synthesis method for ferrite-based materials is critical and depends heavily on the intended application, particularly for the photocatalytic reduction of CO2. While co-precipitation is simple and inexpensive for large-scale production, precise control over particle size and homogeneity is often difficult to achieve, which can impact photocatalytic efficiency. Conversely, hydrothermal synthesis yields highly crystalline and uniformly sized nanoparticles, but the high pressure and temperature required limit its energy efficiency and scalability for industrial applications. Microemulsion methods provide excellent control over size, but suffer from low yields and the need for large volumes of organic solvents. Thermal decomposition can produce high-quality, monodisperse nanoparticles, but it involves the use of toxic organic solvents. Microwave and sonochemical methods offer rapid synthesis and improved crystallinity, but they still require further development for mass production. Biosynthesis, while environmentally friendly, presents challenges in controlling particle size and properties. Therefore, for efficient photocatalytic CO2 reduction, methods that offer a balance between precise control over material properties (e.g., bandgap, surface area, defect concentration) and scalability, cost-effectiveness, and environmental benignity are preferable. Future research should focus on optimizing hybrid approaches or developing novel green synthesis routes that can achieve high yield, purity, and controlled nanostructures suitable for industrial-scale CO2 conversion.

# 5. Physico-chemical properties of ferrites-based magnetic photocatalysts

It is well known that the comprehensive properties of ferrites themselves, including their crystal structural, surface physicochemical, stability, optical, adsorption, electrochemical, photoelectrochemical, and electronic properties, critically determine the photocatalytic efficiency of ferrite-based magnetic photocatalysts. Consequently, fundamental comprehension and deterministic control of the previously mentioned characteristics will allow for the rational design and scalable production of ferrite-based magnetic nano photocatalysts with optimized photocatalytic behavior. This will be advantageous for developing some sturdy ferrites-based magnetic nanomaterial systems for practical photocatalytic applications, as well as fundamental insights into photocatalytic enhancement mechanisms at the single-atom level. The performance of ferrite-based nanomaterials for photocatalytic CO<sub>2</sub> reduction is intricately linked to their intrinsic structural and morphological characteristics. Structural and chemical features determine phase purity and composition, while vibrational analysis reveals bonding and molecular interactions. Surface area and functional groups affect reactivity and dispersion. The specific morphology of nanostructures is vital; two-dimensional (2D) nanosheets, for example, offer maximized surface exposure and reduced charge carrier diffusion distances, facilitating more efficient reactions [106]. Furthermore, controlled defect engineering, such as the introduction of oxygen vacancies, can create

**Table 1**Comparative analysis of synthesis methods for ferrite-based magnetic photocatalysts.

Technique	Advantages	Disadvantages	Ref.
Coprecipitation	Mild conditions; Synthesis in aqueous media; Large quantity	Time-consuming; Low reproducibility; Impurities	[99]
Hydrothermal	Narrow scale-size distribution; Good crystallinity; Synthesis in aqueous media	High T; High P; Special autoclaves	[100]
Sonochemistry	High crystallinity; Saturation magnetization; Narrow size distribution; Good dispersivity	Ultrasound wave irradiation equipment is required; The mechanism is still not well understood	[101]
Microemulsion	Thermodynamically stable; Improved size control	Poor crystallinity; Low reaction yield; Huge quantities of organic solvents are required; High temperature and pressure	[102]
Thermal decomposition	High yield; Controllable size; High crystallinity	High temperature; Toxic organic solvents	[50]
Microwave-assisted	Rapid kinetic for crystallization; High yield of product; high	Homogeneous nucleation occurs Because of uniform heating; Need for organic	[51,
	energy efficiency	solvent	103]
Biosynthesis	Higher biocompatibility; Environmentally-/eco-friendly	Difficult control in terms of size and properties; High temperature; Poor	[104,
	reducing agent	reproducibility	105]

mid-gap states that improve visible light absorption and facilitate charge separation within the ferrite crystal lattice. Magnetic measurements provide insights into spin dynamics and superparamagnetism, and optical/photoelectrochemical properties govern light absorption and charge transfer. Understanding these interconnected features is essential for optimizing MNPs for targeted applications.

#### 5.1. Structural properties

The incorporation of the transition metal oxides with spinel structures brings up the most important magnetic photocatalysts, which are designated as ferrites. Depending on their crystallinity, ferrites can be classified into four distinct categories as presented in Fig. 3: (i) spinel (MFe<sub>2</sub>O<sub>4</sub>, where M is Ni, Fe, Zn, Cu... etc.); (ii) garnet (M<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>, where M is rare earth elements); (iii) hexagonal (MFe<sub>12</sub>O<sub>19</sub>); and (iv) orthoferrite (MFeO<sub>3</sub>) [107–109].

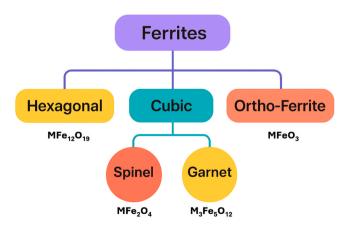
Spinel ferrites are a diverse type of material with a wide range of electronic, magnetic, and chemical aspects. Spinel transition metal oxides (AB $_2$ O $_4$ ) containing two metals have recently shown the ability to tune the energy density and working voltage by regulating the metallic configuration [110,111]. Spinel ferrites have been used in inductors, transformers, magnetic recording, gas sensors, and photocatalysts, amongst other applications. The different spinel types of ferrites are classified into three groups based on the positions of ferric ions on the crystal lattice as follows:

# a) Normal spinel ferrites

A typical spinel structure, in which cations (II) exclusively occupy the tetrahedral site and Fe (III) ions utilize the octahedral site, is characteristic of this class of compounds. The structural formula could be  $[M^{2+}]_{Tetra}[Fe^{3+}]_{Octa}O_4$ , where M denotes divalent cations (II) while 'tetra' and 'octa', refer to tetrahedral, and octahedral sites, respectively. It is imperative to note that only one type of cation is permitted at each location.  $ZnFe_2O_4$  is an example of a normal spinel, in which the divalent  $Zn^{2+}$  accommodates the tetrahedral regions, with the octahedral locations accommodated by  $Fe^{3+}$  [112,113]. Spinel ferrite,  $Fe_3O_4$ , which belongs to the ferromagnetic materials, possesses a cubic system and an inverse spinel structure with Fd3m [114]. The unit cell of magnetite (Fe\_3O\_4) contains  $Fe^{3+}$  and  $Fe^{2+}$  ions with good magnetic properties and 32 oxygen ions in regular cubic closed packs with vacancies in Fe sites, which induce reduced symmetry of crystals [115].

## b) Inverse spinel ferrites

In the inverted spinel structure, cations (II) occupy the octahedral locations, whereas Fe(III) accommodates both tetrahedral and octahedral sites. The inverse spinel has the chemical formula  $[Fe^{3+}]_{Tetra}[M^{2+}\ Fe^{3+}]_{Octa}O_4$ . Two cations, namely the divalent and



**Fig. 3.** Schematic classification of ferrites according to their crystal structure, showing the four major types: spinel, garnet, hexagonal, and ortho-ferrite.

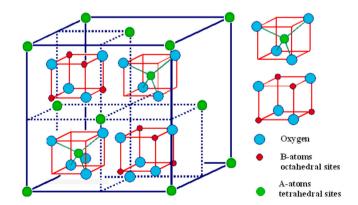
trivalent Fe (III) ones, accommodate the octahedral site [113]. The naturally occurring spinel structure  $\rm Fe_3O_4$  possesses an inverse spinel structure, with  $\rm Fe^{2+}$  accommodating octahedral sites and  $\rm Fe^{3+}$  encompassing both octahedral and tetrahedral positions.

#### c) Mixed spinel ferrites

In a mixed spinel structure, the divalent and trivalent cations occupy both octahedral and tetrahedral positions. These cations are partially housed on octahedral and tetrahedral sites to create the mixed spinel structure [116,117], which has the formula  $[M_{1-}^{2+}Fe^{2+}]_{Tetra} [M_{\delta}^{2+}Fe^{2+}]_{Octa}O_4$ , where  $\delta$  is the inversion degree. In the case of a mixed spinel structure, two metal ions  $(M^{2+})$  and  $(Fe^{3+})$  are distributed on tetrahedral and octahedral sites [118]. A well-known example of mixed spinel ferrite is copper ferrite (CuFe<sub>2</sub>O<sub>4</sub>). It is worth mentioning that the metal cations in both sites are distributed according to their tendency to occupy the positions, which is influenced by many parameters such as stabilization energy, radii of metal cations, interstitial site size, synthesis approach, and reaction conditions during the synthesis [119,120]. The coordination between the cations and oxygen atoms of octahedral and tetrahedral positions for a mixed spinel structure is described in Fig. 4 [121–124].

Mixed metal spinel ferrites possess a single-phase cubic system [126].  $Ni_{0.7}Zn_{0.3}Fe_2O_4$  is a two-mixed spinel ferrite in which  $Zn^{2+}$  ions incline towards tetrahedral sites and  $Ni^{2+}$  ions have a strong tendency to lie in octahedral sites [37], but  $Fe^{3+}$  ions occupy both  $T_h$  and  $O_h$  ones. Upon adding  $Mn^{2+}$  ions, which fully occupy A-sites, we obtain the three mixed spinel ferrite  $Ni_{0.7-x}Zn_{0.3}Mn_xFe_2O_4$ . As a result of the introduction of  $Mn^{2+}$  ions into the A-sites,  $Fe^{3+}$  is shifted from the  $T_h$  sites to the  $O_h$  ones. In the case of  $Ni_{0.7-x}Zn_{0.3}Co_xFe_2O_4$ , when  $Ni^{2+}$  ions are substituted by  $Co^{2+}$  ions to the octahedral sites, a small amount of  $Zn^{2+}$  ions in the  $T_h$  sites change their positions to  $O_h$  sites [127].

Sharma et~al. synthesized CoFe $_2$ O $_4$ , NiFe $_2$ O $_4$ , CuFe $_2$ O $_4$ , and ZnFe $_2$ O $_4$  spinel ferrite [128]. The recorded XRD patterns displayed the formation of a single-phase FCC crystal structure. The lattice parameter "a" value could be calculated from the most intense (311) reflection using the formula  $(1/d_{\rm hkl}^2=(h^2+k^2+l^2)/a^2)$  corresponding to the Fd3m cubic spinel structure. The steady addition of  $\text{Co}^{2+}$  ions resulted in an obvious reduction in the lattice parameter "a" from 8.420 to 8.341 Å, which may be due to the different ionic radii of  $\text{Co}^{2+}$  (0.072 nm) and  $\text{Zn}^{2+}$  (0.074 nm). Furthermore, small scattering domain sizes are indicated in four  $\text{Zn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  (x = 0, 0.03, 0.1, 0.2) samples, as wide diffraction lines can be observed. The coherent diffraction domain size and full width at half maximum (FWHM) values of the (311), (511), and (440) diffractions, were in the range of 9–12 nm. However, due to its higher crystallinity, the  $\text{Zn}_{0.6}\text{Co}_{0.4}\text{Fe}_2\text{O}_4$  sample revealed a 27 nm bigger domain size.



**Fig. 4.** Schematic illustration of the spinel structure of CoFe<sub>2</sub>O<sub>4</sub>, depicting the cation distribution: Fe<sup>3</sup> \* ions in tetrahedral sites (green), oxygen atoms (sky blue), and Fe<sup>3</sup> \*/Co<sup>2\*</sup> ions in octahedral sites (red). Reproduced from reference [125].

The utilization of TEM and high-resolution TEM (HR-TEM) analysis facilitates the acquisition of comprehensive information regarding the morphology of samples, in addition to their structural and textural properties. As demonstrated in the research by Sharma  $\it et al.$ , the TEM image obtained at two distinct annealing temperatures revealed the size and distribution of  $\rm CoFe_2O_4$  [128]. The particles were heavily agglomerated in both micrographs with a permanent magnetic moment equal to their volume. The estimated particle size for the samples annealed at 400  $^{\circ}\rm C$  and 1000  $^{\circ}\rm C$  was about 20 nm and 100 nm, respectively. This may be due to adjacent particles fusing due to surface melting. A similar increase in particle size has also been observed at higher annealing temperatures in previous literature.

#### 5.2. Chemical and vibrational properties

Vibrational spectroscopy techniques, such as Fourier Transform Infrared (FT-IR) spectroscopy and Raman spectroscopy, are essential for characterizing the structural and chemical properties of spinel ferrites. These methods provide insights into the presence of functional groups, metal—oxygen bonding environments, and lattice dynamics.

Fourier transform infrared (FT–IR) was utilized to study the functional groups and composition changes throughout preparation [129–131]. M–O and M–OH functional groups are present in every spinel ferrite. Zinc ferrite (ZFO) samples have been observed to display surface-adsorbed OH group stretching and deformation vibrations at  $3600–3300~\rm cm^{-1}$  and  $1650–1550~\rm cm^{-1}$  [132,133]. The spectra showed three  $T_{2g}$  modes at 174, 480, and 543 cm $^{-1}$ , along with  $E_g$  and  $A_{1g}$  modes at 287 and  $686~\rm cm^{-1}$ . Sharma et~al. identified two fundamental absorption bands, indicative of a spinel-like structure [128]. The greater absorption peak at  $550~\rm cm^{-1}$  ( $\nu_{tet}$ ) is attributable to the tetrahedral metal ion and oxygen complex ( $M_{Td}$ –O) vibration mode, whereas the less intense peak observed at  $420~\rm cm^{-1}$  ( $\nu_{oct}$ ) is due to the stretching vibration of the complex.

Complementary to FT-IR, Raman spectroscopy offers detailed information about the short-range order and cation distribution in spinel lattices. Raman spectra of mixed spinel ferrite show that the transition metals modify the chemical structure and molecular interaction. Mund et al. acquired room-temperature Raman spectra for Co1-xMgxFe2O4 (x = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) in the 180-900 cm<sup>-1</sup> frequency range [134]. In typical inverse spinel ferrite, half of the Fe<sup>3+</sup> cations reside in tetrahedral sites and the rest in octahedral ones. Studying this structure could yield five optical active Raman modes, namely: A<sub>1g</sub>, E<sub>g</sub>, and 3 T<sub>2g</sub>. Previous work on different ferrites has demonstrated higher-frequency Raman modes (A<sub>1g</sub>) above 600 cm<sup>-1</sup>, indicating local lattice effect within the tetrahedral sub-lattice, whereas lower frequency ones ( $E_g$  and  $T_{2g}$ ) conform to the octahedral sub-lattice [127]. Together, FT-IR and Raman analyses play a critical role in confirming the formation of spinel phases and understanding their local bonding environments.

# 5.3. Surface physicochemical properties

X-ray photoelectron spectroscopy (XPS) provides critical insights into the surface chemistry of spinel ferrites, which is largely influenced by the distribution and valence states of transition metals. The surface chemistry of spinel ferrite is based on the transition metal in the structure of spinel ferrite in mixed spinel ferrite. For example, Fan *et al.* used XPS analysis to examine the  $\rm Zn_{0.8}Co_{0.2}Fe_2O_4$  sample [135]. The Zn 2p, Co 2p, and Fe 2p peaks' fine spectra were obtained. The Zn  $\rm 2p_{3/2}$  peak's binding energy (BE) was 1021.3 eV, indicating the existence of  $\rm Zn^{2+}$  species. The Co 2p region's XPS can be subdivided into four contributions. The BE values assigned to Co  $\rm 2p_{3/2}$  and its shakeup satellite are approximately 780.8 and 785.8 eV, respectively, whereas the BE values assigned to Co  $\rm 2p_{1/2}$  and its shakeup satellite are approximately 796.1 and 802.5 eV, respectively. The presence of the  $\rm Co^{2+}$  species in the prepared sample has been indicated by the strong Co 2p shakeup

satellites. The collected Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  spectra display two distinct main peaks with BE values around 710.5 and 724.2 eV, respectively, along with a satellite peak of Fe  $2p_{3/2}$  visible at 718.7 eV, indicating the presence of the Fe<sup>3+</sup> cations. These findings underscore the efficacy of XPS in delineating the chemical structure. Such information is essential for understanding the chemical stability, reactivity, and functional behavior, making XPS an indispensable tool for characterizing spinel ferrite surfaces.

# 5.4. Mössbauer properties

Mössbauer spectroscopy is a highly effective technique for analyzing the electronic and magnetic environments of iron-containing compounds, particularly in spinel ferrites. It provides detailed information on the valence state of iron, typically Fe<sup>0</sup> (metal), Fe<sup>2+</sup>, and Fe<sup>3+</sup>. In addition, the method is employed to ascertain the type of coordination polyhedron occupied by iron atoms (trigonal, tetrahedral, octahedral, etc.). Mössbauer spectroscopy is also utilized to assist in the identification of iron oxide phases based on their magnetic properties. In spinel structures, Mössbauer spectra often display multiple sextets corresponding to iron ions in distinct lattice sites. Fig. 5 shows the Mössbauer absorption spectrum of MnFe<sub>2</sub>O<sub>4</sub> sample measured at room temperature [136]. The spectrum obtained was analyzed using two overlapping sextets, which were found to be consistent with the standard spinel crystal structure (A-ions in Th positions and B-ions in Oh sites). At both the A- and B-sites, the quadrupole splitting (QS) value was zero, suggesting that symmetrical electric fields surround the Mössbauer nuclei, consistent with a well-ordered spinel configuration.

Mössbauer spectroscopy serves as a powerful, non-destructive technique for probing the oxidation states and local environments of iron atoms in spinel ferrites, especially when conventional methods like XRD are insufficient for poorly crystallized phases. Cabrera et al. reported Mössbauer spectra at 298 and 13 K in their manufactured Mg-ferrite samples to determine Fe atom oxidation and check the surrounding environment [137]. MgFe<sub>2</sub>O<sub>4</sub> is donated as [Mg<sub>1-c</sub>Fe<sub>c</sub>](Mg<sub>c</sub>Fe<sub>2-c</sub>)O<sub>4</sub> (c is the inversion degree) and looks like inverted ferrite except for Mg and Fe atoms distributed between the spinel sites of the tetrahedral [A] and octahedral C, which is close to 0.9; however, it changes with the fabrication process and determines ferrite's physical properties and active site types. In MgFe<sub>2</sub>O<sub>4</sub>, Fe nuclei at (B) and [A] spinel locations feature similar average hyperfine magnetic fields, and therefore the zero-field Mössbauer spectroscopy shows an overlap of [A] and (B) sub-spectra, prohibiting c determination. Due to non-equilibrium sites and surface effects' unpredictable occupancy, nanostructured Mg-ferrite spectra investigation may be more difficult. All samples' room temperature spectra display a large central Fe<sup>3+</sup> doublet (Quadrupole Splitting ( $\Delta Q$ )

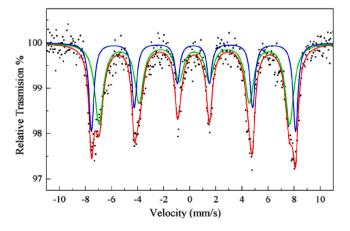


Fig. 5. Room-temperature Mössbauer absorption spectrum of MnFe $_2$ O $_4$  sample. Adapted from [136] with copyright permission from Elsevier, 2010.

 $\sim$ 0.655 mm/s and IS  $\sim$ 0.31 mm/s) and a broad magnetic signal. No Fe<sup>2+</sup> signals were identified. The doublet to Fe ions of MgFe<sub>2</sub>O<sub>4</sub> relax superparamagnetically within the  $(10^{-8} \text{ to } 10^{-9} \text{s})$  Mössbauer time window. Resolved magnetic signals account for blocked ferrite ferric ions. The thermal method increases the crystallinity, raising the magnetic signal's relative region from 10 % Magnesium Ferrite synthesized via Auto-Combustion and Thermal Treatment (MFOAT) to 37 % in auto-combustion samples. This means that MFOAT blocks more particle moments. The Magnesium Ferrite synthesized via Pechini Method (MFOP) room temperature-determined signal area is about 36 %. Spectra at 13 K show a proportionate increase in resolved magnetic signals at the expense of non-resolved signals, which occurs when thermal energy is inadequate to pass the anisotropy barrier in Fe-containing nanomagnetic materials, blocking some of the relaxed particle moments that relaxed SPM at 298 K at 13 K. Both cases show asymmetry and broadness in the lines, suggesting that Fe nuclei at spinel sites sense dispersed iron magnetic fields. Three six-line components were used in Recoil's "dynamic line form site study" to fit the spectra. These findings emphasize the sensitivity of Mössbauer spectroscopy in detecting the subtle structural and magnetic features of Mg-ferrite, especially in its nanostructured forms. Overall, Mössbauer spectroscopy plays a crucial role in confirming structural and magnetic ordering in ferrite materials.

# 5.5. Magnetic properties

Spinel ferrites exhibit remarkable magnetic properties, making them ideal for a variety of applications. Their magnetism arises from a ferrimagnetic ordering of spins in tetrahedral and octahedral lattice sites, where opposing magnetic moments of different strengths result in net magnetization. The magnetic properties of non-mixed spinel ferrite are higher than mixed spinel ferrite due to the contribution of dead magnetic materials such as transition metals. The magnetic properties of spinel ferrites are tuned by their unique crystal size [138,139]. The crystal structure of ionic oxides, particularly Fe oxides, enables a complex structure of magnetic ordering known as ferrimagnetism. The structural design of these ferrites allows for two distinct spins (up and down). Moreover, the total magnetic moment from all directions is not equal to zero [86]. Interestingly, the magnetic moments of atoms are opposed when compared to each other; however, the opposing moments are not balanced for various neighboring sublattices [88,89]. Ni-ferrite (NiFe<sub>2</sub>O<sub>4</sub>) is a ferrimagnetic soft ferrite with high saturation magnetization and low coercivity. Magnesium ferrite (MgFe<sub>2</sub>O<sub>4</sub>) is a soft magnetic material that has found application in a variety of fields [140-143]. In contrast, pure Co-ferrite (CoFe<sub>2</sub>O<sub>4</sub>) is known as a harder magnetic material, exhibiting high coercivity and significant magnetic anisotropy [122].

Tuning the magnetic properties can be achieved by mixing two or more metals in different ratios. Verma et al. reported the magnetic properties of Ni-Zn and Mn-Zn ferrites synthesized using the citrate precursor technique and the structure denoted by Mn<sub>0.2</sub>Ni<sub>0.8-x</sub>Zn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> where x = 0.4-0.6 [144]. The findings reveal that, at sintering temperatures below 1200 °C, the prepared mixed ferrites possessed relatively higher saturation magnetizations. Whereas Bhandare et al. employed a sol-gel auto-combustion route to prepare Mg-doped Co–Ni-mixed ferrite  $Co_{0.5}Mg_xNi_{0.5\text{-}x}Fe_2O_4$  (x = 0–0.4), Wherein Ni and Mg occupied spinel structure octahedral (Oh) and tetrahedral (Td) sites, respectively [126]. While Co occupied both the Td and Oh regions by 2:3 ratios, the observations showed a slight decline in the saturation magnetization upon Mg substitution for Ni, whereas coercivity was not changed. In addition, the ferrimagnetic nature of the prepared structure  $% \left( 1\right) =\left( 1\right) \left( 1\right) \left$ was confirmed by both Fe-the Mössbauer spectroscopy and XRD results. Tailoring these properties through controlled metal substitution and processing conditions, such as sintering temperature or synthesis route, enables the development of ferrites with optimized performance for specific applications.

#### 5.6. Stability properties

The thermal properties of the ferrite-based nanocomposite are considered one of the important characteristics of their application as photocatalysts. Thermogravimetric analysis (TGA) is a critical method for assessing the thermal stability of the prepared composites [145]. In general, all spinel ferrites, mixed and non-mixed, exhibit high thermal stability. Understanding these thermal decomposition patterns is essential for optimizing synthesis conditions and ensuring the structural integrity of the resulting ferrites during application. The decomposition process in all ferrites was divided into two stages [128]. Firstly, weight loss occurred in the 50–100  $^{\circ}\text{C}$  temperature range, which was attributed to water loss adsorbed from the sample. The decomposition of other components such as ethylene glycol and nitrate decomposition into CO<sub>2</sub> and NO<sub>x</sub>, respectively, caused significant weight loss in the second stage in the 300-400 °C temperature range. The curve became almost featureless beyond 400  $^{\circ}$ C, suggesting the development of pure ferrite. Consequently, the optimal annealing temperature was determined to be

Sharma et al. synthesized Zn-incorporated Ni ferrite (Zn<sub>v</sub>Ni<sub>1,v</sub>Fe<sub>2</sub>O<sub>4</sub>) (where x was from 0.0 to 1.0) for MB photocatalytic degradation [146]. The thermal decomposition and crystallization of the synthesized ferrite samples were recorded by TGA. TGA was obtained for both the as-prepared  $Zn_{0.8}Ni_{0.2}Fe_2O_4$  and the annealed at 1000 °C sample in the 50–900  $^{\circ}$ C temperature range, with a 10  $^{\circ}$ C/min heating rate. The thermal decomposition method for the as-obtained sample entailed weight loss in three major steps. The initial weight loss in the 50-100°C range was attributed to the removal of adsorbed water from the investigated sample. The second major step, which occurred within the 300-400°C range, was initiated by the decomposition of nitrates and ethylene glycol, resulting in the formation of NOx and CO2, respectively. The third decomposition stage (which occurred at 550  $^{\circ}$ C) resulted in ferrite crystallization. Additionally, the absence of weight loss indicated the formation of ferrite. The 1000°C annealed sample exhibited an almost straight line, indicative of the formation of stable ferrite. These findings underscore the importance of thermal characterization in guiding the synthesis and functionalization of ferrites for efficient photocatalytic use.

# 5.7. Adsorption properties

Adsorbtion characteristics of spinel ferrite strongly depend on both surface chemical properties and the materials' microstructures [147, 148]. The adsorption of spinel ferrite is a promising prospect, exhibiting a number of attractive characteristics, including a short duration, cost-effectiveness, high efficiencies, and ease of operation [149].

During the adsorption process, a substance (adsorbate) is redistributed from an aqueous solution to a solid surface (adsorbent) [150]. Many parameters influence adsorption efficiency, including adsorbent surface characteristics (surface area, size and number of pores, surface functional groups, thermal stability, and mechanical strength) [151], adsorbate concentration, pH, temperature, and contact time [150].

The adsorption process can take place via different mechanisms, including physical, chemical, and electrostatic interactions [152]. Electrostatic attraction occurs between the positively-charged surface of the adsorbent and negatively-charged anionic dyes [153]. Physical interactions, such as adsorption, occur by means weak intermolecular forces of attraction between adsorbates and adsorbents such as  $\pi$ - $\pi$  electron donor–acceptor interactions, which often occur between a carbonaceous adsorbent's  $\pi$ -electrons and an adsorbate aromatic ring's  $\pi$ -electron, as initially suggested by Coughlin and Ezra (1968) [154]. Finally, in adsorbate–adsorbent chemical adsorption, strong covalent bond formation is the main factor [155]. One way to differentiate between physical and chemical adsorption is adsorption isotherms, especially Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, and Redlich–Peterson isotherms [152,156].

Two other important adsorption characteristics are adsorption kinetics and thermodynamics. Kinetics is concerned with describing the retention rate of a solute from an aqueous solution to an interface (solid phase) at a given pH, temperature, adsorbent dose, and flow rate. Thermodynamics, in contrast, investigates adsorption feasibility, sustainability, and mechanisms, as summarized in Table 2 [157]. The porosity of the prepared nano-ferrites plays an important role in their adsorption capacities. A higher surface area means an optimized quantity and quality of active sites and thus better adsorption capacity. In addition, porosity provides efficient pathways and more active sites [133]. Ferrite nanomaterials not only exhibited promising adsorption capacities for dyes and ions but also potential gas adsorption applications.

# 5.8. Optical properties

The optical properties of ferrite nanoparticles can be evaluated using ultraviolet–visible (UV/Vis) absorption, photoluminescence (PL), and electrochemiluminescence (ECL). Various spinel ferrites possess outstanding optical characteristics, including parasitic light absorption [162] and luminescence [163], which are employed in magneto–optical recording devices [164] and lasers [165]. Optical studies of spinel ferrite may be influenced by many parameters, including the rejoins of  $M^{2+}$  and  $Fe^{3+}$  ions, crystal size, and the type of doping metals as summarized in Table 3 [118]. These parameters affect charge carrier dynamics and light–matter interactions within the material, making optical characterization a key tool in understanding and tuning ferrite nanoparticles for specific applications.

Photoluminescence (PL) studies are important for the measuring, migration, and recombination of light-generated charge carriers in material. Renuka et al. used both sol-gel and combustion methods to prepare NiFe<sub>2</sub>O<sub>4</sub> NPs [175]. PL analysis showed that Ni<sup>2+</sup> ions were present in the octahedral site and Fe<sup>3+</sup> ions in tetrahedral sites, leading to a mixed spinel structure. In addition, at 413, 426, and 513 nm, PL signatures were observed for samples prepared by combustion and sol-gel methods without any peak shift. The presence of Ni<sup>2+</sup> ions in octahedral sites was assured by the 413 nm-located peak with a  ${}^{3}A_{2}$  ( ${}^{3}F$ )  $\rightarrow$   $^{3}\text{T}_{1}$  ( $^{3}\text{P}$ ) transition. 426 and 513 nm bands were attributed to Fe<sup>3+</sup> ions' transitions of  ${}^3d_5 \rightarrow {}^3d_4$  4 s upon electron excitation to the conduction band (CB) as shown in Fig. 6. Hammad et al. illustrated the influential behavior of Co<sup>2+</sup> ions on the optical properties of CuFe<sub>2</sub>O<sub>4</sub> NPs synthesized by a precipitation method [176]. Their results revealed that upon doping Co<sup>2+</sup> ions, the luminescence intensity of the CuFe<sub>2</sub>O<sub>4</sub> sample increased. This can be attributed to the distance increment between the dopant and the array [177]. In summary, spinel ferrite nanoparticles demonstrate remarkable optical characteristics which are crucial for various advanced technological applications. Employing PL and UV/Vis techniques can show how ion distribution and doping significantly affect light absorption and emission behavior.

#### 5.9. Electrochemical and photoelectrochemical properties

Spinel ferrite-based magnetic nanomaterials have emerged as versatile and efficient electrocatalysts for a variety of key electrochemical reactions such as the oxygen reduction reaction (ORR), and hydrogen evolution reaction (HER). These reactions are crucial to energy conversion and storage technologies, particularly in fuel cells and watersplitting systems. The photocatalytic reduction and oxidation reactions on the surface of ferrites-based magnetic nanoparticles are electrocatalytic ones driven by the photogenerated electron and holes, respectively. More interestingly, mixed metal spinel ferrite can also serve as multifunctional electrocatalysts with higher activity than nonmixed spinel ferrite [172], which plays an important role in the improved photocatalytic activity. Das et al. studied the electrochemical properties of cathodes supported by Co<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>, ZnFe<sub>2</sub>O<sub>4</sub>, and Pt/C synthesized materials [178]. The photoelectrochemical behaviour of ferrites, which is facilitated by their semiconductor nature, has garnered significant interest. Many electrochemical parameters such as exchange current density, charge transfer resistance, and electroactive surface can directly affect the performance of ferrite-based photocatalysts. These properties have been elucidated by analytical techniques such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Mott-Schottky (MS) analysis. Recent advances highlight the potential of ferrite nanomaterials as inexpensive, abundant alternatives to precious metals like platinum in sustainable energy technologies.

The ORR kinetics these cathodes were studied in an O2-saturated 100 mM phosphate buffer saline (PBS) solution, as the electrolyte using CV. The current response (Fig. 7) shows a sharp ORR current peak for the cathode using Co<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> at - 0.69 V with a 45 mA peak current, which was considerably higher than the CoFe<sub>2</sub>O<sub>4</sub> ORR current peak (3.2 mA) and that of ZnFe<sub>2</sub>O<sub>4</sub> (6.5 mA), indicating superior catalytic activity of Co<sub>0.5</sub> Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>. EIS assessed the charge transport cathode performance and the exchange current densities using prepared Co<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>. The EIS spectra were simulated in an equivalent circuit in the form of a typical Nyquist plot to obtain the solution resistance (R<sub>s</sub>) and to obtain R<sub>ct</sub>. Fig. 7 shows the virtual Nyquist graphs. The R<sub>s</sub> value for all the cathodes was determined to be about 1.22  $\Omega$ , which is understandable given the related 100 mM PBS electrolyte used in the study. The  $R_{ct}$  value of 0.18  $\Omega$  for the  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  cathode was observed to be 1.33-fold lower than the Pt/C cathode (0.24  $\Omega$ ), five times less than CoFe<sub>2</sub>O<sub>4</sub> (0.9 Ω), and three times less than ZnFe<sub>2</sub>O<sub>4</sub> (0.5  $\Omega$ ), indicating greater ORR operation. Furthermore, the Co<sub>0.5</sub>Zn<sub>0.5</sub>-Fe<sub>2</sub>O<sub>4</sub>-based cathode could achieve a 3.26 A/m<sup>2</sup> exchange current density, which is higher than the Pt/C cathode (2.44 A/m<sup>2</sup>). The electrochemical tests revealed that Co<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> is a good ORR catalyst with low overpotential losses.

Electrochemical water splitting necessitates the utilization of catalysts that exhibit both robust electrocatalytic activity and durability, thereby accelerating the sluggish kinetics inherent to the process [179].

**Table 2**Key adsorption parameters of ferrite nanomaterials in recent studies.

System	Preparation method	Adsorbed dye/ions	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Adsorption isotherm	Adsorption kinetics	Adsorption capacity	Ref.
MnFe <sub>2</sub> O <sub>4</sub> and CoFe <sub>2</sub> O <sub>4</sub>	Co- precipitation	Zn (II)	84.5 and 50.4	0.2769 and 0.1846	Langmuir model (higher R <sup>2</sup> )	Pseudo- second-order	454.5 and 384.6 mg $g^{-1}$ at pH = 6	[157]
MixedCaFe <sub>2</sub> O <sub>4</sub> and MnFe <sub>2</sub> O <sub>4</sub>	Co- precipitation	Methyl orange (MO)	47.67	0.121	Langmuir model	Second-order	99.88 % after 24 min	[158]
CuFe <sub>2</sub> O <sub>4</sub> / Kaoline	Co- precipitation	Methylene blue (MB) and methyl violet (MV)	174.78	0.256	Freundlich model	Quasi-second- order	98.64 % and 99.25 % at pH = 8 and 25°C after 30 min	[159]
NiFe <sub>2</sub> O <sub>4</sub> -GO	Solvothermal	MB	88.027	0.131	Langmuir model	Pseudo- second-order	$1.4~\mathrm{mg~g}^{-1}$ after $240~\mathrm{min}$	[160]
ZnFe <sub>2</sub> O <sub>4</sub> /MgAl- LDH	Hydrothermal	Congo Red (CR)	0.015	$0.257 \text{ mL}$ $\text{g}^{-1}$	Langmuir-type monolayer adsorption	Pseudo- second-order	$294.12 \text{ mg g}^{-1} \text{ with Mg/}$ Al molar of 2	[161]

**Table 3**Optical properties of spinel ferrites: influence of composition, doping, and synthesis method.

Spinel system	System type	Preparation method	Doping metal	Absorbance profile	Bandgap ( $E_g$ )	Ref.
CoFe <sub>2</sub> O <sub>4</sub>	Non-mixed spinel ferrite	Coprecipitation method	-	Blue shift with particle size reduction	2.44 eV	[166]
NiFe <sub>2</sub> O <sub>4</sub>	Non-mixed spinel ferrite	Coprecipitation method	-	Blue shift with particle size reduction	3.54 eV	[166]
ZnFe <sub>2</sub> O <sub>4</sub>	Non-mixed spinel ferrite	Coprecipitation method	-	Blue shift with particle size reduction	3.25 eV	[166]
CuFe <sub>2</sub> O <sub>4</sub>	Non-mixed spinel ferrite	Sol-gel method	-	Strong visible light absorption	2.22 eV	[167]
MnFe <sub>2</sub> O <sub>4</sub>	Non-mixed spinel ferrite	Hydrothermal method	-	Strong visible light absorption	0.98 eV	[168]
$MgFe_2O_4$	Non-mixed spinel ferrite	Solvothermal method	-	UV-visible region broad absorption	1.82 eV	[169]
$\begin{aligned} &\text{Co}_{1x}\text{Zn}_x\text{Fe}_2\text{O}_4 \ (x=0, \ 0.3, \ 0.5, \ 0.7, \\ &\text{and} \ 1) \end{aligned}$	Two-metal mixed spinel ferrite	Co-precipitation method	Zn	Shift toward higher wavelength with increasing (Zn) concentration	$E_{\rm g}$ decreased to 2.258 eV from 2.8306 eV with Zn content increase	[170]
$\mathrm{Co_{1x}Ni_xFe_2O_4}$ (0 $\leq x \leq$ 1, with 0.25 steps)	Two-metal mixed spinel ferrite	Precipitation method	Ni	Blueshift was observed with (Ni) increase	By (Ni) increase, $E_g$ got broadened	[171]
$Cu_{0.5}Zn_{0.5x}Ba_xFe_2O_4$ [ $x = 0.05, 0.1$ ]	Three-metal mixed spinel ferrite	Solid state route	Ba <sup>2+</sup>	Absorption in the visible region	$E_{\rm g}$ increased when ${\rm Ba}^{+2}$ increased	[172]
$Mn_{0.5}Zn_{0.5-x}Mg_xFe_2O_4$ NPs ( $x = 0$ , 0.125, 0.25, 0.375, and 0.5)	Three-metal mixed spinel ferrite	Sol-gel method	$Mg^{2+}$	200–800 nm reflection band was observed	By increasing $Mg^{+2}$ , $E_g$ decreased	[173]
$Ni_{1-x}Cu_xFe_2O_4\ (0\leq x\leq 0.9)$	Two-metal mixed spinel ferrite	Mechanochemical technique	Cu	The blue shift was detected by increasing Cu cations	Upon increasing Cu cations, $E_g$ decreased	[174]

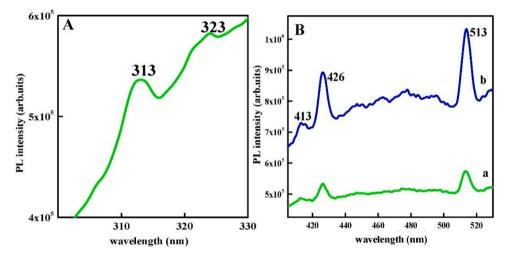


Fig. 6. (A) excitation spectrum of the prepared NiFe<sub>2</sub>O<sub>4</sub> NP; (B) Emission spectra of NiFe<sub>2</sub>O<sub>4</sub> samples synthesized via (a) combustion method and (b) sol-gel method. Adapted from [175], with copyright permission from Elsevier, 2021.

In contrast to the majority of Pt-free electrocatalysts, the most well-known heterogeneous Pt/C composite has been demonstrated to be the most efficient HER electrocatalyst due to its high-exchange current density at low overpotentials, chemical inertness, versatility, high conductivity, and oxidation resistance [180]. Nevertheless, the practical applications of Pt were significantly limited by its high cost and low abundance. An alternative to Pt is represented by earth-abundant transition metals, which have been found to be inexpensive and effective electrocatalysts. These metals include Fe, Co, Ni, Mo, and W. In this context, due to their abundance on earth, customizable molecule architectures, and the special benefits of readily producing a variety of nanostructures, mixed and non-mixed spinel ferrites have also shown tremendous potential as attractive HER electrocatalysts for water-splitting reactions. In recent years, ferrite oxides, including Fe-spinel oxides and Fe<sub>3</sub>O<sub>4</sub>, along with ferrites such as AFe<sub>3</sub>O<sub>4</sub> (A = Mn, Co, Zn, Ni), have emerged as promising anode candidates for

electrocatalysts [181]. *Nivetha et al.* cited electrochemical studies on synthesized graphene-MnFe<sub>2</sub>O<sub>4</sub> (MFG) and graphene-ZnFe<sub>2</sub>O<sub>4</sub> (ZFG) materials [182]. A comprehensive understanding of catalytic efficiency within an acid medium necessitates electrochemical surface area tests to investigate the double-layer capacitance ( $C_{dl}$ ), and electroactive surface areas could be obtained in the non-faradaic zone. The CV technique was used to achieve this objective, with varying scan rates ranging from 0.002 to 0.1 Vs<sup>-1</sup>. The estimation of electroactive site numbers can be achieved through the calculation of the active surface area, derived from electrochemical analysis, which is one of the most critical measurements in the estimation of turnover frequency (TOF).

Mott-Schottky (MS) studies on  $AFe_2O_4$  ferrospinels (where A=Co, Cu, Zn) were published by Helaili *et al.* [183]. The semiconductor (SCs)-electrolyte junction's capacitance (C) and its change with an external bias voltage were calculated at 1 kHz. The MS plot intercept was used to calculate the flat band voltage ( $V_{fb}$ ) potential (Fig. 8) and the

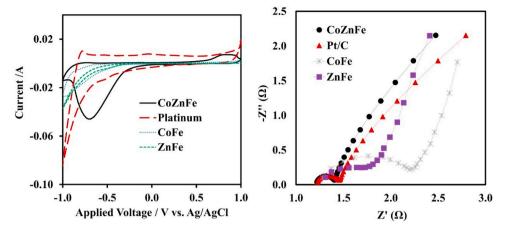


Fig. 7. (a) CV curves; and (b) Nyquist plots of  $Co_{0.5}Zn_{0.5}Fe_2O_4$ ,  $CoFe_2O_4$ ,  $ZnFe_2O_4$ , and Pt/C catalyzed cathodes. Adapted from [178] with copyright permission from Elsevier, 2018.

donor density (ND) was determined by its slope. The MS plot slope, where the +ve sign refers to the n-type and the -ve sign refers to the p-type, also confirms the semiconductor type. The MS relation (Eq. 1) was applied to estimate the density ND and potential  $V_{fb}$  at the SCs/e-lectrolyte interface [183]:

$$\frac{1}{c^2} = \frac{2}{\varepsilon \varepsilon_0 e N_D} \left( V - V_{fb} - \frac{kT}{e} \right) \tag{1}$$

where C,  $\varepsilon$ ,  $\varepsilon$ 0, k and N<sub>D</sub> represent the capacitance of the space charge region, the permittivity of the vacuum, the dielectric constant of the semiconductor, the Boltzmann constant, and the donor density (hole acceptor quantity for the p-type SC or electron donor quantity for the n-type SC), respectively. The electron density (N<sub>D</sub>) was calculated for the

three spinels using the slope; the +ve value approves the n-type character. The flat band voltage ( $V_{fb}$ ) was nearly identical to the onset potential ( $V_{on}$ ), meaning the gap area was devoid of surface states. Upon contact between SC and the electrolyte, the space-charge width (W) arises. In the space charge field, the transition to equilibrium with the redox couple created a Schottky barrier. From the following relationship (Eq. 2), the W amount of semiconductor oxides was determined for a band bending ( $\Delta V = 0.5~V$ ) [183]:

$$W = \sqrt{\frac{\varepsilon \varepsilon_0 (V - V_{fb})}{e N_D}}$$
 (2)

The low photocurrent of a photocatalyst was attributed to the low

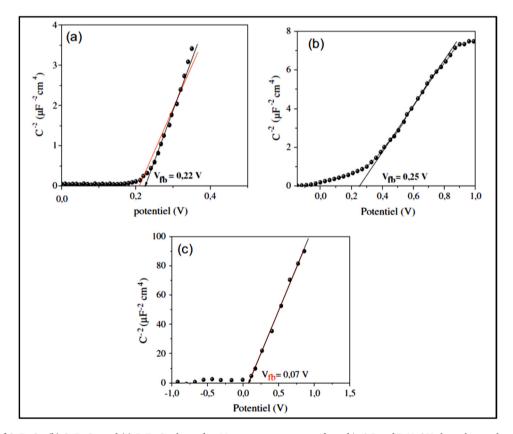


Fig. 8. (a) MS plots of CoFe<sub>2</sub>O<sub>4</sub>; (b) CuFe<sub>2</sub>O<sub>4</sub>; and (c) ZnFe<sub>2</sub>O<sub>4</sub> electrodes. Measurements were conducted in 0.5 mol/L NaOH electrolyte under a nitrogen atmosphere at a scan rate of 0.01 V/s. Adapted from [183] with copyright permission from Elsevier, 2015.

electrical transport properties, which resulted in low conductivities and a small photo response. Furthermore, short charge carrier diffusion lengths were often recorded. As a result, before approaching the SCs/electrolyte interface, the majority of the produced holes could recombine with the existent electrons (present at the CB. The small particles helped the SCs/electrolyte interface move closer to the hole photogeneration, resulting in improved performance collecting holes. Smaller particles, in contrast, increase the depletion-to-diffusion ratio. Because of the low-density  $N_{\rm D}$  calculated W increased from 2.84 nm for  ${\rm CuFe_2O_4}$  to 2760.58 nm for  ${\rm ZnFe_2O_4}$ .

Due to their superior thermal and chemical stability as well as their optimal electronic band structure, spinel ferrite-based magnetic nanoparticles have also shown promise as photoelectrode candidates for solar energy conversion in photoelectrochemical (PEC) cells, in addition to their direct use as electrocatalysts. Ferrite-based nanomaterials for photoelectrocatalytic applications are typically synthesized using the same diverse techniques detailed in Section 4, such as co-precipitation, hydrothermal, and sol-gel methods, which allow for control over size, morphology, and crystallinity crucial for photoelectrode performance. For instance, Singh et al. demonstrated the photoelectrochemical properties of a CoFe<sub>2</sub>O<sub>4</sub> nanostructure film [184]. A three-electrode cell assembly was used for the photoelectrochemical tests, with the photoanode being a CoFe<sub>2</sub>O<sub>4</sub> nanostructure film coated onto a fluoride tin oxide (FTO) substrate, the counter, and reference electrodes being a Pt-wire and Ag/AgCl, respectively, and the electrolyte being 0.1 M Na<sub>2</sub>S solution (Fig. 9a). A tungsten halogen lamp with a ~100 mW/cm<sup>2</sup> illumination rate was applied as the source of photons. To research the effect of an external magnetic field on the CoFe<sub>2</sub>O<sub>4</sub> film photoanodic behavior, a permanent magnet assembly was used to apply a magnetic field parallel to the film plane. The J-V properties of the  $CoFe_2O_4$  photo anode with and without a light source, as well as CoFe<sub>2</sub>O<sub>4</sub> photoanode J-V curves in light conditions in the presence of various strengths of magnetic fields, are shown in Fig. 9b. The J-V curves in CoFe<sub>2</sub>O<sub>4</sub> film reveal a ~1.55 mA/cm<sup>2</sup> significant photocurrent (at 1.9 V vs. RHE) in the absence of a magnetic field. However, on subjecting the CoFe<sub>2</sub>O<sub>4</sub> film to an external magnetic field of 400 Oe, the current increased to  $\sim$ 2.14 mA/ cm<sup>2</sup>. When the magnetic field strength was increased to 600 Oe, the maximum increase in photocurrent was  $\sim$ 3.47 mA/cm<sup>2</sup>. No major change in the photocurrent may be inspected as the magnetic field was increased further. The detected magnetic field-induced shift in the photocurrent correlates to a ~123 % increase in the photocurrent, which is significantly higher than previously reported studies on the magnetic field effect on photocurrents and other photocurrent effects. As magnetic fields vary in frequency, the CoFe<sub>2</sub>O<sub>4</sub> nanostructure films chronoamperometry findings at a 1.23 V fixed potential (vs. RHE) are shown in Fig. 9c. The photocurrent enhancement with magnetic fields follows the same pattern as the chronoamperometry findings. The chemical stability of the CoFe<sub>2</sub>O<sub>4</sub> nanostructure photoanode is also strong.

The combined effects of photocatalysis and electrocatalysis are thought to be responsible for the remarkable increase in activity, which can be attributed to the boosted activity of electrocatalytic (EC) oxidation, improved charge separation, and increased reactive radical species, such as OH and  $\rm O_2$ . Thus, it is expected that spinel ferrite-based magnetic films will soon be widely used in an increasing number of PEC fields. Their activity should also be further improved through better balancing electronic structures (such as band-gap and redox ability), stability, change–carrier mobility, and active sites. In summary, the integration of spinel ferrites into electrocatalytic and photoelectrochemical systems represents a promising avenue for advancing renewable energy technologies through sustainable material solutions.

# 5.10. Density functional theory for electronic and catalytic property tailoring

Density Functional Theory (DFT) has played a vital role in

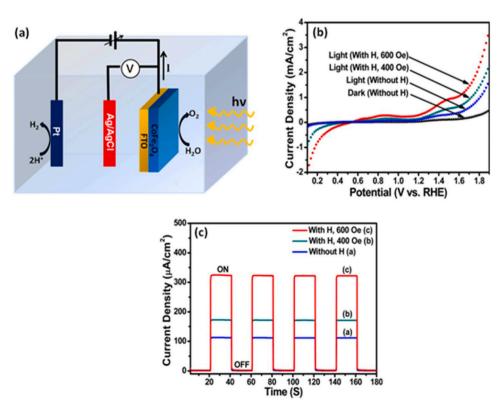


Fig. 9. (a) Schematic illustration of a three-electrode cell configuration for photoelectrochemical performance measurements; (b) Current density-potential (*J-V*) curves of a CoFe<sub>2</sub>O<sub>4</sub> photoanode under dark conditions, and light illumination (100 mW/cm<sup>2</sup>) with and without an external magnetic field; (c) Chronoamperometry results demonstrating the photoresponse of a CoFe<sub>2</sub>O<sub>4</sub> nanostructure film under varying magnetic field strengths. Reproduced from reference [184].

understanding and predicting the electronic properties and bandgap tuning of ferrite-based nanomaterials, particularly in the context of photocatalysis and  $CO_2$  reduction. These theoretical calculations offer atomic-level insight into band structure, density of states (DOS), charge distribution, and magnetic interactions, which are all critical for photocatalytic activity. DFT has been extensively used to predict and tune bandgaps of ferrite nanomaterials, which are typically narrow ( $\sim 1.8-2.2$  eV). This enables visible-light absorption, a desirable trait for photocatalytic  $CO_2$  reduction [185–188]

Salcedo-Rodríguez et al. used DFT to examine the (001) surface terminations of ZnFe<sub>2</sub>O<sub>4</sub> compound [189]. They observed that zinc-terminated surfaces are most stable, and that cationic inversion (Zn-Fe antistites) emerges as a surface defect. This, in turn, promotes ferrimagnetic behavior and modifying electronic structure. However, Fritsch and Ederer explored how epitaxial strain influences cation distribution, electronic structure, and magneto crystalline anisotropy in CoFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>. Their DFT results demonstrated strain-dependent tuning of electronic and magnetic properties, which is useful for engineering band alignments [190]. Another study investigated the properties of Al-doped NiFe<sub>2</sub>O<sub>4</sub>, utilizing both sol-gel and DFT methods. The doping process has been shown to modify surface electronic states and adsorption properties, thereby enhancing CO<sub>2</sub> capture. This represents a significant step towards photocatalytic CO2 reduction [191]. Recently, DFT has become a cornerstone in elucidating reaction mechanisms for electrochemical CO<sub>2</sub> reduction, particularly in identifying intermediates and pathways of photocatalytic CO<sub>2</sub> reduction on metal oxide and ferrite surfaces. These studies aim to model the sequential proton-coupled electron transfer steps by calculating the Gibbs free energies associated with reaction intermediates such as \*CO2, \*COOH, \*CO, \*CHOH, and \*CH<sub>4</sub> [192]

As  $\rm CO_2$  reduction mechanisms often involve multiple intermediates and complex reaction pathways, DFT has become essential in identifying energetically favorable routes and predicting key reaction steps at the molecular level. Liu *et al.* investigated carbon monoxide (CO) oxidation over the surface of MnFe<sub>2</sub>O<sub>4</sub> during chemical looping combustion [193]. Thanks to its distinctive properties such as good thermal stability and

cost-effectiveness,  $MnFe_2O_4$  is a promising oxygen carrier. DFT results revealed that the octahedral  $Fe^{3+}$  site was preferred for CO chemisorption with a C-down orientation, as is shown in Fig. 10. In addition, CO oxidation on the  $MnFe_2O_4$  surface took place in three steps, including CO adsorption, diffusion, and  $CO_2$  desorption. Specifically, some active O sites were occupied by the Mn atomic layer present on the top of the Mn-terminated surface, which led to a weakening of surface activity. Then, in order to generate a  $CO_2$  complex, adsorbed CO reacts with a bridging surface O.  $CO_2$  desorption finally occurs by overlapping an energy barrier.

# 5.11. Properties engineering for efficient photocatalytic reduction of CO<sub>2</sub>

For effective photocatalytic reduction of CO2 using magnetic photocatalysts, several key material properties could be precisely engineered. First and foremost, bandgap tuning is critical to enable visiblelight absorption and align the conduction band potential to match the reduction potentials of CO<sub>2</sub> to value-added products such as CO, CH<sub>4</sub>, and CH<sub>3</sub>OH [194–196]. Tailoring the bandgap could help in reducing electron-hole recombination rates. Secondly, efficient charge separation and transport could be achieved through strategies such as heterojunction formation, Z-scheme architecture, and co-catalyst loading [197]. This facilitates the migration of photogenerated electrons to surface-active sites before recombination occurs. The presence of oxygen vacancies could introduce mid-gap states and serve as active adsorption and activation sites for CO2 molecules. Furthermore, the magnetic separability (intrinsic to ferrites) offers a significant practical advantage, facilitating facile recovery and reuse of photocatalysts in continuous operation setups [198]. Finally, properties such as surface area, porosity, crystallinity, and defect density synergistically influence CO2 capture, light harvesting, and active site availability. A comprehensive understanding of how these properties interplay in ferrite systems provides a rational basis for designing next-generation magnetic nanomaterials tailored for highly efficient and sustainable photocatalytic CO2 reduction.

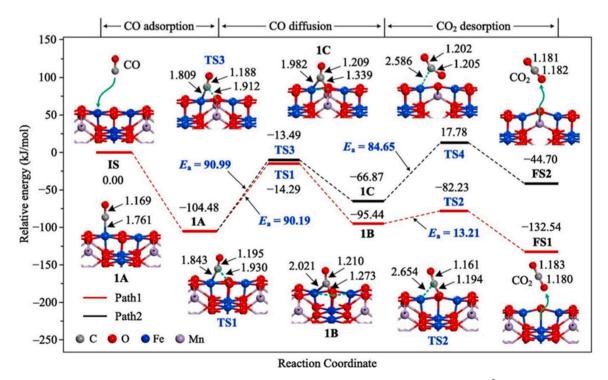


Fig. 10. CO oxidation energy profiles and reaction pathways over Fe-terminated surface. The bond lengths are indicated in Å. Adapted from [193] with copyright permission from Elsevier, 2018.

#### 6. Photocatalytic reduction of carbon dioxide

This section provides a comprehensive overview of the photocatalytic reduction of  $CO_2$ , with a specific focus on the application and enhancement strategies of Spinel Ferrite-Based Magnetic Photocatalysts (SFMPs). It first establishes the global context and fundamental principles of photocatalytic reduction of  $CO_2$ , followed by an in-depth discussion of SFMPs' unique properties and their general catalytic mechanism. Subsequently, various advanced strategies employed to enhance the efficiency and selectivity of SFMPs for  $CO_2$  conversion are detailed, supported by specific research examples.

# 6.1. Global context and fundamental principles of photocatalytic CO<sub>2</sub> reduction

The escalating global atmospheric CO2 levels are significantly intensifying the greenhouse effect, leading to severe environmental challenges and exacerbating the depletion of fossil fuel resources. Addressing these interconnected global challenges necessitates the urgent development of sustainable energy solutions. In this context, the photocatalytic reduction of CO2 into valuable energy-bearing compounds such as CO, methane, and methanol) (Fig. 11). Inoue et al. initially demonstrated the photocatalytic reduction of CO2 in 1979 [199] to hydrocarbons as an ecofriendly method for CO<sub>2</sub> conversion. The utilization of solar light as an illumination source in photoreduction reactions is a significant development due to the inherent advantages of solar energy, including its clean nature, perpetual availability, and cost-free status. The reduction of CO2 in various products is contingent upon the density of photoinduced electrons [200,201] (Table 4). The reaction starts with activating the bonds on both sides of O=C=O with photogenerated e and then the reaction proceeds according to the number of available electrons and the redox potential of each product. Product type (selectivity) and yield could be controlled by engineering a suitable photocatalyst. Semiconductors are known to provide good photocatalytic activity, as some of the photoexcited electrons in the conduction band undergo redox reactions while others recombine. Therefore, we must design an effective photocatalyst for CO<sub>2</sub> reduction with a minimum recombination rate, the highest activity, and lowest cost. Semiconductors with wide band gaps (<3 ev) like TiO2, SiC, and ZnS are not active under solar irradiation. On the other hand, iron oxides are solar-activated photocatalysts with a narrow band gap, but their conduction band is more positive than the redox potential of CO<sub>2</sub> [202]. Mixing different semiconductors with iron oxides creates photocatalysts that have the advantages of both types. The conduction band potential of the photocatalyst must be lower than the reduction potential of the

**Table 4** Equilibrium potentials for CO<sub>2</sub> reduction products and the corresponding density of activated electrons [201].

$CO_2 + 2 H^+ + 2 e^- \rightarrow CO + H_2O$	$E^0=-0.52\;V$
$CO_2 + 2 H^+ + 2 e^- \rightarrow HCOOH$	$E^0 = -0.61 \text{ V}$
$CO_2 + 4 H^+ + 4 e^- \rightarrow HCHO + H_2O$	$E^0 = -0.48 \text{ V}$
$CO_2 + 6 H^+ + 6 e^- \rightarrow CH_3OH + H_2O$	$E^0 = -0.38 \text{ V}$
$CO_2 + 8 H^+ + 8 e^- \rightarrow CH_4 + 2 H_2O$	$E^0 = -0.24 \text{ V}$
$CO_2 + e^- \rightarrow CO_2^{-\bullet}$	$E^0=-1.90\;V$

reaction to occur [203]. Spinel ferrites are also known for their magnetic properties, which facilitate their recovery and reusability. Nano-catalysis is preferred rather than bulk catalysis, as it provides a larger surface area, improved light harvesting, more active sites, and enhanced adsorption of  $CO_2$ . The three-step mechanism of illumination $\rightarrow$  charge activation $\rightarrow$  catalyzed reaction is involved in  $CO_2$  conversion [204].

The activation of inert  $CO_2$  molecules requires a considerable amount of energy. Generally,  $CO_2$  hydrogenation into  $C^{2+}$  hydrocarbons goes through two consecutive reaction steps: firstly, a reduction of  $CO_2$  to CO via the reverse water–gas shift (RWGS),  $CO_2 + H_2 \rightarrow CO + H_2O$ , followed by the hydrogenation of CO to  $C^{2+}$  hydrocarbons via Fischer–Tropsch synthesis (FTS, n CO + 2n  $H_2 \rightarrow C_nH_{2n} + nH_2O$ ) using traditional FTS catalysts (e.g., Fe, Co, Ni and Ru). However, the product follows the Anderson–Schulz–Flory (ASF) distribution, which is mainly straight-chain paraffins. Promoters (e.g., sodium, kalium, manganese, etc.) are added to FTS catalysts to improve the selectivity towards light olefin products by promoting the dissociation and adsorption of CO and enhancing surface basicity [205].

A photoelectron participating in the reduction of  $CO_2$  into products has been reported in some studies. The photocatalytic activity of various photocatalysts was compared by a measurement standard: the total utilized photoelectron number (UPN) [206–209], calculated by the Eq. 3:

$$N_{UPN} = 2 N_{H2} + 2 N_{CO} + 8 N_{CH4}$$
 (3)

where (N) represents the molar number of generated products. Not all studies that are discussed in this section paid attention to that important factor (UPN), although it identifies the photocatalytic activity of the catalyst under investigation.

The selectivity of the reduction products depends on the density of activated charges and the reaction medium. The photocatalytic  $CO_2$  reduction can operate in vaporous or aqueous media [210], each one of which pushes the reaction to a specific pathway (Fig. 11).

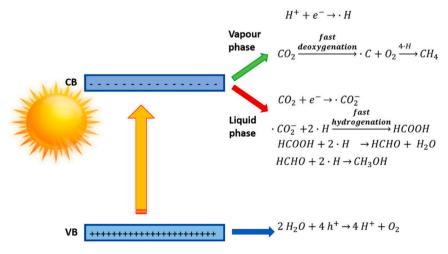


Fig. 11. Possible pathways of photocatalytic CO2 reduction in vapor and aqueous media. Adapted from [210] with copyright permission from MDPI, 2017.

#### 6.2. SFMPs: properties and general mechanism

A deeper understanding of the photocatalytic reduction mechanism of CO<sub>2</sub> over SFMPs is imperative for guiding future design strategies. When exposed to light, SFMPs absorb visible photons, which could generate electron-hole pairs. The photogenerated electrons in the CB migrate to the surface and could participate in the multi-electron reduction of adsorbed CO2 molecules while holes in the valence band (VB) could react with water or other sacrificial agents. The reduction pathway typically involves key intermediates including CO<sub>2</sub>, COOH, and HCOO<sup>-</sup>, with subsequent formation of products like CO, HCHO, CH<sub>3</sub>OH, and CH<sub>4</sub>. The outcome is contingent on the number of electrons transferred and the redox potentials of the reaction steps. The efficiency and selectivity of these pathways are closely tied to catalyst properties like band gap, surface adsorption energy, and charge separation efficiency. All of these properties can be tuned by means of structural modifications [211]. Upon light irradiation, these photocatalysts (e.g., ZnFe<sub>2</sub>O<sub>4</sub>, CuFe<sub>2</sub>O<sub>4</sub>, MnFe<sub>2</sub>O<sub>4</sub>) generate electron-hole pairs, where the excited electrons reducing CO2 into valuable hydrocarbons or solid carbon, while holes often oxidize water or sacrificial donors. The mechanistic pathway of photocatalytic CO<sub>2</sub> reduction on SFMPs, can be simplified as follows:

$$CO_2 + e^- \rightarrow CO_2^{\bullet -} \tag{4}$$

$$CO_2^{\bullet-} + H^+ \rightarrow COOH^* \text{ or } HCOO^*$$
 (5)

$$COOH^* \rightarrow CO + OH^- \tag{6}$$

$$HCOO^* \rightarrow HCHO \rightarrow CH_3OH \rightarrow CH_4$$
 (7)

The overall efficiency and selectivity of these pathways are critically linked to intrinsic catalyst properties, including band gap, surface adsorption energy, and charge separation efficiency. Metal doping, for instance with Ce or Mn, introduces mid-gap states and oxygen vacancies, enhancing visible-light absorption and facilitating CO<sub>2</sub> activation and conversion via intermediate species like COOH\* and HCOO\* [212]. Heterojunction and Z-scheme architectures (e.g., CuFe<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub>, ZnFe<sub>2</sub>O<sub>4</sub>/Ag/TiO<sub>2</sub>) could promote directional charge separation, allowing more electrons to participate in CO<sub>2</sub> reduction and suppressing recombination, thus improving the yield of CH<sub>3</sub>OH or CH<sub>4</sub> [213]. Furthermore, vacancy engineering (e.g., in MgFe<sub>2</sub>O<sub>4</sub> or Co-Fe<sub>2</sub>O<sub>3</sub>)

increases the density of oxygen vacancies, which serve as  $CO_2$  adsorption and activation sites, thereby stabilizing COOH\* intermediates and enhancing CO or  $H_2$  production [214].

# 6.3. Modification strategies and their impact on SFMP performance

To significantly boost the photocatalytic activity and efficiency of SFMPs for CO2 reduction, a diverse array of advanced modification approaches has been developed and extensively explored (Fig. 12). These strategies include doping with metal/nonmetal elements to tailor bandgaps and introduce defects, creating oxygen vacancies to enhance adsorption and charge separation, and controlling morphology for improved light harvesting and active site exposure. Moreover, incorporating the plasmonic effect has been demonstrated to enhance light absorption and the generation of hot electrons. Concurrently, the construction of Type II heterojunctions and Z-scheme systems has been shown to effectively separate charges and maintain strong redox potentials. Each approach contributes uniquely to enhancing CO<sub>2</sub> activation and conversion efficiency, as further discussed below. The following sections delve into specific examples of how different modification strategies enhance the photocatalytic CO2 reduction efficiency of SFMPs, building upon the general principles outlined previously and referencing the summarized data in Table 5.

# 6.3.1. Doping

The modification of SFMP by doping introduces tailored electronic and surface properties that enhance light absorption, charge separation, and redox activity. The incorporation of metal dopants (e.g., Ce, Mn) allows for the manipulation of the band structure, thereby ensuring a more precise alignment with solar irradiation. This, in turn, facilitates enhanced electron transfer, contributing to an optimized energy conversion process. Guo et al. [215] fabricated Ce-doped ZnFe<sub>2</sub>O<sub>4</sub> spinels, which demonstrated considerable adsorption capacities and high photocatalytic CO<sub>2</sub> reduction with H<sub>2</sub>O vapor, producing CO, H<sub>2</sub>, and CH<sub>4</sub> under sunlight illumination and a temperature of 200 °C for four hours. The photocatalytic reduction activity of Ce doped ZnFe<sub>2</sub>O<sub>4</sub> was four times higher than that of the undoped one. The introduction of Ce<sup>3+</sup> into the ZnFe<sub>2</sub>O<sub>4</sub> crystal resulted in the formation of a heterojunction between the ZnFe<sub>2</sub>O<sub>4</sub> and CeO<sub>2</sub> phases. This heterojunction led to several notable improvements in optical properties. Firstly, it enhanced the

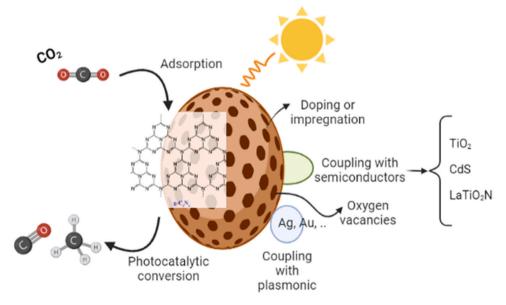


Fig. 12. Schematic illustration of common modification strategies for enhancing the photocatalytic CO<sub>2</sub> reduction efficiency of ferrite-based materials. The figure depicts approaches such as doping, coupling with other semiconductors, introducing oxygen vacancies, and incorporating plasmonic effects to optimize light absorption, charge separation, and CO<sub>2</sub> conversion. The figure was created with BioRender.com.

Table 5
SFMP modification strategies for enhanced photocatalytic co<sub>2</sub> reduction: performance and mechanisms.

Photocatalyst	synthesis approach	Morphology	Optical properties	Irradiation spectrum and source	Reduction product	Proposed Enhancement Mechanism	Ref.
Ce doped ZnFe <sub>2</sub> O <sub>4</sub>	Sol–gel	Polyhedralparticles	1.78, 2.07, 2.22, 2.32, 2.40, 2.47 and 3.4 eV for ZFC <sub>x</sub> (x = 0, 0.1, 0.15, 0.2, 0.25 and 0.3) respectively	Visible light	H <sub>2</sub> , CO and CH <sub>4</sub>	Band-gap tailoring, visible-light utilization, enhanced CO <sub>2</sub> adsorption	[215]
Mn-Fe <sub>3</sub> O <sub>4</sub>	Dispersion of Mn on Fe <sub>3</sub> O <sub>4</sub> microspheres	Microspheres	-	Not applicable (thermal hydrogenation)	Light olefins	Increased BET area, C=O bond activation, inhibited C-C coupling	[205]
Co-α-Fe $_2$ O $_3$	Alcohol-thermal reaction	Platelet-like	-	Visible light	80.2 % CO (37.8 μmol/h)	Synergistic Co/oxygen vacancies, enhanced selectivity towards CO <sub>2</sub> reduction	[216]
MgFe <sub>2</sub> O <sub>4</sub>	Coprecipitation followed by calcination	Hollow-Cubic structure	1.99–2.04 eV	Visible light	CO and $H_2$ (24.4 and 34.3 $\mu$ mol/g/h)	Oxygen vacancies: modified electronic structure, extended photoabsorption, minimized e'/h <sup>+</sup> recombination	[214]
CuFe <sub>2</sub> O <sub>4</sub> /TiO <sub>2</sub>	Sol–gel	Flocculent shapewith a diameter of 1–10 $\mu m$	TiO <sub>2</sub> (3.1 eV) CuFe <sub>2</sub> O <sub>4</sub> /TiO <sub>2</sub> (2.61 eV) CuFe <sub>2</sub> O <sub>4</sub> (1.24 eV)	Visible light (500 W xenon lamp) for 8 h	Methanol(651 lmol/gcat L)	$\text{CuFe}_2\text{O}_4$ CB shift, Type-II heterostructure for e $^{+}/\text{h}^{+}$ separation	[217]
Co <sub>x</sub> Zn <sub>1-x</sub> Fe <sub>2</sub> O4@TiO <sub>2</sub>	Co-precipitation followed by calcination of titania anatase	Aggregates of different sizes (less than 150 nm)	3.14 – 3.19 eV	UVC light irradiation via6 UVC-lamps (Philips TUV 6 W TL mini)	CO and CH <sub>4</sub>	Z-scheme (ZnFe <sub>2</sub> O <sub>4</sub> @TiO <sub>2</sub> ); Type-I heterojunction (CoFe <sub>2</sub> O <sub>4</sub> @TiO <sub>2</sub> )	[218]
α-Fe <sub>2</sub> O <sub>3</sub> /LaTiO <sub>2</sub> N	Solvothermal	Fine particles distributed on plates	2.05 eV	300 W Xe lamp simulated light source/3h	CO and CH <sub>4</sub>	Synergistic CO <sub>2</sub> adsorption & direct Z- scheme charge transfer	[207]
α-Fe <sub>2</sub> O <sub>3</sub> /CdS	Two-step solvothermal	Hierarchical flower-like microsphere	2.05 and 2.75 eV for $\alpha$ -Fe2O3 and CdS	Solar light	СО	Direct Z-scheme enhanced charge separation & lifetime; Interfacial electronic coupling	[219]
g-C <sub>3</sub> N <sub>4</sub> QDs/Au NPs/ CeO <sub>2</sub> /Fe <sub>3</sub> O <sub>4</sub>	Hydrothermal- calcination, deposits grow and self-assembly processes	Micro flowers	$2.83~{\rm eV}$ and $1.46~{\rm eV}$ for ${\rm CeO_2}$ MFs and CN QDs	UV–vis light	CO and CH <sub>4</sub>	Enhanced charge separation via Ce <sup>4+</sup> → Ce <sup>3+</sup> , oxygen defects, Z- scheme, heterojunctions; Magnetic recovery	[220]
ZnFe <sub>2</sub> O <sub>4</sub> /Ag/TiO <sub>2</sub>	Photo-deposition assisted solvothermal	${ m ZnFe_2O_4}$ microspheres deposited over ${ m TiO_2}$ NRs	2.15 eV	UV-light irradiation with 200 Hg lamp	CO, CH <sub>4</sub> and CH <sub>3</sub> OH	Z-scheme heterojunction; Ag-NPs as metal mediator	[221]
Fe <sub>3</sub> N/Fe <sub>2</sub> O <sub>3</sub> /C <sub>3</sub> N <sub>4</sub>	Thermal pyrolysis	Structure includes three different phases:a) layered g-C <sub>3</sub> N <sub>4</sub> nanosheets.b) Spherical Fe <sub>3</sub> N grains.c) dark black particles of Fe <sub>2</sub> O <sub>3</sub>	2.23 eV	300 W xenon lamp with 420 nm cut-off filter	CO 8.03 and CH <sub>4</sub> 1.6 µmol/ g/h	Z-scheme charges pathway; $Fe_2O_3$ increases photosensitivity & mediates $e^{\cdot}$	[222]
$\begin{array}{l} K_4Nb_6O_{17}/Fe_3N/\\ \alpha\text{-}Fe_2O_3/C_3N_4 \end{array}$	One-step thermal pyrolysis	Nanoflakes (diameter of a few hundred nm)	2.75 eV	300 W xenon lamp with a 420 nmcut-off filter	CO and CH <sub>4</sub> (7.01 and 1.3 µmol/g/h respectively).	Coexistence of 4 photosensitive compounds; 4 interfacial junctions for charge transport; Fe <sub>3</sub> N electron mediator	[223]
$\alpha\text{-Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$	Hydrothermal	Honeycomb-like porous structure	2.79 and 2.04 eV for g- $C_3N_4$ and $\alpha$ - $Fe_2O_3$ respectively	Visible light 300 W Xenon lamp with a 420 nm cut-off filter	СН₃ОН	Band-gap tailoring; Z- scheme transfer mechanism	[224]
rGO@CuZnO@Fe <sub>3</sub> O <sub>4</sub>	Ionic interaction followed by hydrothermal	Core-shell microspheres	1.44 eV	Visible light 20 W white cold LED light	CH <sub>3</sub> OH(2656 μmol/g cat)	rGO facilitated electron transport; Fe <sub>3</sub> O <sub>4</sub> facilitated charge migration & magnetic recovery; Cu captured electrons	[225]
Fe <sub>3</sub> O <sub>4</sub> @NC/Cu <sub>2</sub> O	Cu <sup>2+</sup> reduction followed by aerobic oxidation	Rod-shaped core-shell	Optical band gap is difficult to determine for black catalysts	5 W Xenon HID lamp (irradiance of 12.5 cm <sup>-2</sup> )	СН₃ОН	Nitrogen doping inhibited recombination; Surface $\text{Cu}_2\text{O}$ NPs increased $\text{S}_{\text{BET}}$ ; $\text{Fe}_3\text{O}_4$ core retarded photo-corrosion &	[226]

Table 5 (continued)

Photocatalyst	synthesis approach	Morphology	Optical properties	Irradiation spectrum and source	Reduction product	Proposed Enhancement Mechanism	Ref.
CoO <sub>x</sub> /ZnFe <sub>2</sub> O <sub>4</sub> @H- TiO <sub>2</sub> /Au-Cu	Stepwise solvothermal	Double-shell hollow nanospheres	1.89 and 2.91 eV	Visible light irradiation. by 300 W Xe lamp with AM1.5 filter	CH <sub>4</sub> 21.39 µmol/g/h with 93.8 % selectivity	enabled magnetic recovery Double-shell inhibited bulk recombination; Type-II heterojunction; Au-Cu/CoO cocatalysts trapped e'/h <sup>+</sup>	[227]
Co <sub>3</sub> O <sub>4</sub> @CoFe <sub>2</sub> O <sub>4</sub>	Solvothermal synthesis followed by thermal treatment	Hierarchical hollow double-shelled nano- boxes	$1.42$ and $1.69$ eV for $CoFe_2O_4$ and $Co_3O$ respectively	300 W Xelamp	CH₄ and CO	Hierarchical hollow cubic structure increased photo- utilization/absorption; Z- scheme facilitated e*/h+ transfer	[228]

absorption of visible light, resulting in an increase in photoinduced charges. Secondly, it reduced PL emissions by delaying recombination. Thirdly, it enhanced chemisorption and activation of CO<sub>2</sub>, thereby forming the reduction precursor CO2 in the presence of water vapor. Jiang et al. [205] used Mn-Fe<sub>3</sub>O<sub>4</sub> catalyst for the highly selective conversion of CO<sub>2</sub> to light olefins via reductive hydrogenation. The manganese promoter has demonstrated a number of significant effects, including an increase in the BET area, an enhancement of surface adsorption toward CO2 by virtue of its provision of active sites, a facilitation of the activation of C=O bonds cleavages on both sides, a maximization of the effective yield of hydrocarbons, and a retardation of the formation of long C-C chains via secondary hydrogenation, thereby favoring the selectivity of light olefins. The mechanism involves two steps, namely first adsorption and the reduction of CO2 on the catalyst surface producing CO via reverse water–gas shift (RWGS,  $CO_2 + H_2 \rightarrow$  $CO + H_2O$ ). The second step involves activation of the C=O bond and hydrogenation to form C-C chains via Fischer-Tropsch synthesis (FTS, n  $CO + 2n H_2 \rightarrow C_n H_{2n} + n H_2 O$ ).

The discussion now includes the transformative potential of twodimensional (2D) materials, such as graphene, layered double hydroxides, molybdenum disulfide (MoS2), bismuthene, and MXenes, in enhancing the photocatalytic reduction of CO2 [229-231]. These materials have significant key advantages, including an exceptionally large specific surface area, abundant active sites, and atomic thickness that facilitates efficient charge transfer, and tunable electronic properties [229]. For example, 2D graphene oxide (GO)-diketopyrrolopyrrole (DPP) film photocatalysts have shown remarkable CO production rates of 32.62 µmol g<sup>-1</sup> h<sup>-1</sup> in aqueous solutions, achieving almost 100 % selectivity without the need for sacrificial agents [232]. Similarly, MXenes (e.g., Ti<sub>3</sub>C<sub>2</sub>Xy) coupled with ZrO<sub>2</sub> photocatalysts have significantly boosted CO formation rates by 6.6 times to 4.6  $\mu$ mol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> [233]. MXenes function as efficient co-catalysts due to their high electrical conductivity and rich surface functionalities, which promote electron-hole separation and enhance CO2 adsorption and activation. The ability to control magnetism in 2D van der Waals materials using heat or laser pulses suggests exciting avenues for integrating magnetic separability with advanced photocatalytic properties, potentially offering a new dimension for catalyst recovery and manipulation [234]. This widespread adoption of 2D materials signifies a conceptual shift in catalyst design, moving towards engineering interfaces at the nanoscale to optimize charge dynamics and catalytic performance.

# 6.3.2. Oxygen vacancies

The incorporation of oxygen vacancies into SFMP has been demonstrated to enhance its photocatalytic activity. This enhancement is attributed to the creation of defect sites, which facilitate charge separation and improve  $\text{CO}_2$  adsorption. These vacancies narrow the band gap and serve as active centers for electron transfer, enabling more efficient photocatalytic reduction of  $\text{CO}_2$ . For example, Yang \textit{et al.} [216] designed an efficient cocatalyst by decorating  $\alpha\text{-Fe}_2\text{O}_3$  with 1~% Co

Fu et al. [214] successfully improved the CO2 photocatalytic reduction activity of MgFe<sub>2</sub>O<sub>4</sub> by introducing oxygen vacancies via high-temperature calcination (650-850 °C) under visible light illumination, giving a high yield of CO and H<sub>2</sub>. The results show an increase in the oxygen vacancies' concentration within increasing calcination temperature, followed by decreasing vacancies beyond 750 °C. The Mg-Fe-750 displayed the highest EPR signal, implying the highest oxygen vacancies concentration. The increase in oxygen vacancies upon calcination is attributed to the formation of spinel phase crystals below 750 °C. TG analysis shows a decrease in sample weight with increasing temperature (600–750 °C) then weight gain at (800–850 °C) as a result of iron oxide formation resulting from reacting MgFe<sub>2</sub>O<sub>4</sub> with O<sub>2</sub> at higher temperatures. The introduction of oxygen vacancies boosted the PCA by: (i) enhancing visible light absorption; (ii) the inhibition of e<sup>-</sup>/h<sup>+</sup> recombination; and (iii) increasing the chemical adsorption of the catalyst towards CO2.

# 6.3.3. Morphology

Modifying the morphology of SFMP offers a powerful strategy to enhance their photocatalytic efficiency for CO₂ reduction. The strategic tailoring of structures such as core-shell microspheres, nanorods, or hollow nanospheres, researchers can improve light harvesting, charge separation, and reactant accessibility. These morphological designs enable synergistic interactions among multi-component systems, facilitating selective and efficient CO2 conversion into valuable fuels under visible light. Kumar et al. fabricated magnetically-recoverable core-shell microspheres of CuZnO@Fe<sub>3</sub>O<sub>4</sub> wrapped in reduced graphene oxide (rGO@CuZnO@Fe<sub>3</sub>O<sub>4</sub>) and used it for the selective reduction of CO<sub>2</sub> to CH<sub>3</sub>OH with H<sub>2</sub>O under visible irradiation [225]. The restoration of the sp<sup>2</sup> hybridized aromatic system in rGO facilitated electron transportation resulting in better charge separation. The photocatalytic effect is due to the synergism between hetero-catalytic components providing high electron mobility, which is detailed in the following points: (I) the efficient transfer of e<sup>-</sup>/h<sup>+</sup> of Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> to ZnO; (II) copper content trapped photoinduced electrons and reduced electron-hole pair recombination; (III) rGO wrap onto ZnO@Fe<sub>3</sub>O<sub>4</sub> microspheres enhances methanol selectivity due to efficient electron transfer from the CB of ZnO to the rGO sheets. The catalyst is magnetically-recoverable for six cycles without a significant decrease in methanol yield.

Movahed et al. [226] developed Cu<sub>2</sub>O NP<sub>S</sub> decorated on Fe<sub>3</sub>O<sub>4</sub>@N-C

NRs-shaped core-shell and investigated its photocatalytic activity on the selective photoreduction of  $CO_2$  to  $CH_3OH$  under visible light illumination. Photocatalytic  $CO_2$  reduction with  $Fe_3O_4@N\text{-}C/Cu_2O$  was found to be four times higher than that of  $Fe_3O_4/Cu_2O$ , with the catalyst retaining its reactivity for only four cycles. The unique PCA is a result of three factors: (I) surface-immobilized  $Cu_2O$  NPs increase  $S_{BET}$  that not only facilitates the absorption and utilization of sunlight but also makes better contact between photocatalysts and  $CO_2$ . (II)  $Fe_3O_4$  core rods retarded the photocorrosion of  $Cu_2O$ , enhanced the photogeneration of  $e^-/h^+$ , and enabled the magnetic recovery of the catalyst. (III) Nitrogen doping into the carbon layer increased the hydrophilicity, improving the dispersibility of the magnetic core and hindering their agglomeration in the solution. Furthermore, nitrogen moieties on the carbon layer served as anchoring sites of the Cu species and the N-C layer retards the recombination of the photoinduced  $e^-$ .

Liu et al. designed and fabricated double-shell hollow heterostructure nanospheres of  $ZnFe_2O_4@Hollow-TiO_2$  anchored with a dualseparated cocatalyst of CoO and Au-Cu [227]. They claimed the creation of surface oxygen vacancies for enhancing visible light utilization, improving carriers' separation and enabling photocatalytic CO2 reduction with 93.8 % selectivity towards CH<sub>4</sub>. A CoO oxidation cocatalyst was used for trapping holes, while Au-Cu reduction cocatalysts were trapping electrons. A high PCA was obtained when oxidation and reduction cocatalysts were separately loaded, which facilitates carriers' separation and inhibits their recombination (Fig. 13). The hollow spherical structure might result in bulk recombination of the photoinduced charges, a phenomenon that was overcome by the formation of a staggered heterojunction between ZnFe<sub>2</sub>O<sub>4</sub> and H-TiO<sub>2</sub>, which strongly accelerated the transfer and separation of the photogenerated e<sup>-</sup>/h<sup>+</sup> pairs. The hollow structure also provides a large surface area and high light exploitation. The mechanism involves visible light photosensitization of the composite, which provides e that in turn migrates across the heterojunction and is trapped by the reduction cocatalyst Au-Cu and then, finally, participates in CO2 reduction to CH4. Meanwhile, photoinduced h<sup>+</sup> also migrates across the junction and is trapped by the oxidizing cocatalyst CoO before participating in water oxidation.

Long et al. developed a hierarchical hollow double-shelled nanoboxes of  $\text{Co}_3\text{O}_4$ @ $\text{CoFe}_2\text{O}_4$  photocatalyst utilizing [Ru(bpy)\_3]Cl\_2·6 H<sub>2</sub>O as a photosensitizer [228]. The unique morphology provides a large surface area that boosts light absorption and enhances the adsorption of  $\text{CO}_2$  molecules. The Z-scheme heterojunction provided a short electron transport pathway and strengthened the charge density, giving a stronger oxidation/reduction ability. Under UV–vis irradiation, the photocatalyst exhibited a high reduction strength for  $\text{CO}_2$  to CO and  $\text{CH}_4$ . The reaction mechanism postulated that the CO was formed from activated  $\text{CO}_2^-$ , whereas  $\text{CH}_4$  was produced from either the formate

intermediate (COO') or the consumption of CO by six electrons, when sufficient electrons are provided by the photocatalyst [228].

# 6.3.4. Plasmonic effect

The incorporation of plasmonic nanostructures into SFMP significantly enhances their photocatalytic performance for CO2 reduction by exploiting localized surface plasmon resonance (LSPR). Plasmonic metals such as Au and Ag generate energetic "hot electrons" under light irradiation, facilitating charge separation and direct injection of electrons into ferrite conduction bands or adjacent semiconductors. This synergistic interaction boosts light absorption, promotes efficient charge transfer, and increases the overall yield and selectivity of CO2 photoreduction products. Wei et al. [220] co-modified CeO2/Fe3O4 micro-flowers with g-C<sub>3</sub>N<sub>4</sub> QDs (CN QDs) and Au nanoparticles for the purpose of preparing a photocatalytic composite nominated (CACeF). The composite was examined for CO<sub>2</sub> reduction to CO and CH<sub>4</sub>. The modified composite showed, respectively 5- and 8-times higher yield than that of pure CeO<sub>2</sub> under the illumination of UV-visible light. The enhanced photocatalytic activity was attributed to some factors. First, (I) the conversion of Ce<sup>4+</sup> to Ce<sup>3+</sup> conversion and oxygen defects on the CeO<sub>2</sub> surface were observed to enhance the separation of photogenerated e<sup>-</sup>/h<sup>+</sup>; (II) a Z-scheme charges pathway formed between Fe<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>; (III) a heterojunction between CeO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> that facilitates charge separation; (IV) LSPR of Au, which not only photosensitized CeO2 but also produced hot electrons participated directly in CO2 reduction; and (V) Fe2O3 enabled the magnetic recovery and promoted light utilization of the composite.

Tahir [221] synthesized  $ZnFe_2O_4$  microspheres, coupled with  $Ag/TiO_2$  nanorods, to develop a Z/scheme heterojunction that facilitates photocatalytic reduction of  $CO_2$  to CO,  $CH_4$ ,  $CH_3OH$ , and  $C_2H_6$  under UV and visible light irradiation in the presence of  $H_2O$  in a fixed bed reactor system. 1D  $TiO_2$  NRs facilitate a one-directional flow of photogenerated electrons to VB of  $ZnFe_2O_4$  microspheres due to the Z-scheme assembly  $(ZnFe_2O_4/TiO_2)$  obtained under UV irradiation, whereas Ag acts as a metallic mediator. Water oxidation would occur at a VB of  $TiO_2$  NRs and  $CO_2$  reduction at a CB of  $ZnFe_2O_4$ . The photocatalyst was found to be effective and stable for four cycles; after the fourth cycle, the amount of CO was 1.06-fold lower compared to the first cyclic run, while  $CH_4$  was increased by 1.07-fold higher than it was produced in the first cycle.

# 6.3.5. Type II heterojunction

The formation of type-II heterojunctions between SFMP and semi-conductors presents a powerful strategy to enhance photocatalytic CO<sub>2</sub> reduction efficiency. In such systems, staggered band alignments facilitate spatial separation of photogenerated electrons and holes, reducing recombination and boosting charge carrier lifespan. By coupling ferrites

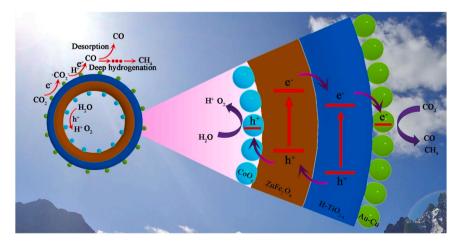


Fig. 13. Mechanism of photocatalytic CO<sub>2</sub> reduction showing charge transfer across the hollow structured photocatalyst ZnFe<sub>2</sub>O<sub>4</sub>@H-TiO<sub>2</sub> and separately loaded cocatalysts (CoO and Au–Cu) Adapted from [227] with copyright permission from Elsevier, 2021.

like CuFe<sub>2</sub>O<sub>4</sub> or ZnFe<sub>2</sub>O<sub>4</sub> with TiO<sub>2</sub> or other narrow-bandgap materials, the heterostructure not only tailors band positions to match redox potentials but also improves visible-light absorption and catalytic selectivity toward CO2 reduction products such as methanol or CO. Uddin et al. [235] investigated the photocatalytic reduction of CO2 to methanol using CuFe<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> under visible irradiation, giving a three times higher yield than that of CuFe<sub>2</sub>O<sub>4</sub> (with the stepwise addition of the catalyst). A low formation rate of methanol on CuFe<sub>2</sub>O<sub>4</sub> alone was observed due to the large difference between the potential of CuFe<sub>2</sub>O<sub>4</sub> CB (-1.03 V) and the redox couple (-0.38 V) of photoreduction. Loading TiO2 onto CuFe2O4 raised the methanol yield and increased the photocatalytic reduction activity due to three reasons: (I) The band gap of the material was modified to align with the standard reaction potential by adjusting the CB of CuFe<sub>2</sub>O<sub>4</sub> to a more negative level; (II) CuFe<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> Type-II hetero-structure promoted the e<sup>-</sup>/h<sup>+</sup> separation and retard their recombination. The methanol formation mechanism follows Eq. 8:

$$CO_2 + 6 H^+ + 6 e^- \rightarrow CH_3OH + H_2O E_{ox}^0 = -0.38 V$$
 (8)

In a related study, Ciocarlan  $\it et al. [218]$  coupled doped Ferrite nanocomposites of  $Co_xZn_{1-x}Fe_2O_4$  with  $TiO_2$  for improving the photocatalytic  $CO_2$  reduction with hydrogen under UVC light irradiation within a fixed-bed batch reactor. The  $CO_2$  reduction to CO exhibited a direct proportionality to the Zn:Co ratio, thereby confirming that Zn ferrites demonstrate significantly higher activity compared to CO ferrites. This is evidenced by an 80 % increase in CO yield, which possesses the potential to further react with CO in the rector-producing syngas. The reduction of CO to CO to CO is more favorable when using a CO ferrite photocatalyst. Mott-Schottky plots provide evidence that the junction across CO free CO functions as a CO ferroge transfer pathway mechanism. In contrast, a type I heterojunction was observed across CO for CO functions.

Song et al. [207] converted CO2 into CO and CH4 via visible light photocatalytic reduction using  $\alpha\text{-Fe}_2O_3/\text{LaTi}O_2N$ .  $\alpha\text{-Fe}_2O_3$  has been demonstrated to enhance the photocatalytic activity of LaTiO2N in three ways: (I) an increase in SSA from 6.8 (pristine LTON) to 15.0 m<sup>2</sup>/g, which increases CO<sub>2</sub> adsorption ability; (II) a direct Z-scheme pathway that facilitate charge separation (proved by Nyquist plots with a semicircular shape), which in turns improves charge generation and migration (as proven by the TPC plot), and inhibits recombination by elongating a carrier's lifetime (proved by the TRPL spectra); (III) bandgap shifting towards longer wavelengths. Furthermore, α-Fe<sub>2</sub>O<sub>3</sub> showed a strong water oxidation capacity with a lower VB edge position, whereas LaTiO<sub>2</sub>N displayed a strong CO<sub>2</sub> reduction ability with a higher CB edge position. The formation of the heterojunction between α-Fe<sub>2</sub>O<sub>3</sub> and LaTiO2N was confirmed by the XPS spectra of the composite, which showed shifting O 1 s, N 1 s, and Fe 2p peaks of α-Fe<sub>2</sub>O<sub>3</sub>/LaTiO<sub>2</sub>N towards lower binding energies, whereas La 3d and Ti 2p peaks of the LATN were shifted towards the opposite direction. This shift in binding energies is indicative of the formation of a built-in electric field with direction from LTON to α-Fe<sub>2</sub>O<sub>3</sub>.

Long et al. constructed a 2D/2D  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/CdS bilayer heterostructure and applied it to photocatalytic CO<sub>2</sub> reduction [219]. The photocatalytic enhancement was mainly attributed to: (i) effective interfacial electronic coupling resulting in a favorable internal built-in electric field (IEF); (ii) a short diffusion distance to the interface between 2D-CdS and 2D- $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>; and (iii) a direct Z-scheme charge transfer pathway across the large bilayer interface.

# 6.3.6. Z-scheme

Z-scheme ferrites were introduced for photocatalytic reduction of  ${\rm CO}_2$  primarily to overcome the limitations of traditional single-component systems. The primary function of these materials is to provide efficient charge separation, strong redox ability, and enhanced light absorption. These elements are indispensable for driving the complex,

multi-electron CO2 reduction process. For example, Padervand et al. [222] synthesized a novel ternary Fe<sub>3</sub>N/Fe<sub>2</sub>O<sub>3</sub>/C<sub>3</sub>N<sub>4</sub> photocatalyst from cheap raw material and applied it to the photocatalytic reduction of CO2 with H<sub>2</sub>O vapors (gas phase reduction) under visible light irradiation. The ternary composite showed CO<sub>2</sub> photoreduction activity seven times higher than that of C<sub>3</sub>N<sub>4</sub>. That enhancement could be attributed to: (i) The presence of Fe<sub>2</sub>O<sub>3</sub> resulted in an increase in photosensitivity, leading to the generation of greater quantities of e<sup>-</sup>/h<sup>+</sup> pairs following visible light irradiation; (ii) The presence of Fe2O3 resulted in an increase in photosensitivity, leading to the generation of greater quantities of e<sup>-</sup>/h<sup>+</sup> pairs following visible light irradiation; and (iii) the Z-scheme pathway, which facilitated carriers' migration across the ternary interfaces and inhibited their recombination. Products of photocatalytic CO2 reduction detected by gas chromatography were CO (produced at the beginning of the reaction and it started fading smoothly after 1 h) and CH<sub>4</sub> (evolution rate increased slowly along the reaction time). Another study reported of a magnetically fabrication reusable  $K_4Nb_6O_{17}/\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>N/g-C<sub>3</sub>N<sub>4</sub> photocatalyst, which exhibited boosted photoreduction activity of CO2 14.6-fold higher than that of g-C3N4 [223]. The enhanced photocatalytic activity could be ascribed to the coexistence of various photosensitive compounds that increase light harvesting and the presence of four interfacial junctions, facilitating charge transportation. Moreover, the coexistence of a large number of active sites on the surface of the four crystalline phases can efficiently enhance the photocatalytic reduction process. Fe<sub>3</sub>N exhibits unique magnetic and electronic properties that play an essential role in photocatalyst reusability and prolong the carriers' lifetimes by acting as an electron mediator [222]. Guo et al. [224] analyzed the photocatalytic activity of α-Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> for the photo-reduction of CO<sub>2</sub> to methanol under visible irradiation at 20 °C and 0.6 MPa. The composite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> showed a three times higher level of CO<sub>2</sub> reduction activity than that of lone g-C<sub>3</sub>N<sub>4</sub> for two reasons: (i) α-Fe<sub>2</sub>O<sub>3</sub> enhanced visible light utilization; and (ii) Z-scheme transfer mechanism (heterojunction) facilitated separation of photogenerated e<sup>-</sup>/h<sup>+</sup> and suppresses their recombination. The mechanism involves the photooxidation of H<sub>2</sub>O in the VB of Fe<sub>2</sub>O<sub>3</sub> and photocatalytic CO<sub>2</sub> reduction to CH<sub>3</sub>OH in the CB of g-C<sub>3</sub>N<sub>4</sub>.

# 7. Future perspectives

While significant progress has been made in ferrite-based nanomaterials for photocatalytic CO<sub>2</sub> reduction, several critical challenges and unresolved questions must be addressed to translate laboratory success into practical applications. These challenges span fundamental mechanistic understanding, experimental methodologies, scalable system design, and environmental sustainability.

This review has highlighted recent progress and issues associated with the properties and synthesis of magnetic nanoparticle ferrites with controlled size, crystallinity, and composition as active photocatalysts for different photo-based applications. Numerous synthetic approaches have been developed and explored including coprecipitation, hydrothermal, microemulsion, simple thermal decomposition, microwaveassisted, and bio-based methodologies. Hydrothermal, coprecipitation, and sol-gel methods are the most prevalent approaches for producing MNPs. Despite substantial progress, significant gaps remain in synthetic methodology for controlling key variables, including the cost of chemical design, particle size, the chemistry of the desired structure, and the material quality for the photocatalytic application. Furthermore, a deeper understanding of which of the aforementioned factors is the most significant for evaluating photochemical stability and performance. From a morphological perspective, the controlled addition of surfactants offers advantages during the synthetic of MNPs strategy, due to the interaction between metallic contents and the surfactant, which can control particle aggregation and enable controllable particle growth. Furthermore, the remaining surfactant content on the prepared MNPs might block some active sites, creating performance issues, therefore

complete surfactant removal is essential to maintain catalytic activity. The hydrothermal process is often preferred over sol-gel and other approaches because it could produce NPs of the desired size, crystallinity, and compositional consistency. However, the requirement for high temperatures and pressures, as well as specialized reactors, makes this strategy less energy-efficient compared to other synthesis techniques.

Improved photocatalytic performance could be achieved by designing MNPs with high porosity characteristics. The porosity of prepared MNPs plays a crucial role in their photocatalytic performance and adsorption capacities. Higher surface area provides better quantity and quality of active sites, resulting in enhanced adsorption capacity. Additionally, porosity creates efficient pathways and more active sites for charge transfer during photocatalytic applications. The overall properties of MNPs can be tailored through additional design considerations, including doping to introduce vacancies or crystal defects. The presence of dopant elements during material processing can modify ion distribution and significantly affect physicochemical characteristics. Moreover, novel or enhanced properties can be achieved through exchange coupling between soft and hard MNPs for specific applications. Therefore, optimization between the synthetic cost, desired physicochemical character (including morphology, porosity, and crystallinity), and photocatalytic performance should be discussed in future studies.

Commercial-scale production of MNPs represents one of the key factors for accelerating the commercialization of photocatalysts. Unfortunately, most of the reported synthesis strategies that have been studied ignored commercial requirements, often employing toxic solvents, complex reactors, high-cost precursors, and extreme pressure and temperature. To attract industrial application of MNPs, environmentally friendly and reproducible chemical strategies that can be optimized for commercial use are essential. This requires elaborate studies from multiple research groups to confirm reproducible, low-cost, and efficient MNP production.

The transition from laboratory-scale synthesis to commercial production necessitates a thorough environmental assessment. For instance, a recent study utilizing the Waste Reduction Algorithm (WAR) for large-scale magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticle production via co-precipitation (806.87 tons/year capacity) indicated that the process, when optimized, can be environmentally friendly, showing negative Potential Environmental Impacts (PEI)[236]. However, this assessment also

highlighted that the main environmental impacts often arise from downstream processes, such as the centrifugation unit for separation, rather than the core synthesis reaction itself.[256] This finding underscores the need for holistic life cycle assessments (LCA) that consider the entire product lifecycle, from raw material extraction to end-of-life management, rather than focusing solely on 'green synthesis' at the initial stage. Currently, the literature lacks comprehensive LCA studies for many nanomaterials, which can lead to misleading conclusions about their overall environmental performance.

A promising future trend in synthetic methods involves the utilization of industrial waste as a raw material for ferrite production, as summarized in Fig. 14. This approach aligns with circular economy principles and addresses both waste management and resource sustainability challenges. The design process typically begins with the identification of waste sources, which may include industrial waste (e.g., ash, mud, sludge), agricultural biomass, and electronic waste (e.g., computers, batteries, phones, and circuit boards) [237]. These wastes often contain significant quantities of transition metals (Fe. Co. Ni. Mn) critical for magnetic nanoparticle fabrication. After waste sorting, a pre-treatment phase is essential to prepare raw materials for further processing. Pre-treatment procedures often involve drying, grinding, sieving, and, in certain instances, heat activation (e.g., calcination or pyrolysis) to improve metal accessibility and eliminate organic materials. Following extraction, these materials undergo various material synthesis procedures, including co-precipitation, sol-gel methods, hydrothermal or solvothermal approaches, and, progressively, green synthesis utilizing plant extracts or biotemplates. These methods facilitate control over material shape, crystallinity, and dimensions, all critical for photocatalytic efficacy. Fig. 14 provides a comparative overview, contrasting recent advancements and conventional challenges with the future prospects enabled by waste-driven material design.

Another primary challenge lies in the ambiguous reaction pathways and unclear charge transfer mechanisms within complex photocatalytic systems. Despite numerous heterojunction photocatalysts being reported, direct evidence for the precise charge transfer pathways (e.g., built-in electric fields, specific electron/hole migration routes) frequently remains insufficient, and theoretical computations can still be speculative. The dynamic nature of photocatalyst surfaces, which can undergo kinetic state or even shape changes during reactions, further

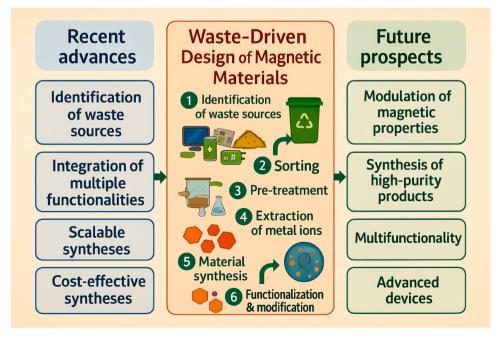


Fig. 14. Schematic illustration of the design pathway for waste-derived magnetic photocatalysts. The comparative overview within the figure further highlights recent advancements and conventional challenges alongside the promising future prospects enabled by this sustainable waste valorization approach.

complicates understanding. Future efforts must prioritize a clever combination of advanced spectroscopic characterizations (e.g., in situ XPS, femtosecond transient absorption spectra, Kelvin probe force microscopy) and sophisticated theoretical calculations to elucidate these intricate mechanisms at an atomic and molecular level.

Artificial intelligence (AI) and machine learning tools are expected to play a more significant role in forecasting waste composition and customizing synthesis settings for optimal efficacy. Moreover, the integration of photocatalysis with other technologies, such as photosupercapacitors and solar fuel generation systems, creates opportunities for hybrid devices that simultaneously purify the atmosphere and store energy. Ultimately, comprehensive legislative backing and industrial collaboration will be essential for the widespread adoption of these materials, facilitating the transition from laboratory synthesis to pilot or large-scale applications that utilize municipal and agricultural waste streams.

#### 8. Conclusions

This review offers a comprehensive of the advancements in ferrite-based magnetic nanomaterials for photocatalytic CO<sub>2</sub> reduction, distinguishing itself by focusing specifically on the unique advantages, synthesis, and modification strategies pertinent to ferrites. Ferrite-based magnetic nanomaterials exhibit significant potential in photocatalytic applications, particularly in terms of environmental remediation and sustainable energy production. Their unique properties, such as low toxicity, cost-effectiveness, and efficient magnetic separation, make them viable candidates for the photocatalytic CO<sub>2</sub> reduction. Magnetic photocatalysts are typically composed of a magnetic core, which facilitates easy separation and recovery, and a photoactive semiconductor shell. This dual structure ensures both high photocatalytic activity and catalyst reusability. The review has detailed various synthetic approaches, and emphasized how these strategies influence the final structure, stability, and photocatalytic efficiency of the materials.

The enhanced photocatalytic performance of ferrite-based nanoparticles is achieved through various advanced design strategies, including dimensional tuning, co-catalyst integration, heterojunction formation, and the engineering of oxygen vacancies. By modifying physicochemical properties like bandgap energy, surface area, and charge separation efficiency, the photocatalytic activity of these materials can be optimized for the selective conversion of CO2 into valuable products. This review underscores the importance of the further development of ferrite-based photocatalysts to overcome current limitations and advance sustainable solutions for environmental challenges. The strategic design of waste-driven magnetic photocatalysts presents a versatile, promising frontier. This approach paves the way to green synthesis techniques and application-driven design, redefining the role of waste in next-generation catalytic technologies. Future progress will depend on integrating these innovative material designs with a deeper mechanistic understanding to create practical and scalable systems for a sustainable future.

# CRediT authorship contribution statement

Khaled M. Amin: Writing – original draft, Supervision, Visualization, Conceptualization, Writing – review & editing, Data curation.

Nada A. Eldeeb: Writing – original draft, Writing – review & editing, Data curation, Visualization. Zineb Gargar: Visualization, Writing – review & editing, Data curation, Writing – original draft. Ibrahim M.A.

Mohamed: Conceptualization, Visualization, Writing – review & editing, Supervision, Writing – original draft, Data curation. Mohamed Elsenety: Visualization, Conceptualization, Writing – original draft, Data curation, Writing – review & editing, Supervision. Mahmoud M. Emara: Supervision, Conceptualization, Writing – review & editing, Data curation, Writing – original draft. M. Abd Elkodous: Writing – original draft, Data curation, Writing – review & editing, Visualization.

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#### **Declaration of Competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

# Acknowledgement

Open Access publication is funded by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) grant number 491111487. Hesham Hamad acknowledges the financial support from the MOPGA 2022 Visiting Fellowship Program for Young Researchers provided by the Ministry of Europe and Foreign Affairs (France) and MAEC-AECID fellowship by the Ministry of Foreign Affairs and Cooperation (Spain).

#### Data availability

Data will be made available on request.

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