

Band-Gap Engineering and Magnetic Enhancement of Mn–Ni and Mn–Cu Co-Doped ZnFe₂O₄ Nanoceramics via Green Microwave-Assisted Synthesis for Visible-Light Photocatalysis

Michael Jegan1 M

m.jagan8888@gmail.com

Chikkaiah Government Arts and Science College

Selleswari D

Chikkaiah Government Arts and Science College

Sarala Rubi C

Vel Tech Rangarajan Dr Sagunthala R&D Institute of Science and Technology

ArulMurugan P

Sir Theagaraja College

Research Article

Keywords: ZnFe₂O₄ nanoparticles, Mn–Ni co-doping, Mn–Cu co-doping, Green microwave-assisted synthesis, Visible-light photocatalysis, Magnetic recoverability, Wastewater treatment

Posted Date: September 2nd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10660354/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.
[Read Full License](#)

Additional Declarations: No competing interests reported.

Abstract

Developing sustainable visible-light-driven photocatalysts for wastewater treatment remains a significant challenge. In this study, Mn–Ni and Mn–Cu co-doped ZnFe_2O_4 nanoparticles were synthesized via a green microwave-assisted method using *Azadirachta indica* (neem) leaf extract. XRD confirmed single-phase cubic spinel ferrites, while TEM revealed nanosized quasi-spherical particles. UV–Vis DRS showed reduced band gaps and enhanced visible-light absorption after co-doping, whereas VSM confirmed enhanced soft ferrimagnetic behavior with increased saturation magnetization, enabling efficient magnetic recovery. Under visible-light irradiation, Mn–Ni and Mn–Cu co-doped ZnFe_2O_4 achieved methyl orange degradation efficiencies of 98.2% and 96.0%, respectively, outperforming pristine ZnFe_2O_4 . The enhanced photocatalytic performance is attributed to band-gap narrowing, improved charge separation, suppressed electron–hole recombination, and enhanced magnetic properties. These findings demonstrate that green microwave-assisted co-doping is an effective strategy for developing efficient, magnetically recyclable ZnFe_2O_4 photocatalysts for sustainable wastewater remediation.

1. Introduction

Green synthesis has emerged as an environmentally friendly and sustainable approach for preparing nanomaterials by minimizing hazardous chemicals and reducing environmental pollution. Plant extracts serve as effective natural reducing, stabilizing, and capping agents because of their rich phytochemical constituents, including flavonoids, phenolics, alkaloids, and terpenoids, which facilitate controlled nanoparticle formation. Compared with conventional chemical methods, green synthesis offers several advantages, including simplicity, low cost, biocompatibility, and eco-friendliness. In addition, microwave-assisted synthesis has gained considerable attention owing to its rapid and uniform heating, shorter reaction time, high energy efficiency, improved crystallinity, and better control over particle size and morphology. The integration of green chemistry with microwave-assisted processing provides an efficient route for producing highly crystalline ferrite nanomaterials with enhanced physicochemical properties for environmental applications [1–6].

Among spinel ferrites, ZnFe_2O_4 is considered a promising visible-light-responsive photocatalyst because of its narrow band gap, excellent chemical stability, magnetic recoverability, and low toxicity. However, its practical application is limited by rapid electron–hole recombination and relatively poor visible-light utilization, resulting in moderate photocatalytic efficiency. Transition-metal doping has proven to be an effective strategy for overcoming these limitations by tailoring the electronic structure, narrowing the band gap, enhancing visible-light absorption, promoting charge-carrier separation, and improving magnetic properties. In particular, Mn, Ni, and Cu dopants have shown remarkable potential for enhancing the photocatalytic performance of ZnFe_2O_4 through modifications of its structural, optical, and magnetic characteristics [7–12].

Recent studies have demonstrated that microwave-assisted green synthesis significantly improves the crystallinity, morphology, and catalytic activity of ferrite nanoparticles while greatly reducing synthesis time. Although several investigations have reported individually doped ZnFe_2O_4 photocatalysts, systematic comparative studies on different transition-metal co-doping strategies synthesized under identical green microwave-assisted conditions remain scarce. In particular, a direct comparison between Mn–Ni and Mn–Cu co-doped ZnFe_2O_4 nanoparticles and their combined effects on crystal structure, optical band-gap engineering, magnetic behavior, and visible-light photocatalytic performance has not been comprehensively explored [13–16].

In the present work, Mn–Ni and Mn–Cu co-doped ZnFe_2O_4 nanoparticles were successfully synthesized through a rapid green microwave-assisted method using *Azadirachta indica* (neem) leaf extract as a natural reducing, stabilizing, and capping agent. The synthesized nanoparticles were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS), transmission electron microscopy/high-resolution transmission electron microscopy (TEM/HRTEM), and vibrating sample magnetometry (VSM). Their structural, optical, magnetic, and visible-light photocatalytic properties toward methyl orange degradation were systematically investigated, together with magnetic recoverability and photocatalytic kinetics. The novelty of this work lies in the development of an eco-friendly microwave-assisted green synthesis route, the direct comparison of Mn–Ni and Mn–Cu co-doping under identical conditions, and the establishment of the relationship between band-gap reduction, enhanced magnetic properties, and photocatalytic performance. These findings provide valuable insights into the design of highly efficient, magnetically recyclable ZnFe_2O_4 -based photocatalysts for sustainable wastewater treatment.

2. Experimental

2.1 Materials

Analytical-grade zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 98\%$), manganese(II) nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\geq 98\%$), nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 98\%$), and copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\geq 99\%$) were purchased from **Merck (India)** and used as received without further purification. Fresh neem (*Azadirachta indica*) leaves were collected locally, thoroughly washed with distilled water to remove dust and impurities, air-dried, and used for the preparation of the plant extract, which served as a natural reducing, stabilizing, and capping agent during nanoparticle synthesis.

2.2 Microwave-assisted green synthesis of ZnFe_2O_4

Pristine ZnFe_2O_4 nanoparticles were synthesized by a green microwave-assisted method using *Azadirachta indica* (neem) leaf extract. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were dissolved in distilled water under constant magnetic stirring. Neem leaf extract was added slowly to the precursor solution, and the mixture was stirred for 30 min. The

resulting solution was irradiated in a domestic microwave oven at 800 W for 15 min. The obtained precipitate was washed several times with distilled water and ethanol, dried at 80°C for 12 h, and finally calcined at 650°C for 5 h to obtain crystalline ZnFe₂O₄ nanoparticles.

2.3 Microwave-assisted green synthesis

Mn–Ni and Mn–Cu co-doped ZnFe₂O₄ nanoparticles were synthesized via a rapid green microwave-assisted method. Appropriate stoichiometric amounts of the metal nitrate precursors were dissolved in distilled water under continuous magnetic stirring to obtain a homogeneous solution. Subsequently, the freshly prepared neem leaf extract was added dropwise to the precursor solution while maintaining constant stirring. The resulting reaction mixture was subjected to microwave irradiation at a power of 800 W for 15 min, promoting rapid nucleation and the formation of ferrite nanoparticles. The obtained precipitates were repeatedly washed with distilled water and ethanol to remove residual impurities and phytochemical residues, followed by drying at 80°C for 12 h. Finally, the dried powders were calcined at 650°C for 5 h in air to obtain highly crystalline Mn–Ni and Mn–Cu co-doped ZnFe₂O₄ nanoparticles [17–20].

2.4 Photocatalytic Activity

The visible-light photocatalytic performance of the synthesized pristine ZnFe₂O₄, Mn–Ni co-doped ZnFe₂O₄, and Mn–Cu co-doped ZnFe₂O₄ nanoparticles was evaluated through the degradation of methyl orange (MO) aqueous solution under visible-light irradiation. In a typical experiment, 10 mg of the photocatalyst was dispersed in 100 mL of MO solution with an initial concentration of 10 mg L⁻¹. The suspension was ultrasonicated for 10 min to ensure homogeneous dispersion and subsequently magnetically stirred in the dark for 30 min to establish adsorption–desorption equilibrium between the photocatalyst surface and dye molecules. The photocatalytic degradation experiments were carried out in a quartz reactor under continuous magnetic stirring using a 12 W blue LED light source with a peak emission wavelength of 463 nm. The LED was positioned approximately 10 cm from the reaction vessel to provide uniform visible-light irradiation throughout the experiment. During irradiation, 3 mL aliquots were withdrawn from the reaction mixture at 15 min intervals and centrifuged to separate the photocatalyst from the solution. The concentration of methyl orange was determined using a UV–Vis spectrophotometer by monitoring the characteristic absorption maximum of the dye at 464 nm (λ_{max}). The decrease in absorbance at 464 nm was used to calculate the photocatalytic degradation efficiency as a function of irradiation time.

The degradation efficiency was calculated using the following equation:

$$\text{Degradation (\%)} = \frac{A_0 - A_t}{A_0} \times 100$$

where A_0 is the initial absorbance of the methyl orange solution after adsorption–desorption equilibrium, and A_t is the absorbance measured after visible-light irradiation for time t .

The photocatalytic degradation kinetics were analyzed using the pseudo-first-order Langmuir–Hinshelwood model:

$$\ln \left(\frac{A_0}{A_t} \right) = kt$$

2

where k (min^{-1}) is the apparent first-order reaction rate constant and t (min) is the irradiation time. The photocatalytic performances of the pristine ZnFe_2O_4 , Mn–Ni co-doped ZnFe_2O_4 , and Mn–Cu co-doped ZnFe_2O_4 nanoparticles were compared under identical experimental conditions to evaluate the influence of transition-metal co-doping on the visible-light-driven degradation of methyl orange.

2.5 Analytical Characterizations

The crystal structure of the synthesized nanoparticles was analyzed using X-ray diffraction (XRD) with Cu–K α radiation ($\lambda = 1.5406 \text{ \AA}$). Fourier-transform infrared spectroscopy (FTIR) was employed in the wavenumber range of $4000\text{--}400 \text{ cm}^{-1}$ to identify the characteristic vibrational modes of the spinel ferrite structure. The optical properties and band-gap energies were investigated using UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS), whereas the particle morphology, size distribution, and lattice structure were examined by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). The magnetic properties were evaluated at room temperature using a vibrating sample magnetometer (VSM).

3. Results and discussion

3.1 X-ray Diffraction Analysis

Figure 2. presents the X-ray diffraction (XRD) patterns of the synthesized Mn–Ni and Mn–Cu co-doped ZnFe_2O_4 nanoparticles. All diffraction peaks can be indexed to the characteristic reflections of the cubic spinel ferrite structure corresponding to the (220), (311), (400), (422), (511), and (440) crystallographic planes, confirming the successful formation of single-phase ZnFe_2O_4 without detectable secondary impurity phases. The diffraction peaks are in good agreement with the standard JCPDS/PDF card of cubic ZnFe_2O_4 , indicating that the incorporation of Mn^{2+} , Ni^{2+} , and Cu^{2+} ions does not alter the crystal symmetry but is accommodated within the spinel lattice.

The average crystallite size (D) was estimated from the most intense (311) diffraction peak using the Debye–Scherrer equation and was found to be in the range of 20–28 nm, confirming the nanocrystalline nature of the synthesized samples. The slight broadening of the diffraction peaks after co-doping is attributed to the reduction in crystallite size together with the development of lattice strain. Moreover, a

small shift in the diffraction peak positions was observed for the co-doped samples, suggesting successful substitution of Mn^{2+} , Ni^{2+} , and Cu^{2+} ions into the ZnFe_2O_4 crystal lattice. These shifts originate from differences in the ionic radii of the dopant cations relative to Zn^{2+} and Fe^{3+} , resulting in local lattice distortion and modification of the lattice parameters [21–24].

The enhanced peak intensity and sharp diffraction profiles indicate improved crystallinity, which can be attributed to the rapid and homogeneous heating provided by microwave-assisted synthesis. The phytochemicals present in neem (*Azadirachta indica*) leaf extract also play an important role in controlling crystal nucleation and particle growth, resulting in highly crystalline nanoparticles with reduced structural defects. The absence of secondary phases further confirms that the selected co-doping concentrations are within the solubility limit of the ZnFe_2O_4 spinel structure.

The improved crystallinity together with the induced lattice distortion is expected to influence the electronic structure and magnetic exchange interactions of ZnFe_2O_4 , thereby contributing to enhanced visible-light absorption and photocatalytic performance. These XRD results demonstrate that the green microwave-assisted synthesis route is an effective approach for producing highly crystalline Mn–Ni and Mn–Cu co-doped ZnFe_2O_4 nanoparticles suitable for visible-light-driven photocatalytic applications.

3.2 Fourier Transform Infrared (FTIR) Analysis

Figure 3. shows the FTIR spectra of the synthesized Mn–Ni and Mn–Cu co-doped ZnFe_2O_4 nanoparticles recorded in the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$. The spectra exhibit the characteristic absorption bands of the spinel ferrite structure, confirming the successful formation of ZnFe_2O_4 after green microwave-assisted synthesis. Two prominent absorption bands are observed at approximately 580 cm^{-1} (ν_1) and 430 cm^{-1} (ν_2), corresponding to the intrinsic stretching vibrations of metal–oxygen (M–O) bonds at the tetrahedral (A) and octahedral (B) sites, respectively. These characteristic bands are the fingerprint of the cubic spinel ferrite structure and are in good agreement with previously reported ZnFe_2O_4 ferrites.

Compared with pristine ZnFe_2O_4 , slight shifts in the ν_1 and ν_2 absorption bands are observed after Mn–Ni and Mn–Cu co-doping, indicating the successful incorporation of Mn^{2+} , Ni^{2+} , and Cu^{2+} ions into the ZnFe_2O_4 lattice. The substitution of transition-metal ions with different ionic radii modifies the local crystal field, resulting in variations in the metal–oxygen bond lengths and bond strengths. These changes lead to lattice distortion and confirm that the dopant ions are effectively accommodated within the spinel lattice without altering the crystal structure. The observed band shifts are consistent with the lattice distortion inferred from the XRD analysis.

A broad absorption band centered around 3400 cm^{-1} is assigned to the stretching vibration of hydroxyl ($-\text{OH}$) groups originating from surface-adsorbed water molecules and phytochemical constituents of the neem (*Azadirachta indica*) leaf extract used during green synthesis. In addition, the weak absorption band near 1630 cm^{-1} corresponds to the bending vibration of molecular water ($\text{H}-\text{O}-\text{H}$), indicating the presence of physically adsorbed moisture on the nanoparticle surface. The residual phytochemical

species from the neem extract may act as natural capping and stabilizing agents, preventing excessive particle agglomeration during microwave-assisted synthesis [25–26].

The characteristic metal–oxygen stretching vibrations observed at the tetrahedral and octahedral sites verify the local bonding environment of the spinel lattice. The slight shifts in these absorption bands after Mn–Ni and Mn–Cu co-doping indicate successful incorporation of the transition-metal ions and reveal changes in metal–oxygen bond strength caused by local lattice distortion. These observations complement the XRD results by providing evidence of local structural modifications induced by co-doping, which facilitate improved charge-carrier transport, enhanced visible-light absorption, and superior photocatalytic performance.

3.3 UV–Vis Diffuse Reflectance Spectroscopy (UV–Vis DRS) Analysis

Figure 4. presents the UV–Vis diffuse reflectance spectra (DRS) and the corresponding Tauc plots of Mn–Ni co-doped ZnFe₂O₄ and Mn–Cu co-doped ZnFe₂O₄ nanoparticles. Both samples exhibit broad absorption extending from the ultraviolet to the visible region, indicating their excellent visible-light harvesting capability. The Mn–Ni co-doped ZnFe₂O₄ sample exhibits characteristic absorption maxima at approximately 217 nm and 373 nm, whereas the Mn–Cu co-doped ZnFe₂O₄ sample shows absorption peaks around 220 nm and 426 nm. The broad absorption in the visible region confirms the successful incorporation of transition-metal dopants into the ZnFe₂O₄ lattice, resulting in enhanced optical absorption.

The optical band-gap energy (E_g) was determined using the Tauc relation:

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

2

where α is the absorption coefficient, h is Planck's constant, ν is the frequency of the incident photon, A is a proportionality constant, and E_g represents the optical band-gap energy.

The band-gap energies were estimated by extrapolating the linear portion of the Tauc plots $(\alpha h\nu)^2$ versus $h\nu$ to the photon-energy axis. The calculated optical band-gap values were found to be approximately 1.50 eV for the Mn–Ni co-doped ZnFe₂O₄ nanoparticles and 1.60 eV for the Mn–Cu co-doped ZnFe₂O₄ nanoparticles.

The slight variation in band-gap energy can be attributed to the incorporation of Mn²⁺, Ni²⁺, and Cu²⁺ ions into the ZnFe₂O₄ crystal lattice. The substitution of transition-metal ions introduces localized impurity levels and defect states within the forbidden energy gap, facilitating electronic transitions from the valence band to the conduction band. Moreover, the difference in ionic radii and electronic configurations

of the dopant ions induces lattice distortion and modifies the electronic band structure, thereby influencing the optical properties of the ferrite nanoparticles [27].

Among the synthesized samples, Mn–Ni co-doped ZnFe₂O₄ exhibits the lower optical band-gap energy (1.50 eV), indicating a greater degree of band-gap narrowing than the Mn–Cu co-doped ZnFe₂O₄ sample (1.60 eV). This lower band-gap value facilitates easier excitation of electrons under visible-light irradiation, thereby improving the utilization of solar energy. In contrast, the Mn–Cu co-doped ZnFe₂O₄ nanoparticles display a comparatively broader absorption band extending toward longer wavelengths, suggesting enhanced visible-light absorption despite their slightly higher band-gap energy. Such behavior may arise from defect-induced absorption and charge-transfer transitions associated with Cu²⁺ ions.

The reduced band-gap energies of both co-doped ferrites promote efficient generation of photogenerated electron–hole pairs under visible-light illumination. Furthermore, the dopant-induced defect states act as charge-carrier trapping centers, suppressing the recombination of photogenerated electrons and holes and thereby enhancing the formation of reactive oxygen species such as hydroxyl (•OH) and superoxide (•O₂[−]) radicals. Consequently, the improved optical characteristics of the Mn–Ni and Mn–Cu co-doped ZnFe₂O₄ nanoparticles are expected to significantly enhance their visible-light-driven photocatalytic efficiency, making them promising candidates for wastewater treatment and environmental remediation [28–29].

Table 1
Structural, Optical and Morphological Properties of ZnFe₂O₄ and Mn–Ni, Mn–Cu co-doped ZnFe₂O₄ nanocomposites

Sample	Crystal Structure	Crystallite Size (nm)	Particle Size (nm)	Band Gap (eV)
ZnFe ₂ O ₄	Cubic spinel	20–28	20–35	1.90
Mn–Ni@ZnFe ₂ O ₄	Cubic spinel	20–28	20–35	1.50
Mn–Cu@ZnFe ₂ O ₄	Cubic spinel	20–28	20–35	1.60

3.4 Transmission Electron Microscopy (TEM) Analysis

Transmission electron microscopy (TEM), selected area electron diffraction (SAED), and high-resolution transmission electron microscopy (HRTEM) were employed to investigate the morphology, crystallinity, and microstructural characteristics of the synthesized pristine ZnFe₂O₄, Mn–Ni co-doped ZnFe₂O₄, and Mn–Cu co-doped ZnFe₂O₄ nanoparticles. The corresponding TEM, SAED, and HRTEM images are shown in Figs. (5–7)

The TEM micrographs of the Mn–Ni co-doped ZnFe₂O₄ nanoparticles (Fig. 5a–c) reveal predominantly quasi-spherical particles with slight agglomeration arising from magnetic interactions and high surface

energy. The particles are uniformly distributed with an average particle size of approximately 20–35 nm, which agrees well with the crystallite size estimated from XRD analysis. The incorporation of Mn^{2+} and Ni^{2+} ions does not significantly alter the particle morphology but results in a homogeneous nanostructure with improved crystallinity.

Similarly, the Mn–Cu co-doped ZnFe_2O_4 nanoparticles (Fig. 6a–c) exhibit quasi-spherical morphology with a narrow particle size distribution and slight agglomeration. The average particle size remains within the range of 20–35 nm. Compared with the Mn–Ni co-doped sample, a slight variation in particle morphology is observed, which may be attributed to lattice distortion induced by the substitution of Cu^{2+} ions into the ZnFe_2O_4 lattice during microwave-assisted synthesis [30–32].

The TEM images of the pristine ZnFe_2O_4 nanoparticles (Fig. 7a–c) also demonstrate uniformly distributed quasi-spherical nanoparticles with an average particle size of 20–35 nm. The microwave-assisted green synthesis using *Azadirachta indica* (neem) leaf extract effectively controlled particle nucleation and growth, resulting in nanosized particles with relatively uniform morphology and limited agglomeration.

The SAED patterns of the Mn–Ni co-doped (Fig. 5d), Mn–Cu co-doped (Fig. 6d), and pristine ZnFe_2O_4 (Fig. 7d) nanoparticles display distinct concentric diffraction rings that can be indexed to the (220), (311), (400), (422), (511), and (440) crystallographic planes of the cubic spinel ZnFe_2O_4 structure. The absence of additional diffraction rings or spots confirms the formation of phase-pure spinel ferrite nanoparticles without detectable impurity phases. The well-defined diffraction rings further indicate the polycrystalline nature and high crystallinity of all synthesized samples, in good agreement with the XRD results.

The HRTEM images of the Mn–Ni co-doped ZnFe_2O_4 (Fig. 5e,f), Mn–Cu co-doped ZnFe_2O_4 (Fig. 6e,f), and pristine ZnFe_2O_4 (Fig. 7e,f) nanoparticles exhibit clear and well-resolved lattice fringes, confirming their excellent crystallinity. The measured interplanar lattice spacing (d-spacing) is approximately 0.25 nm, corresponding to the (311) crystallographic plane of the cubic spinel ZnFe_2O_4 structure. The incorporation of Mn^{2+} , Ni^{2+} , and Cu^{2+} ions into the ZnFe_2O_4 lattice does not alter the fundamental spinel crystal structure but induces slight lattice distortion, which is consistent with the peak shifts observed in the XRD analysis.

The uniform nanoscale morphology and well-resolved lattice fringes indicate excellent crystallinity and short diffusion pathways for photogenerated charge carriers. The reduced particle size increases the available active surface area, facilitating efficient interfacial charge transfer and providing more active sites for photocatalytic reactions. These structural characteristics contribute to enhanced visible-light photocatalytic performance compared with pristine ZnFe_2O_4 .

3.5 Vibrating Sample Magnetometer (VSM) Analysis

Figure 8 presents the room-temperature magnetic hysteresis (M–H) curves of pristine ZnFe₂O₄, Mn–Ni co-doped ZnFe₂O₄, and Mn–Cu co-doped ZnFe₂O₄ nanoparticles measured using a vibrating sample magnetometer (VSM). All the samples exhibit narrow hysteresis loops with low coercivity (H_c) and remanent magnetization (M_r), confirming their soft ferrimagnetic nature. Such soft magnetic behavior is advantageous for photocatalytic applications because it enables rapid magnetic separation and efficient recovery of the photocatalyst from wastewater using an external magnetic field.

The magnetic parameters, including saturation magnetization (M_s), remanent magnetization (M_r), coercivity (H_c), and the squareness ratio (M_r/M_s), were extracted from the hysteresis loops and are summarized in Table 2. The pristine ZnFe₂O₄ nanoparticles exhibited a saturation magnetization of 17.5 ± 0.5 emu g⁻¹, which increased remarkably to 72 ± 2 emu g⁻¹ for Mn–Ni co-doped ZnFe₂O₄ and 76 ± 2 emu g⁻¹ for Mn–Cu co-doped ZnFe₂O₄. This enhancement in saturation magnetization is attributed to the redistribution of cations between the tetrahedral (A) and octahedral (B) sites of the spinel lattice, which strengthens the Fe³⁺–O²⁻–M²⁺ (M = Mn, Ni, Cu) superexchange interactions. Furthermore, the substitution of magnetic transition-metal ions modifies the cation distribution and increases the net magnetic moment of the spinel ferrite structure, thereby improving the overall magnetic response [33–37].

The coercivity increased from 18 ± 2 Oe for pristine ZnFe₂O₄ to 35 ± 3 Oe and 42 ± 3 Oe for the Mn–Ni and Mn–Cu co-doped samples, respectively, while retaining their soft magnetic characteristics. The increase in coercivity is associated with enhanced magnetocrystalline anisotropy, lattice distortion caused by co-doping, and the nanoscale crystallite size of the ferrite nanoparticles. Likewise, the remanent magnetization increased from 1.8 ± 0.2 emu g⁻¹ for pristine ZnFe₂O₄ to 8.0 ± 0.4 emu g⁻¹ for Mn–Ni co-doped ZnFe₂O₄ and 9.0 ± 0.5 emu g⁻¹ for Mn–Cu co-doped ZnFe₂O₄, indicating stronger magnetic ordering and enhanced exchange interactions within the spinel lattice.

The enhanced magnetic response originates from the combined effects of transition-metal substitution, improved crystallinity, and reduced surface spin disorder. Redistribution of magnetic cations between the tetrahedral and octahedral sites strengthens the superexchange interactions, leading to increased saturation magnetization while preserving the soft ferrimagnetic behavior. These magnetic characteristics facilitate rapid magnetic separation and efficient recovery of the photocatalyst after wastewater treatment.

Table 2
Magnetic parameters of pristine ZnFe₂O₄, Mn–Ni co-doped ZnFe₂O₄, and Mn–Cu co-doped ZnFe₂O₄ nanoparticles.

Sample	M _s (emu g ⁻¹)	M _r (emu g ⁻¹)	H _c (Oe)	M _r /M _s
ZnFe ₂ O ₄	17.5 ± 0.5	1.8 ± 0.2	18 ± 2	0.103
Mn–Ni@ZnFe ₂ O ₄	72 ± 2	8.0 ± 0.4	35 ± 3	0.111
Mn–Cu@ZnFe ₂ O ₄	76 ± 2	9.0 ± 0.5	42 ± 3	0.118

3.6 Visible-Light Photocatalytic Activity

The visible-light photocatalytic performance of the synthesized Mn–Ni and Mn–Cu co-doped ZnFe₂O₄ nanoparticles was evaluated by monitoring the degradation of methyl orange (MO) dye under visible-light irradiation. The photocatalytic behavior was systematically investigated through degradation efficiency, pseudo-first-order kinetic analysis, normalized concentration (C/C_0) profiles, radical scavenger experiments, and catalyst reusability, as illustrated in Fig. 9(a–f).

1. Degradation Efficiency as a Function of Irradiation Time

Figure 9(a,b) shows the variation of photocatalytic degradation efficiency with irradiation time. For both photocatalysts, the degradation efficiency increases steadily with prolonged visible-light exposure, indicating continuous generation of reactive species during the photocatalytic process. The degradation proceeds rapidly during the initial stage because of the high concentration of methyl orange molecules and the abundance of active catalytic sites, followed by a gradual increase until equilibrium is approached.

Among the synthesized samples, Mn–Ni co-doped ZnFe₂O₄ achieved the highest degradation efficiency of approximately 98.2% within 90 min, whereas Mn–Cu co-doped ZnFe₂O₄ exhibited 96.0% degradation under identical experimental conditions. The superior photocatalytic activity of the Mn–Ni co-doped ZnFe₂O₄ is mainly attributed to its lower optical band-gap energy (1.50 eV), enhanced visible-light absorption, efficient charge separation, and suppressed electron–hole recombination. These results demonstrate that transition-metal co-doping significantly improves the visible-light photocatalytic performance of ZnFe₂O₄ nanoparticles [38–40].

1. Pseudo-First-Order Kinetic Analysis

As shown in Fig. 9(c) the linear relationship between $\ln(C_0/C_t)$ and irradiation time indicates that the degradation process follows pseudo-first-order kinetics. The linear fitting exhibits excellent correlation coefficients ($R^2 \approx 0.98–0.99$), confirming the applicability of the Langmuir–Hinshelwood model. The Mn–Ni co-doped ZnFe₂O₄ photocatalyst exhibits a higher apparent rate constant than the Mn–Cu co-doped sample, demonstrating faster degradation kinetics. The improved reaction rate originates from enhanced visible-light absorption, efficient charge transfer, and prolonged lifetime of photogenerated charge carriers induced by Mn–Ni co-doping.

(c) Variation of C/C_0 with Irradiation Time

Figure 9(d) illustrates the variation of the normalized dye concentration (C/C_0) as a function of irradiation time. Before light irradiation, the photocatalyst suspension was stirred in the dark to establish adsorption–desorption equilibrium. During this period, only a slight decrease in C/C_0 was observed, indicating that adsorption contributes minimally to dye removal.

After visible-light illumination, the C/C_0 value decreased continuously with increasing irradiation time for both photocatalysts, confirming efficient photocatalytic degradation. The Mn–Ni co-doped $ZnFe_2O_4$ exhibited a more rapid decrease in C/C_0 than the Mn–Cu co-doped $ZnFe_2O_4$, consistent with its higher degradation efficiency. The faster decline in C/C_0 reflects more efficient photogenerated charge separation, accelerated formation of reactive oxygen species, and enhanced oxidation of methyl orange molecules.

(d) Radical Scavenger Experiments

To identify the active species responsible for photocatalytic degradation, scavenger experiments were performed using tert-butanol (t-BuOH), p-benzoquinone (p-BQ), and potassium iodide (KI) as scavengers for hydroxyl radicals ($\cdot OH$), superoxide radicals ($\cdot O_2^-$), and photogenerated holes (h^+), respectively.

As presented in Fig. 9(e) the degradation efficiency decreased only slightly in the presence of t-BuOH, indicating that hydroxyl radicals play a relatively minor role in the degradation process. However, the addition of p-BQ and KI resulted in a significant decrease in photocatalytic activity, confirming that superoxide radicals ($\cdot O_2^-$) and photogenerated holes (h^+) are the dominant reactive species responsible for methyl orange degradation. The enhanced generation of these reactive species results from efficient charge separation induced by transition-metal co-doping, thereby promoting rapid oxidation and mineralization of dye molecules.

(e) Photocatalyst Reusability

The long-term stability and practical applicability of the synthesized photocatalysts were evaluated through four successive photocatalytic degradation cycles, as shown in Fig. 9(f). After each cycle, the photocatalysts were magnetically separated, washed, dried, and reused under identical experimental conditions.

Both Mn–Ni and Mn–Cu co-doped $ZnFe_2O_4$ nanoparticles retained excellent photocatalytic performance after repeated use, exhibiting only a slight reduction in degradation efficiency after four cycles. The negligible loss in activity demonstrates the outstanding structural stability, chemical durability, and resistance to photocorrosion of the synthesized ferrite nanoparticles. Furthermore, their enhanced magnetic properties enable rapid magnetic recovery with minimal catalyst loss, highlighting their excellent recyclability and suitability for practical wastewater treatment applications.

Overall, the photocatalytic results clearly demonstrate that Mn–Ni and Mn–Cu co-doped $ZnFe_2O_4$ nanoparticles exhibit outstanding visible-light-driven photocatalytic performance, excellent kinetic behavior, efficient charge separation, high stability, and superior magnetic recoverability. Among the synthesized samples, Mn–Ni co-doped $ZnFe_2O_4$ exhibited the best overall photocatalytic performance, achieving 98.2% degradation of methyl orange within 90 min, confirming its potential as an efficient, reusable, and environmentally sustainable photocatalyst for wastewater purification.

Table 3
Comparison of ZnFe₂O₄-Based Photocatalysts

Photocatalyst	Synthesis Method	Pollutant	Light Source	Degradation (%)	Time (min)	Reference
ZnFe ₂ O ₄	Sol–gel	Methyl orange	Visible light	82	120	[41]
Mn-doped ZnFe ₂ O ₄	Hydrothermal	Methyl orange	Visible light	90	120	[42]
Dy-doped ZnFe ₂ O ₄	Sol–gel	Methylene blue	Visible light	94	120	[43]
Sm-doped ZnFe ₂ O ₄	Hydrothermal	Organic dye	Visible light	95	120	[44]
La ³⁺ -substituted ZnFe ₂ O ₄	Co-precipitation	Organic dye	Visible light	95	120	[45]
Cu-doped ZnFe ₂ O ₄	Sol–gel	Organic dye	Visible light	96	100	[46]
Ni/Mn co-doped ZnFe ₂ O ₄ /rGO	Hydrothermal	Organic dye	Visible light	98	120	[47]
Mn–Cu co-doped ZnFe ₂ O ₄	Green microwave-assisted	Methyl orange	Visible light	96.0	90	Present work
Mn–Ni co-doped ZnFe ₂ O ₄	Green microwave-assisted	Methyl orange	Visible light	98.2	90	Present work

3.7 Photocatalytic Mechanism

The enhanced visible-light photocatalytic activity of Mn–Ni and Mn–Cu co-doped ZnFe₂O₄ nanoparticles can be explained by the synergistic effects of transition-metal co-doping, which modifies the electronic band structure and promotes efficient charge separation. Under visible-light irradiation ($\lambda = 463$ nm), photons with energy greater than or equal to the optical band-gap energy excite electrons (e[−]) from the valence band (VB) to the conduction band (CB), leaving positively charged holes (h⁺) in the valence band [48–51].



The incorporation of Mn²⁺ together with Ni²⁺ or Cu²⁺ introduces localized defect states and intermediate energy levels within the ZnFe₂O₄ band structure. These defect states serve as charge-trapping centers that effectively suppress the rapid recombination of photogenerated electron–hole pairs and prolong the lifetime of charge carriers. Consequently, more electrons and holes participate in surface redox reactions.

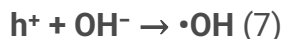
The photogenerated electrons react with dissolved oxygen molecules adsorbed on the catalyst surface to generate superoxide radicals:



The photogenerated holes oxidize water molecules or surface hydroxyl ions to produce hydroxyl radicals:



or



The generated reactive oxygen species, particularly superoxide ($\cdot O_2^-$) and hydroxyl ($\cdot OH$) radicals, possess strong oxidative ability and attack methyl orange molecules, breaking the azo bonds and aromatic rings into intermediate products, which are finally mineralized into harmless products such as carbon dioxide and water.



Among the synthesized photocatalysts, Mn–Ni co-doped $ZnFe_2O_4$ exhibited the highest photocatalytic degradation efficiency (98.2%), indicating that Mn–Ni co-doping provides more efficient charge separation and slower electron–hole recombination than Mn–Cu co-doping under the present experimental conditions. The improved crystallinity, nanoscale particle size, increased surface-active sites, and enhanced visible-light absorption further contribute to the superior photocatalytic performance. In addition, the soft magnetic nature of the co-doped $ZnFe_2O_4$ nanoparticles enables rapid magnetic separation and catalyst recovery after photocatalytic treatment, making them promising recyclable photocatalysts for wastewater purification.

4. Conclusion

In this work, Mn–Ni and Mn–Cu co-doped $ZnFe_2O_4$ nanoparticles were successfully synthesized through a rapid, eco-friendly microwave-assisted green synthesis using *Azadirachta indica* (neem) leaf extract as a natural reducing, stabilizing, and capping agent. This sustainable synthesis approach provides an efficient alternative to conventional chemical methods for the preparation of highly crystalline spinel ferrite photocatalysts with minimal environmental impact. Structural characterization by XRD confirmed the formation of single-phase cubic spinel $ZnFe_2O_4$ without detectable impurity phases, while FTIR analysis verified the characteristic metal–oxygen vibrations corresponding to the tetrahedral and octahedral sites of the spinel lattice. TEM and HRTEM observations revealed uniformly distributed quasi-spherical nanoparticles with particle sizes in the range of 20–35 nm and well-resolved lattice fringes, confirming the excellent crystallinity of the synthesized materials. UV–Vis diffuse reflectance spectroscopy demonstrated that transition-metal co-doping effectively narrowed the optical band gap from approximately 1.90 eV for pristine $ZnFe_2O_4$ to 1.60 eV for Mn–Cu co-doped $ZnFe_2O_4$ and 1.50 eV for

Mn–Ni co-doped ZnFe₂O₄, thereby enhancing visible-light absorption. Magnetic measurements revealed typical soft ferrimagnetic behavior with significantly enhanced saturation magnetization after co-doping, enabling rapid magnetic separation and efficient recovery of the photocatalyst following photocatalytic treatment. The superior magnetic response, combined with high crystallinity and nanoscale morphology, makes these materials suitable for repeated practical applications. Photocatalytic experiments under visible-light irradiation demonstrated outstanding degradation efficiencies toward methyl orange, achieving 98.2% degradation within 90 min for Mn–Ni co-doped ZnFe₂O₄ and 96.0% for Mn–Cu co-doped ZnFe₂O₄, both markedly higher than pristine ZnFe₂O₄. The enhanced photocatalytic activity is attributed to the synergistic effects of transition-metal co-doping, including band-gap narrowing, defect-state formation, improved visible-light harvesting, efficient charge-carrier separation, suppressed electron–hole recombination, and enhanced generation of reactive oxygen species ($\cdot\text{OH}$ and $\cdot\text{O}_2^-$), which accelerate dye mineralization. Overall, this study demonstrates that green microwave-assisted Mn–Ni and Mn–Cu co-doping is an effective strategy for tailoring the structural, optical, magnetic, and photocatalytic properties of ZnFe₂O₄ nanoparticles. Among the synthesized photocatalysts, Mn–Ni co-doped ZnFe₂O₄ exhibited the best overall photocatalytic performance owing to its lower band-gap energy (1.50 eV) and higher methyl orange degradation efficiency, whereas Mn–Cu co-doped ZnFe₂O₄ showed superior magnetic properties, facilitating easier catalyst recovery. These findings provide valuable insights into the rational design of sustainable, visible-light-active, and magnetically recoverable spinel ferrite photocatalysts with significant potential for wastewater purification and other environmental remediation applications.

Declarations

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.

Funding:

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Author Contribution

Author Contributions M. Michael Jegan: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Visualization, Writing – original draft. D. Selleswari: Supervision, Validation, Resources, Writing – review & editing. C. Sarala Rubi: Investigation, Data curation, Formal analysis. P. ArulMurugan: Supervision, Project administration, Validation. All authors read and approved the final manuscript.

Data Availability

XRDTIRUV–Vis/DRSTEMVSMPhotocatalytic

References

1. Q. Zhao, Z. Yan, C. Chen, J. Chen, Spinel: Controlled preparation, oxygen reduction/evolution reaction, application, and beyond, *Chem. Rev.* **117** (2017) 10121–10211
2. B.F. Bogacz, R. Gargula, P. Kurzydło, A.T. Pędziwiatr, T. Tatarchuk, N. Palychuk, Two-level model description of superparamagnetic relaxation in nanoferrites (Co, Zn)Fe₂O₄. *Acta Phys. Pol. A* **134**, 993–997 (2018)
3. S.N. Kane, S. Raghuwanshi, M. Satalkar, V.R. Reddy, U.P. Deshpande, T.R. Tatarchuk, P. Mazaleyrat, Synthesis, characterization and nanostructure modeling of Ni nano ferrite, *AIP Conf. Proc.* **1953** (2018) 030830
4. S. Sheenu Jauhar, J. Kaur, A. Goyal, S. Singhal, J. Jauhar, A. Goyal, S. Singhal, Tuning the properties of cobalt ferrites: A road towards diverse applications. *RSC Adv.* **6**, 97694–97719 (2016)
5. B.R. Rose Vergis, N. Kottam, B.M. Harikrishna, B.M. Nagabhushana, Removal of Evans blue dye from aqueous solution using magnetic spinel ZnFe₂O₄ nanomaterial: Adsorption isotherms and kinetics, *Nano-Struct. Nano-Objects.* **18**, 100290 (2019)
6. P. Tiwari, R. Verma, S.N. Kane, T. Tatarchuk, F. Mazaleyrat, Effect of Zn addition on structural, magnetic properties and anti-structural modeling of magnesium–nickel nano ferrites. *Mater. Chem. Phys.* **229**, 78–86 (2019)
7. A. Abu El-Fadl, A.M. Hassan, M.H. Mahmoud, T. Tatarchuk, I.P. Yaremiy, A.M. Gismelsed, M.A. Ahmed, Synthesis and magnetic properties of spinel Zn_{1-x}Ni_xFe₂O₄ (0.0 ≤ x ≤ 1.0) nanoparticles synthesized by microwave combustion method. *J. Magn. Magn. Mater.* **471**, 521–528 (2019)
8. M.A. Ahmed, H.E. Hassan, M.M. Eltabey, K. Latif, T.R. Tatarchuk, Mössbauer spectroscopy of Mg_xCu_{1.5-x}Zn_{0.5}Fe₂O₄ (x = 0.0, 0.2 and 0.5) ferrite system irradiated by γ-rays. *Phys. B* **550**, 195–200 (2018)
9. M.T. Nguyen, M.D. Nguyen, M. Gao et al., Microwave-assisted synthesis of copper ferrite nanocatalysts for synergistic plasma–Fenton degradation of Rhodamine B, *Colloids Surf. Physicochem Eng. Asp.* **705**, 135681 (2025)
10. C.N. Lakshmi, M. Irfan, N. Singh, One-pot microwave-assisted green synthesis of carbon-embedded cobalt ferrite nanoparticles for enhanced photocatalytic degradation of ciprofloxacin with mechanistic insights. *Ind. Eng. Chem. Res.* **64**, 16518–16530 (2025)
11. S.P. Keerthana, R. Yuvakkumar, P. Senthil Kumar, G. Ravi, D. Velauthapillai, Rare earth metal (Sm)-doped ZnFe₂O₄ for improved photocatalytic elimination of toxic dye from aquatic system. *Environ. Res.* **197**, 111047 (2021)

12. K.M. Srinivasamurthy, A.V. Jagadeesha, S.P. Kubrin, S.M. Teppanavar, D.A. Satychev, P. Mohan Kumar, H.W. Azale, B. Rudraswamy, Tuning of ferromagnetic nature and hyperfine interaction of Ni²⁺-doped cobalt ferrite nanoparticles for power transformer applications. *Ceram. Int.* **44**, 9194–9203 (2018)
13. K.K. Kefeni, B.B. Mamba, T.A.M. Msagati, Application of spinel ferrite nanoparticles in water and wastewater treatment: A review. *Sep. Purif. Technol.* **188**, 399–422 (2017)
14. L.T.T. Nguyen, H.T.T. Nguyen, L.T.H. Nguyen, A.T.T. Duong, H.Q. Nguyen, N.D. Bui, V.T.M. Ngo, D.T.C. Nguyen, T.V. Tran, Toward enhanced visible-light photocatalytic dye degradation and reusability of La³⁺-substituted ZnFe₂O₄ nanostructures. *Environ. Res.* **214**, 114130 (2022)
15. D. Ghanbari, M. Salavati-Niasari, Synthesis of urchin-like CdS–Fe₃O₄ nanocomposite and its application in flame retardancy of magnetic cellulose acetate. *J. Ind. Eng. Chem.* **24**, 284–292 (2015)
16. X. Zhao, L. Baharinikoo, M.D. Farahani, B. Mahdizadeh, A.A. Kazemzadeh, Farizhandi, Experimental modelling studies on the removal of dyes and heavy metal ions using ZnFe₂O₄ nanoparticles. *Sci. Rep.* **12**, 5987 (2022)
17. H. Bayahia, High activity of ZnFe₂O₄ nanoparticles for photodegradation of crystal violet dye solution in the presence of sunlight. *J. Taibah Univ. Sci.* **16**, 988–1004 (2022)
18. N. Nadeem, M. Zahid, Z.A. Rehan, M.A. Hanif, M. Yaseen, Improved photocatalytic degradation of dye using coal fly ash-based ZnFe₂O₄ composite. *Int. J. Environ. Sci. Technol.* **19**, 3045–3060 (2022)
19. F. Ansari, A. Sobhani, M. Salavati-Niasari, Facile synthesis, characterization, and magnetic properties of CuFe₁₂O₁₉ nanostructures via a sol–gel auto-combustion process. *J. Magn. Magn. Mater.* **401**, 362–369 (2016)
20. K. Charradi, Z. Ahmed, M.A. BenMoussa, Z. Beji, A. Brahmia, I. Othman, M.A. Haija, R. Chtourou, S.M.A.S. Keshk, A facile approach for the synthesis of spinel ZnFe₂O₄/cellulose as an effective photocatalyst for the degradation of methylene blue in aqueous solution. *Cellulose.* **29**, 3411–3428 (2022)
21. M. Alam, N. Dhanda, H. Almutairi et al., Green ferrites: Eco-friendly synthesis to applications in environmental remediation, antimicrobial activity and catalysis—A comprehensive review. *Appl. Organomet. Chem.* **39**, e7962 (2025)
22. F. Ansari, M. Salavati-Niasari, Simple sol–gel auto-combustion synthesis and characterization of lead hexaferrite using cherry juice as a novel fuel and green capping agent. *Adv. Powder Technol.* **27**, 2025–2031 (2016)
23. S. Tantuvoy, S. Bose, A. Ghosh et al., Microwave catalytic treatment using magnetically separable CoFe₂O₄ spinel catalyst for high-rate degradation of malachite green dye. *J. Environ. Manage.* **373**, 123772 (2025)
24. K. Moghaddari, L. Schumacher, R. Pöttgen, G. Kickelbick, Optimizing superparamagnetic ferrite nanoparticles: Microwave-assisted versus thermal decomposition synthesis methods. *Nanoscale*

25. F. Bibi, Fabrication of Ni and Mn co-doped ZnFe₂O₄ spinel ferrites and their nanocomposites with rGO as an efficient photocatalyst for the remediation of organic dyes. *Polyhedron*. **250**, 116826 (2024)
26. M.L. da Costa, D.M. Druzian, C. dos Santos, Y.P.M. Ruiz, G. Pavoski, J.A.S. Tenório, D.C.R. Espinosa, W.L. da Silva, Green lithium niobate synthesized from Citrus latifolia extract: Development, characterization and photocatalytic activity for the rose bengal dye photodegradation with mechanistic insights using machine learning models. *Mater. Today Nano*. **27**, 100868 (2026)
27. I. Marouani, W.H. Hassan, D.J. Jasim, N. Almadani, H.A. El-Sabban, I. Mahariq, G. Mustafayeva, F. Jalilov, S. Usanov, R.A. Haggam, Engineering a ZnFe₂O₄–CuCo₂O₄ Z-scheme heterojunction with interfacial charge transfer for enhanced visible-light hydrogen evolution and pharmaceutical contaminant degradation. *Surf. Interfaces*. **57**, 110075 (2026)
28. A. Begum, K. Hamid, M.Z.B. Mukhlis, M.T. Uddin, Development of dual functional heterostructured g-C₃N₄/CdS nanocomposites for visible-light photocatalytic dye degradation and electrochemical hydrogen production. *Mater. Adv.* **7**, 6850–6865 (2026)
29. M. Moharrami, M.R. Omidkhah, F. Shojaei, A. Akbari, Multifunctional visible-light photocatalytic ceramic membrane based on a magnetic Cu/Cu₂O–In₂O₃–NiZnFe₂O₄ double Z-scheme nanocomposite for efficient dye removal. *J. Water Process. Eng.* **68**, 110415 (2026)
30. B. Zhao, N. Chen, M. Li, C. Sun, T. Xue, Y. Xing, Y. Xue, S. Wang, B. Ma, Y. Tang, Magnetic OV_s-CoFe₂O₄/g-C₃N₄ heterojunction for enhanced tribocatalytic degradation of RhB: Performance and mechanism. *J. Environ. Chem. Eng.* **14**, 123807 (2026)
31. M. Pannerselvam, S. Zameer Basha, A. Shameem, R. Suresh, V. Siva, A. Murugan, Facile microwave preparation of Ce₂(WO₄)₃ nanocatalyst for dual-light-driven photocatalytic degradation of methylene blue. *J. Mater. Sci. Mater. Electron.* **37**, 1346 (2026)
32. A. Ravitchandiran, A.K. Subramania, N. Renuga Devi, N. Chandrasekar, S. Angaiah, Green synthesis of metal nanoparticles using plant extracts and their biomedical applications: An overview. *J. Iran. Chem. Soc.* **23**, 213 (2026)
33. M.N. Aliabadi, A.O. Moghanlou, Z. Doroudi, M.R.A.G. Ghasri, J. Najafpour, Photocatalytic degradation of Congo red dye using N- and S-doped rGO/NiFe₂O₄ heterogeneous nanocomposite under visible light. *J. Chem. Technol. Biotechnol.* (2026)
34. D. Umaru, J.S. Alnawmasi, N.Y. Elamin, I.F. Alshdoukhi, S.B. Alotaibi, H.Y. Hafeez, J. Mohammed, I.M. Musa, Enhanced hydrogen production via photocatalytic water splitting using rGO-coated CdS–CoFe₂O₄ photocatalysts. *Synth. Met.* **318**, 118221 (2026)
35. G. Kallawar, P.D. Tanwade, B.A. Bhanvase, B.R. Sathe, Electrocatalytic degradation of malachite green dye using Fe₃O₄/TiO₂/rGO nanocomposite: Implication towards environmental remediation. *Ceram. Int.* (2026)
36. B. Khaled, A. Bouafia, A. Guerram, C. Salmi, D. Barani, M.M.S. Abdullah, S.E. Laouini, Z. Zelca, Microwave-assisted synthesis of Mn_{1.92}O₄@carbon nanocomposite for enhanced photocatalytic

- degradation of thiophene and cadmium chloride under simulated solar irradiation. *J. Mater. Sci. Mater. Electron.* **37**, 1359 (2026)
37. M. Bilal, J. Ali, Z. Bibi, T. Munir, E.M. Bakhsh, K. Akhtar, S.B. Khan, Chicken bile-mediated silver nanoparticles: Performance in antibacterial activity and photodegradation of Disperse Orange 1, *Catalysts* **16** (2026) 549
 38. F. Farahmandzadeh, E. Molahosseini, S. Salehi, M. Molaei, H. Zare, Simple and fast dark degradation of methylene blue and *Escherichia coli* bacteria by Fe₃O₄/AC/Ag₂S magnetic nanocomposites. *Polyhedron*. **282**, 118226 (2026)
 39. L. Harikrishnan, I. Pakkiri, S. Venkatesan, A. Rajaram, T. Vembuli, Vibration-enhanced photocatalytic performance of magnetically recyclable CoFe₂O₄-anchored Ni-MOF heterojunction for polluted water remediation. *Next Mater.* **5**, 102505 (2026)
 40. A. Liaqat, I. Bibi, S. Kamal, Q. Raza, G. Mustafa, S. Lim, K. Ajmal, N. Alwadai, A. Nazir, M. Iqbal, Band gap engineering in Cu-substituted ZnCo₂O₄ spinel nanoparticles: Experimental and DFT insights into photocatalytic and antimicrobial performance. *J. Alloys Compd.* **1030**, 188766 (2026)
 41. N.A. Jasim, Preparation of Zn_xMn_{1-x}Fe₂O₄ ferrites for photocatalytic degradation of dyes. *Results Chem.* **5**, 100852 (2023)
 42. Q. Xie, Regulating spin polarization of Mn-doped ZnFe₂O₄ photocatalysts for improved activity. *J. Clean. Prod.* **430**, 139723 (2024)
 43. S. Kumar, Photocatalytic and adsorption behavior of Dy-doped ZnFe₂O₄ ferrites. *Appl. Phys. A* **130**, 231 (2024)
 44. W.S. Sarifuddin, Cu-doped ZnFe₂O₄ photocatalysts for enhanced hydrogen production and visible-light dye degradation. *J. Photochem. Photobiol Chem.* **453**, 115658 (2024)
 45. S.P. Keerthana, R. Yuvakkumar, P. Senthil Kumar, G. Ravi, D. Velauthapillai, Rare earth metal (Sm)-doped ZnFe₂O₄ for improved photocatalytic elimination of toxic dye from aquatic system. *Environ. Res.* **197**, 111047 (2021)
 46. L.T.T. Nguyen, H.T.T. Nguyen, L.T.H. Nguyen, A.T.T. Duong, H.Q. Nguyen, N.D. Bui, V.T.M. Ngo, D.T.C. Nguyen, T.V. Tran, Toward enhanced visible-light photocatalytic dye degradation and reusability of La³⁺-substituted ZnFe₂O₄ nanostructures. *Environ. Res.* **214**, 114130 (2022)
 47. F. Bibi, Fabrication of Ni and Mn co-doped ZnFe₂O₄ spinel ferrites and their nanocomposites with rGO as an efficient photocatalyst for the remediation of organic dyes. *Polyhedron*. **250**, 116826 (2024)
 48. A. Ayala-Fonseca, J. Oliva, C. Martinez-Sanchez, P. Salas, E. Aldeco-Perez, C. Rodríguez-González, Rapid electro-Fenton and photocatalytic degradation of methyl orange dye using graphene oxide nanoparticles supported on carbon felt. *J. Indian Chem. Soc.* **103**, 102862 (2026)
 49. A. Barani, B.R. Esboei, H.R. Goli, M.A. Ebrahimzadeh, Selective detection of Hg(II) via green synthesis of silver/silver chloride nanoparticles using *Astrodaucus persicus*: Optimization, comprehensive evaluation of biological activities, photodegradation, and heavy metal ion removal performances. *Surf. Interfaces*. **57**, 110022 (2026)

50. C.-Y. Tsay, T.-T. Ho, Hydrothermally synthesized spinel nanoferrites as magnetically separable and recyclable visible-light photocatalysts for degradation of hydrophilic organic pollutant. *Catalysts*. **16**, 531 (2026)
51. R. Kumar, V. Yadav, V.K. Gagnish, Rishu, Bhardwaj, Green synthesis of Fe₂O₃ nanoparticles using sunflower seed extract for enhanced photodegradation of rhodamine B. *Mater. Chem. Phys.* **327**, 132662 (2026)

Figures

Image not available with this version

Figure 1

This image is not available with this version.

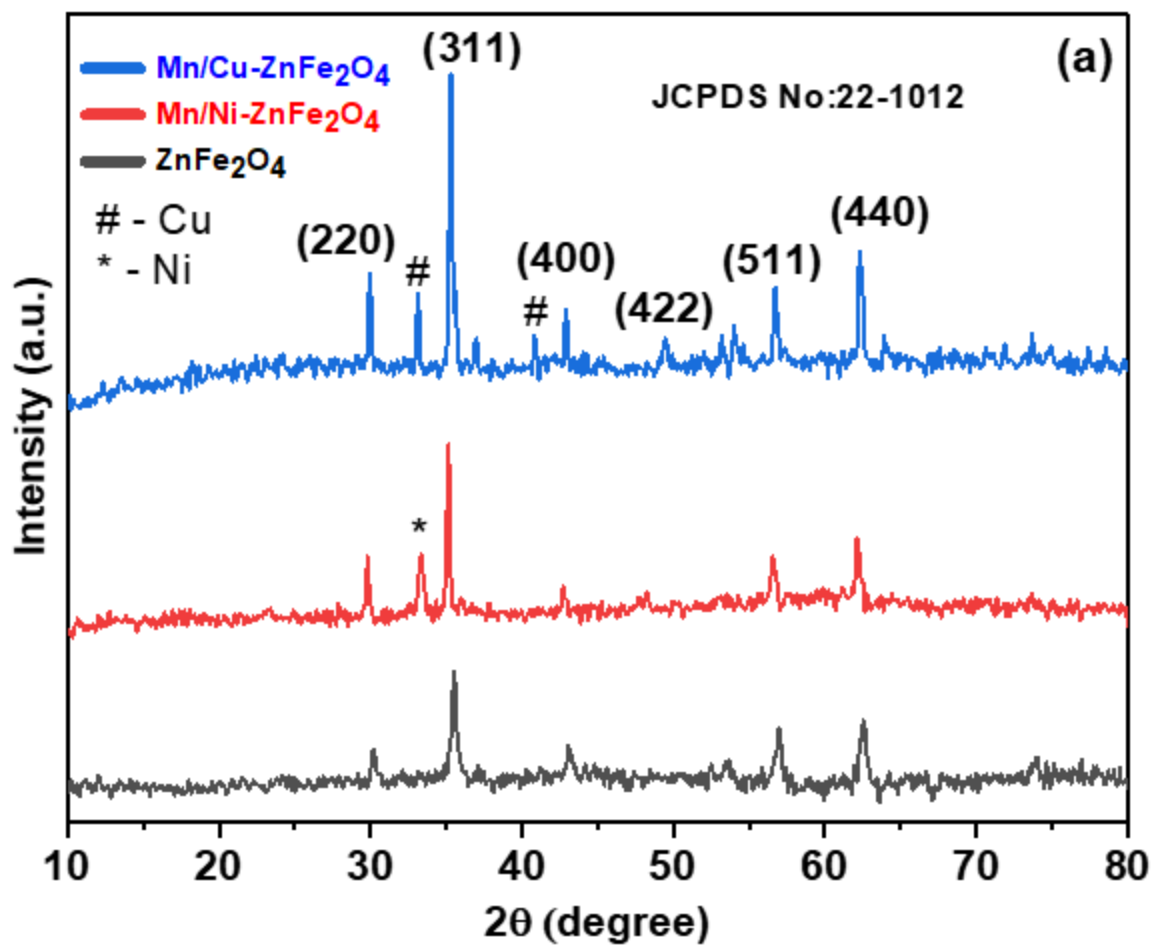


Figure 2

X-ray diffraction (XRD) patterns of pristine ZnFe₂O₄, Mn–Ni co-doped ZnFe₂O₄, and Mn–Cu co-doped ZnFe₂O₄ nanoparticles, confirming the formation of single-phase cubic spinel ferrite structures.

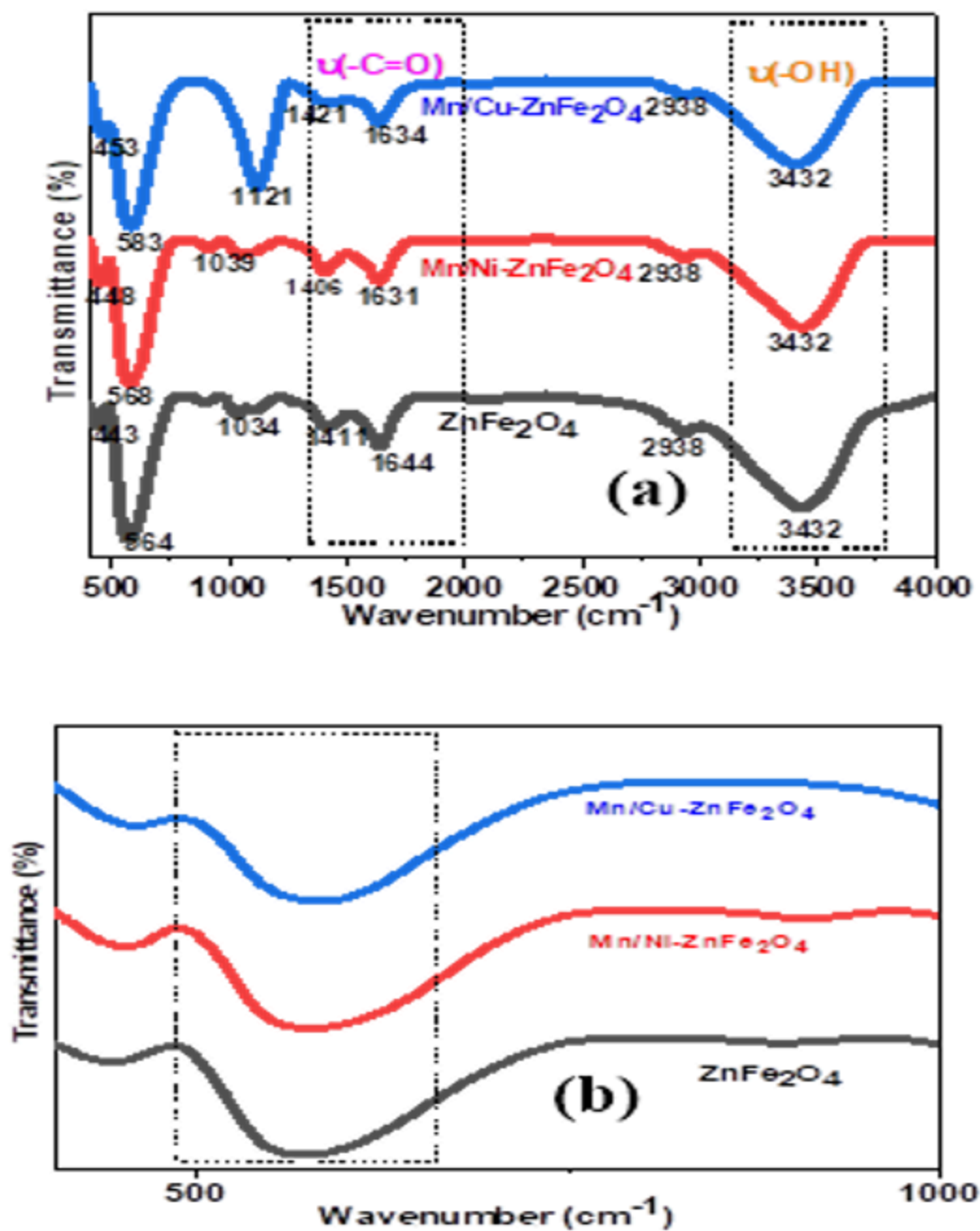


Figure 3

(a) FTIR spectra of pristine ZnFe₂O₄, Mn–Ni co-doped ZnFe₂O₄, and Mn–Cu co-doped ZnFe₂O₄ nanoparticles synthesized via the green microwave-assisted method; (b) enlarged view of the characteristic metal–oxygen vibration region (400–1000 cm^{-1}) for pristine ZnFe₂O₄, Mn–Ni co-doped ZnFe₂O₄, and Mn–Cu co-doped ZnFe₂O₄ nanoparticles.

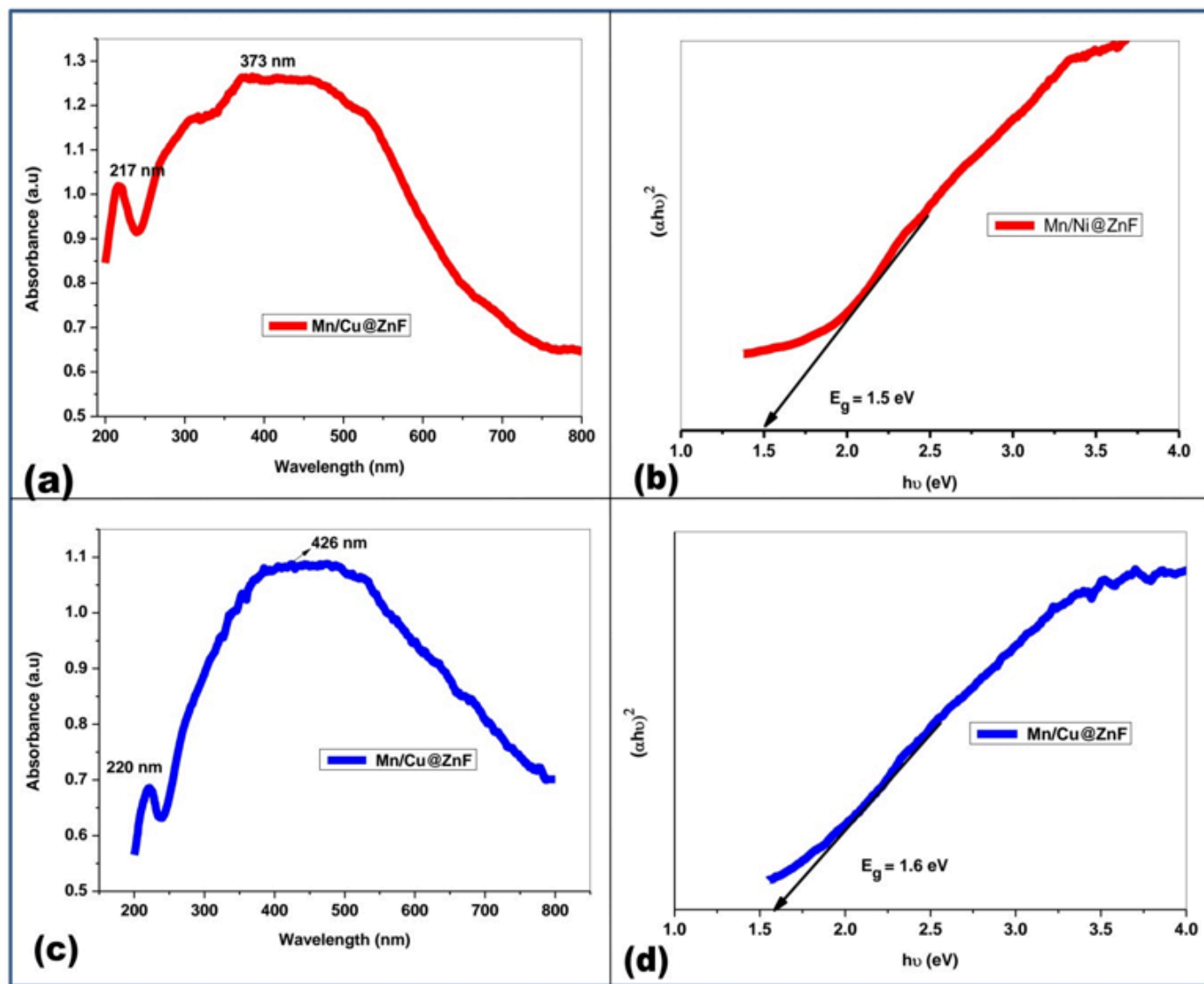


Figure 4

UV-Vis diffuse reflectance spectra (DRS) and corresponding Tauc plots of (a,b) Mn-Ni co-doped ZnFe₂O₄ and (c,d) Mn-Cu co-doped ZnFe₂O₄ nanoparticles.

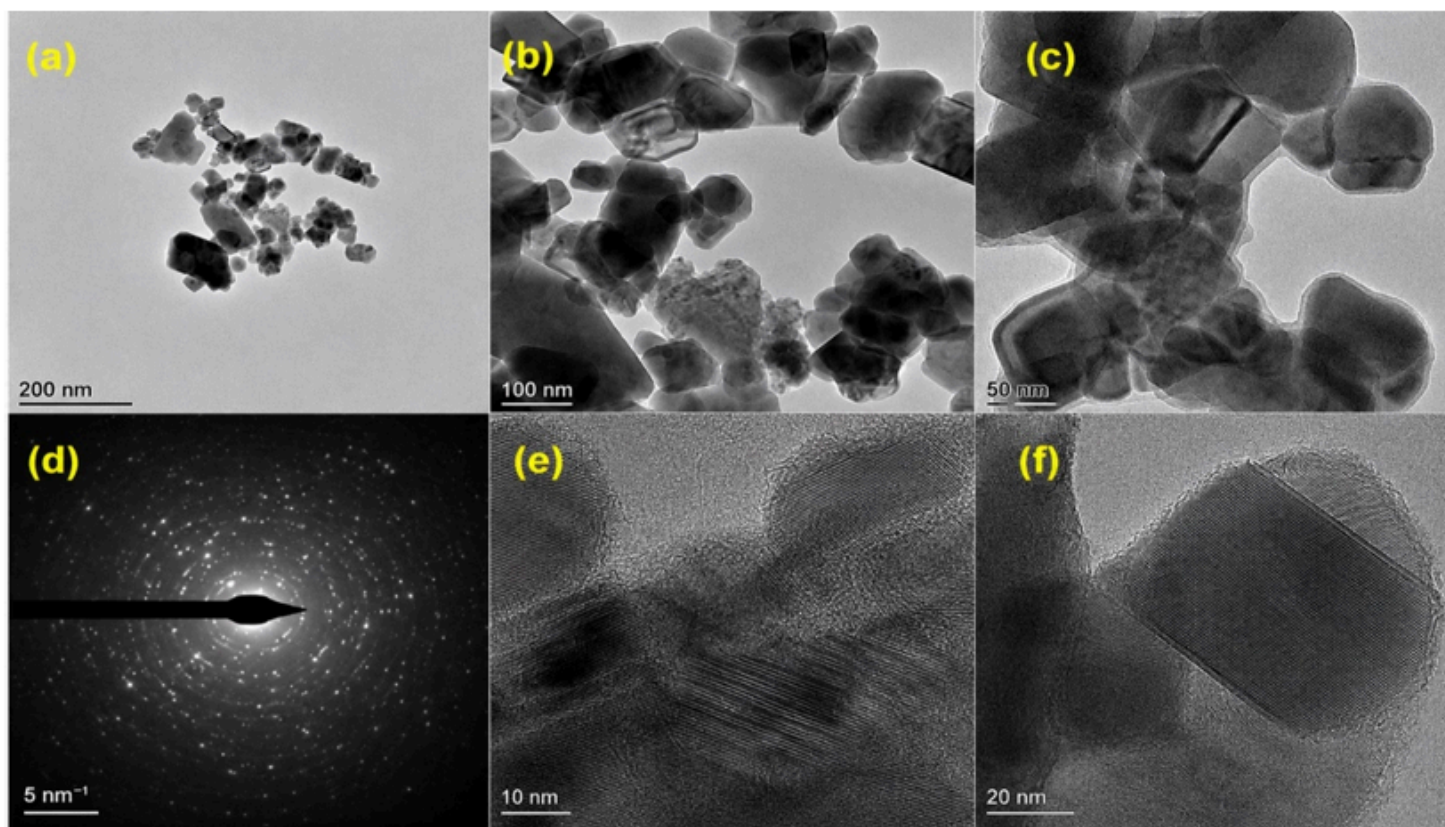


Figure 5

TEM, HRTEM, and SAED images of (a–f) Mn–Ni co-doped ZnFe_2O_4 .

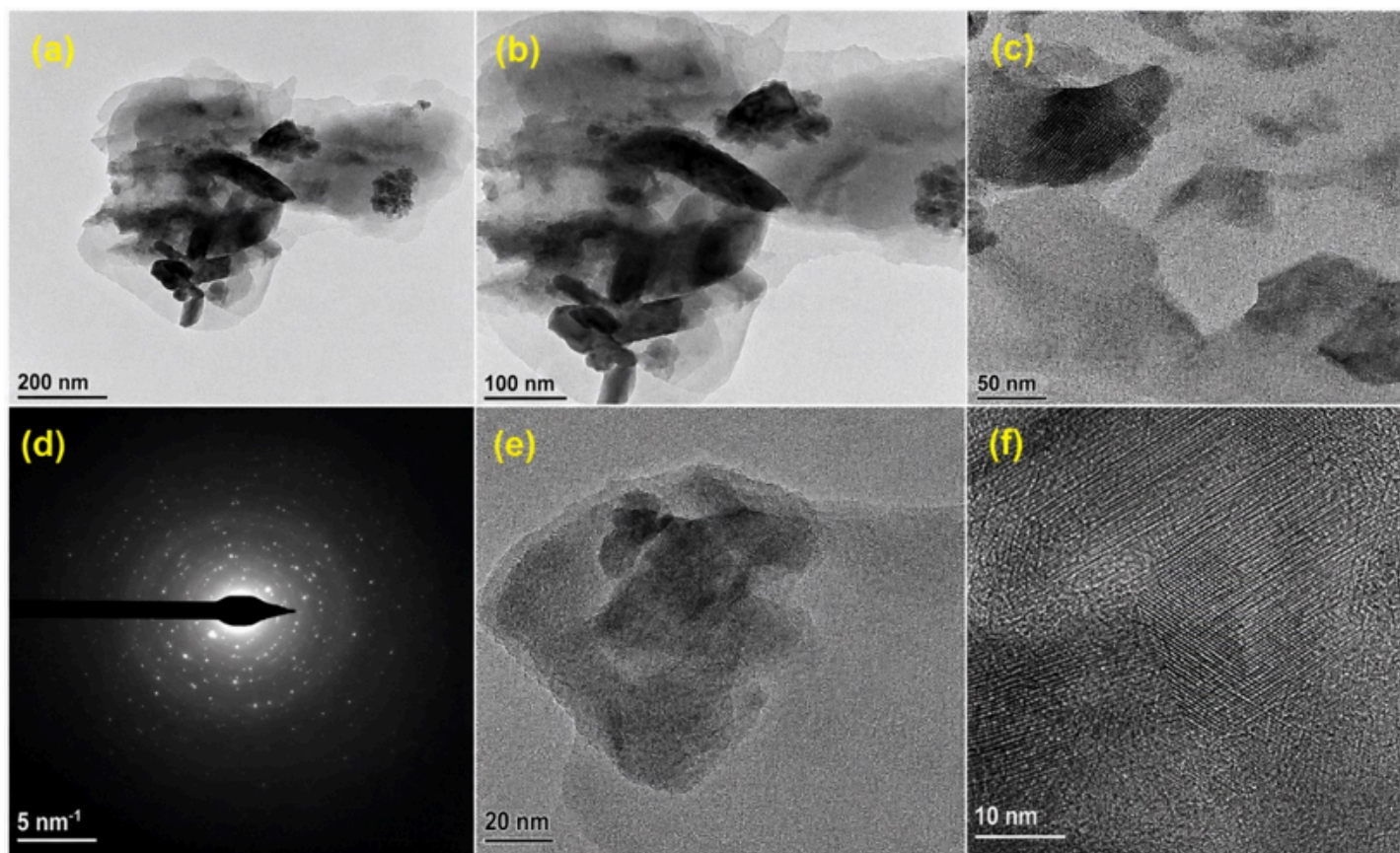


Figure 6

TEM, HRTEM, and SAED images of (a–f) Mn–Cu co-doped ZnFe_2O_4 .

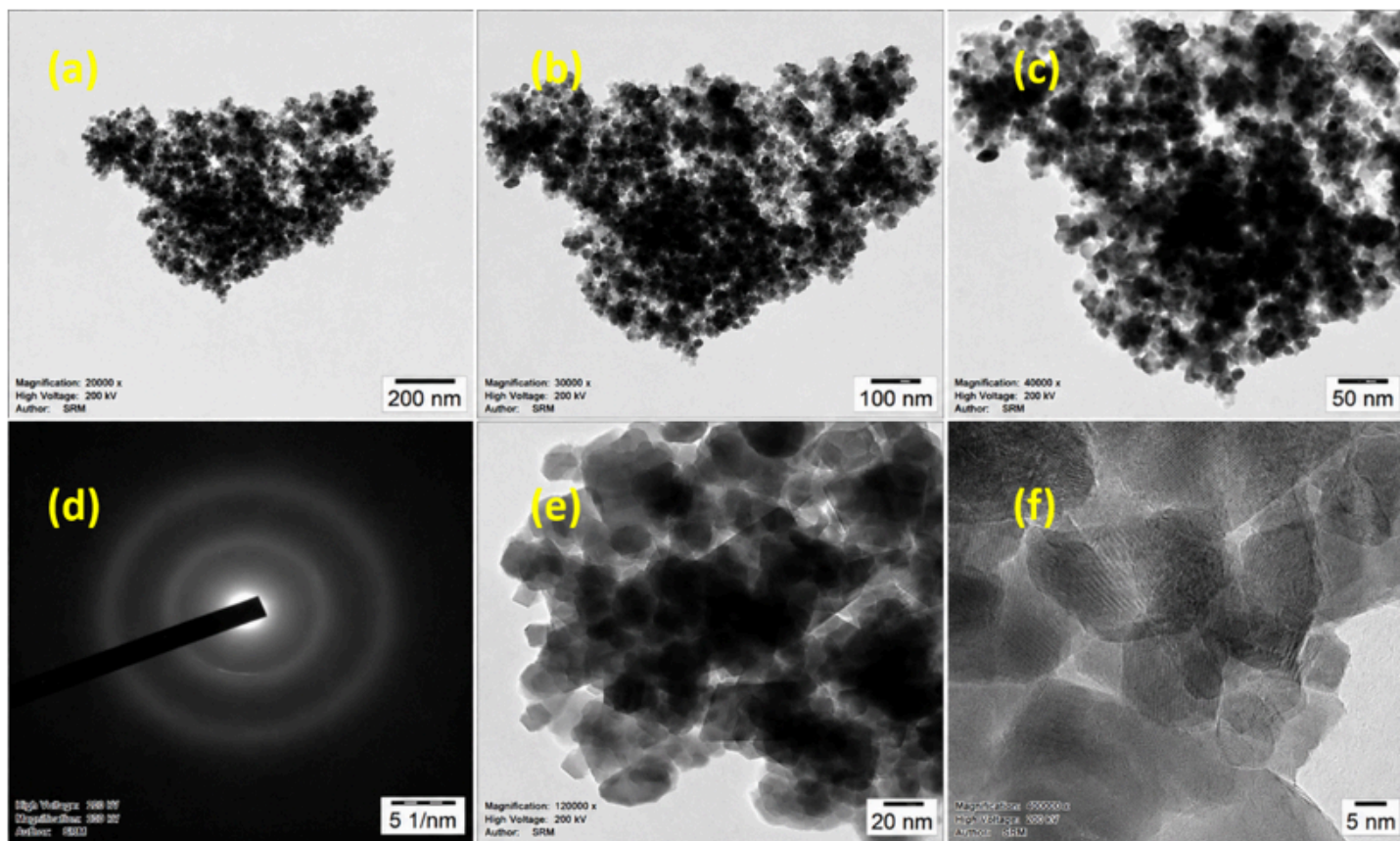


Figure 7

TEM, HRTEM, and SAED images of (a–f) ZnFe_2O_4 .

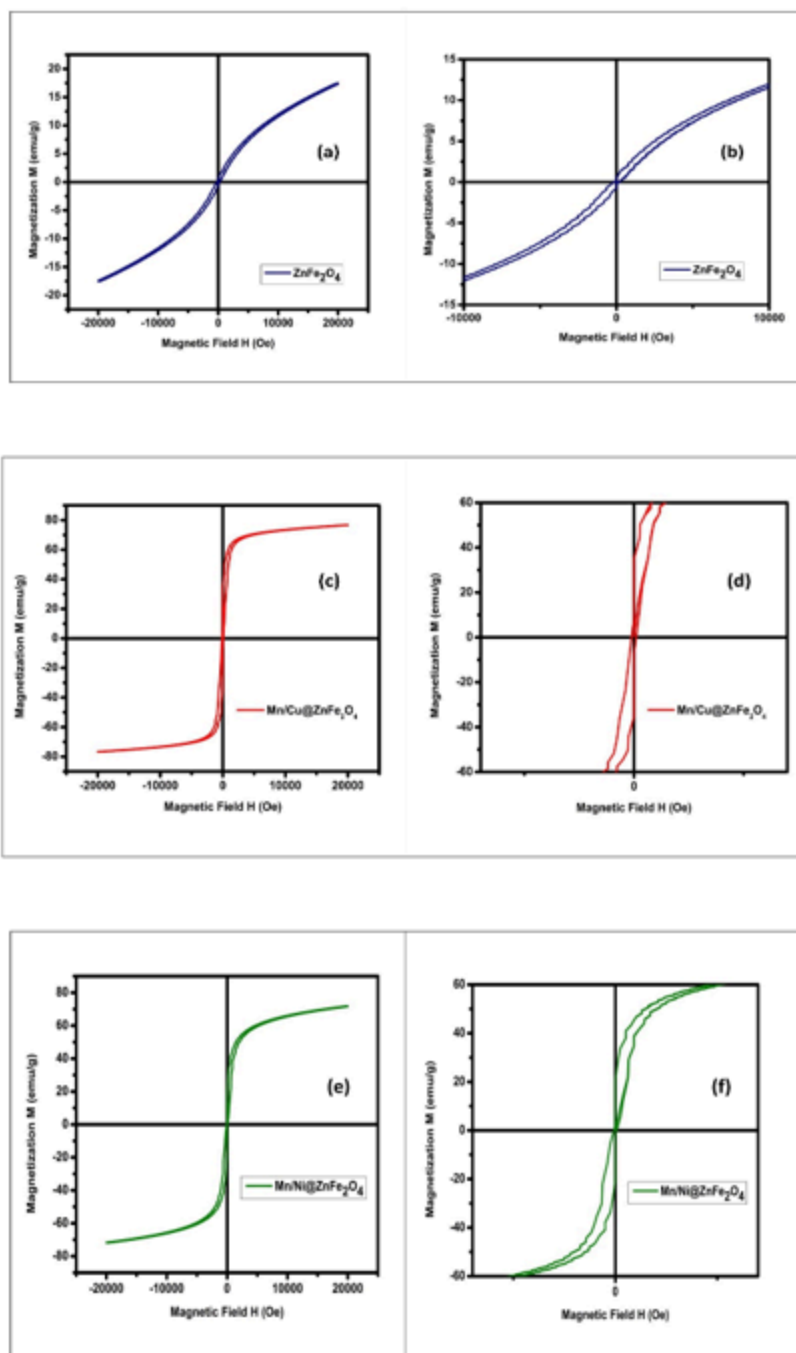


Figure 8

Magnetic hysteresis (M-H) curves of (a,b) pristine ZnFe_2O_4 , (c,d) Mn-Cu co-doped ZnFe_2O_4 , and (e,f) Mn-Ni co-doped ZnFe_2O_4 nanoparticles

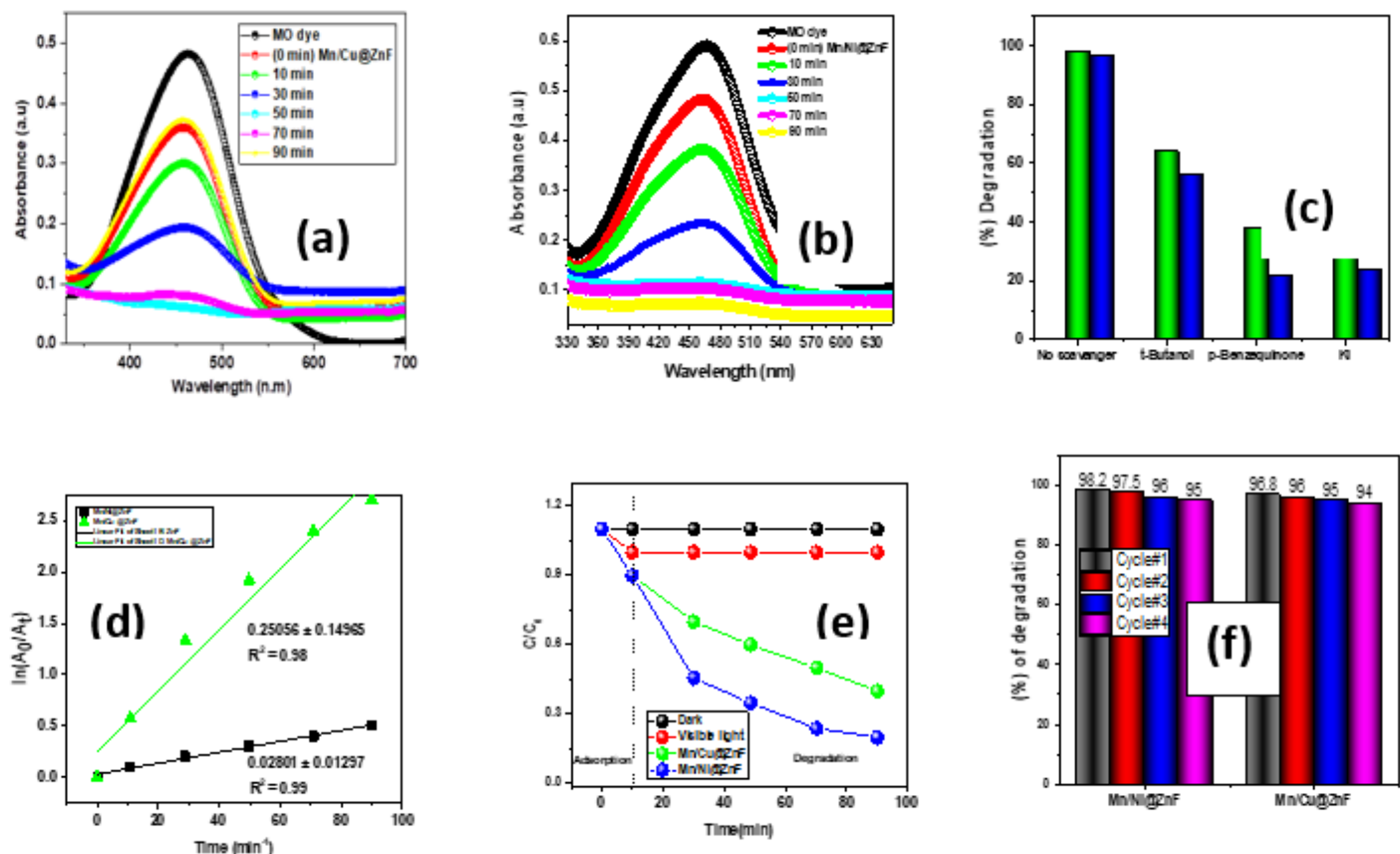


Figure 9

(a, b) UV-Vis absorption spectra of MO degradation using Mn-Cu and Mn-Ni co-doped ZnFe_2O_4 nanocomposites, respectively; (c) degradation efficiency; (d) pseudo-first-order kinetic plots; (e) C/C_0 versus irradiation time; and (f) recyclability of the photocatalysts over four successive cycles.

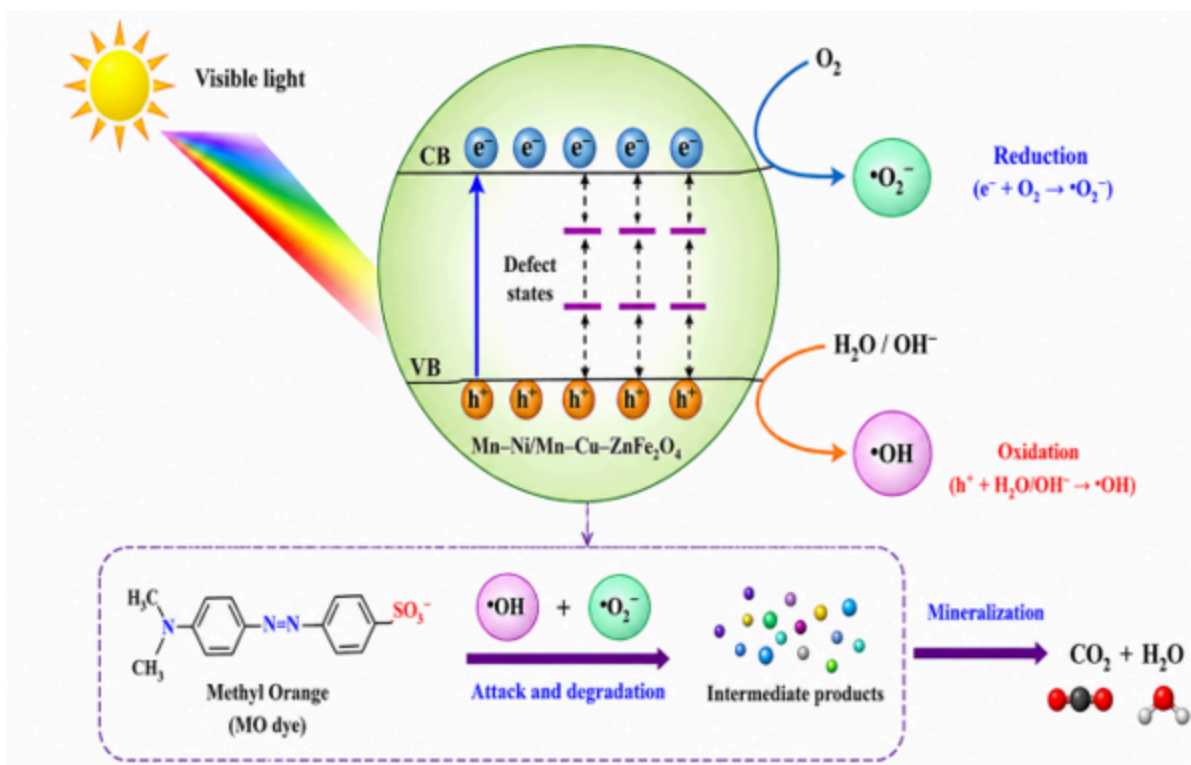


Figure 10

Proposed photocatalytic mechanism of Mn-Ni/Mn-Cu co-doped ZnFe₂O₄ under visible-light irradiation.