



Hydrothermal–Ball Milling Synthesis and Physicochemical Characterizations of Cu₂O/ZnFe₂O₄ Heterojunction Nanocomposite for Photocatalytic Applications

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ABSTRACT: This study reports the successful synthesis of Cu₂O/ZnFe₂O₄ heterojunction nanocomposite via a facile hydrothermal method followed by ball milling. The pristine Cu₂O and ZnFe₂O₄ nanoparticles were synthesized using hydrothermal techniques at optimized temperatures (140–160 °C) and reaction times (6–10 hours). The composite formation was confirmed through comprehensive characterization including X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM), Photoluminescence (PL) spectroscopy, and nitrogen adsorption–desorption analysis. XRD analysis confirmed the cubic cuprite phase of Cu₂O (JCPDS No. 05-0667) and the cubic spinel structure of ZnFe₂O₄ (JCPDS No. 89-1012), with crystallite sizes of approximately 25 nm. FTIR spectra revealed characteristic metal–oxygen vibrations at 1339–924 cm⁻¹ (Cu–O) and 699 cm⁻¹ (Fe–O/Zn–O), confirming successful synthesis. The composite exhibited a BET surface area of 36.37 m²/g, significantly higher than pristine Cu₂O (7.28 m²/g), with a mesoporous structure (Type IV isotherm, H3 hysteresis loop). FESEM micrographs revealed agglomerated nanoparticles with rough, porous morphology and intimate interfacial contact between Cu₂O and ZnFe₂O₄ phases. PL spectroscopy demonstrated significant quenching of emission intensity in the composite, indicating effective suppression of electron–hole recombination. UV–Vis–NIR analysis yielded an optical band gap of approximately 2.6 eV, confirming visible light absorption capability. This comprehensive characterization confirms the successful formation of a type II heterojunction with enhanced charge separation properties, suitable for photocatalytic applications in wastewater treatment.

KEYWORDS: Cu₂O/ZnFe₂O₄ nanocomposite, hydrothermal synthesis, heterojunction, photocatalytic, characterization, spinel ferrite.

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1. INTRODUCTION

Photocatalysis has emerged as a promising advanced oxidation process (AOP) for wastewater treatment, offering complete mineralization of organic pollutants using renewable solar energy (Koe *et al.*, 2020; Fujishima *et al.*, 2007). Among various photocatalysts, copper(I) oxide (Cu₂O) has attracted significant attention due to its narrow band gap (2.0–2.2 eV), high absorption coefficient in visible light, nontoxicity, low cost, and environmental acceptability (Li *et al.*, 2022). However, practical applications of Cu₂O are severely limited by photocorrosion, poor stability, and rapid recombination of photogenerated electron–hole pairs (Yang *et al.*, 2022).

Zinc ferrite (ZnFe₂O₄) presents an excellent candidate for heterojunction formation due to its high physicochemical stability, narrow band gap (1.9–2.0 eV), high porosity, paramagnetism enabling easy recovery, and good reusability (Zhang *et al.*, 2010; Wu *et al.*, 2016; Sharafinia *et al.*, 2022). The formation of p–n heterojunctions between p-type Cu₂O and n-type ZnFe₂O₄ can effectively promote charge separation, reduce recombination, and enhance photocatalytic activity (Wang *et al.*, 2024; Zhang *et al.*, 2025).

This manuscript focuses on the synthesis and detailed characterization of a Cu₂O/ZnFe₂O₄ heterojunction nanocomposite, providing a comprehensive understanding of its structural, morphological, optical, and textural properties essential for photocatalytic applications.

2. MATERIALS AND METHODS

2.1 Chemicals

Copper(II) sulfate pentahydrate (CuSO₄·5H₂O, ≥99%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, ≥98%), iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, ≥98%), sodium hydroxide (NaOH, ≥97%), ascorbic acid (C₆H₈O₆, ≥99%), ethanol (C₂H₅OH, ≥99.5%), and deionized water were used. All chemicals were of analytical grade and used without further purification.

2.2 Synthesis of Cu₂O Nanoparticles

Cu₂O nanoparticles were synthesized using a hydrothermal method adapted from Ho and Huang (2009). Typically, 0.6 g of CuSO₄·5H₂O was dissolved in 15 mL of deionized water. Under continuous stirring, 12 mL of 1.2 mol/L NaOH solution was added dropwise over 10 minutes (Solution A). Subsequently, 4 mL of 0.2 mol/L ascorbic acid was added with stirring for 30 minutes. The mixture was transferred to a 50 mL Teflon-lined stainless-steel autoclave and maintained at 140–160 °C for 6–10 hours. After cooling to room temperature, the product was collected by centrifugation, washed three times with ethanol and deionized water, and dried at 60 °C for 4 hours.

2.3 Synthesis of ZnFe₂O₄ Nanoparticles

ZnFe₂O₄ nanoparticles were synthesized via a hydrothermal method. 10 mmol Zn(NO₃)₂·6H₂O and 20 mmol Fe(NO₃)₃·9H₂O were dissolved in 100 mL distilled water with stirring until homogeneous. 2 M NaOH was added gradually until pH 12 was achieved, forming a suspension. The mixture was transferred to a Teflon-lined autoclave and heated at 180 °C for 3 hours. The product was filtered, washed with distilled water until pH 7–8, and dried.

2.4 Synthesis of Cu₂O/ZnFe₂O₄ Composite

The Cu₂O/ZnFe₂O₄ composite (1.5:1.5 ratio) was prepared by ball milling using a planetary ball mill at 300 rpm for 2 hours in ethanol medium. The mixture was dried at 60 °C for 4 hours.

2.5 Characterization Techniques

X-ray Diffraction (XRD): Phase identification was performed using a 6100 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å) at 40 kV and 30 mA, scanning from 10° to 80° 2 θ . Crystallite sizes were calculated using the Debye–Scherrer equation: $D = K\lambda/(\beta \cos \theta)$, where $K = 0.94$, $\lambda = 1.5406$ Å, β is the FWHM in radians, and θ is the Bragg angle.

Fourier Transform Infrared Spectroscopy (FTIR): FTIR spectra were recorded using the KBr pressed disk technique on an FTIR spectrophotometer at a resolution of 1 cm⁻¹ in the range 3500–400 cm⁻¹.

Field Emission Scanning Electron Microscopy (FESEM): Morphological analysis was conducted at 10 kV using a field emission scanning electron microscope. Samples were deposited on alumina stubs and gold-sputtered before analysis.

Photoluminescence Spectroscopy (PL): PL spectra were obtained at room temperature using a spectrofluorometer with an excitation wavelength of 325 nm.

Nitrogen Adsorption–Desorption Analysis: BET surface areas and pore structures were determined using nitrogen adsorption–desorption isotherms at liquid nitrogen temperature (−196 °C). Surface areas were calculated using the BET equation, and pore volumes from the Barrett–Joyner–Halenda (BJH) method.

UV–Vis–NIR Spectroscopy: Optical properties were studied using a UV–Vis–NIR scanning spectrophotometer in diffuse reflectance mode.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction Analysis

The XRD patterns (Figure 1) confirmed the formation of pure crystalline phases. Cu₂O exhibited characteristic peaks at 2 $\theta = 29.5^\circ$, 36.4°, 42.3°, 61.3°, and 73.5° corresponding to (110), (111), (200), (220), and (311) planes of cubic cuprite (JCPDS No. 05-0667). ZnFe₂O₄ showed reflections at 30.1°, 35.3°, 43.1°, 53.4°, 56.9°, and 62.5° assigned to (220), (311), (400), (422), (511), and (440) planes of cubic spinel (JCPDS No. 89-1012). The composite pattern displayed peaks from both phases without impurities, confirming successful heterojunction formation. Average crystallite sizes were approximately 25 nm for ZnFe₂O₄ and in the nano-range for Cu₂O, consistent with literature (Raja *et al.*, 2017; Ren *et al.*, 2009).

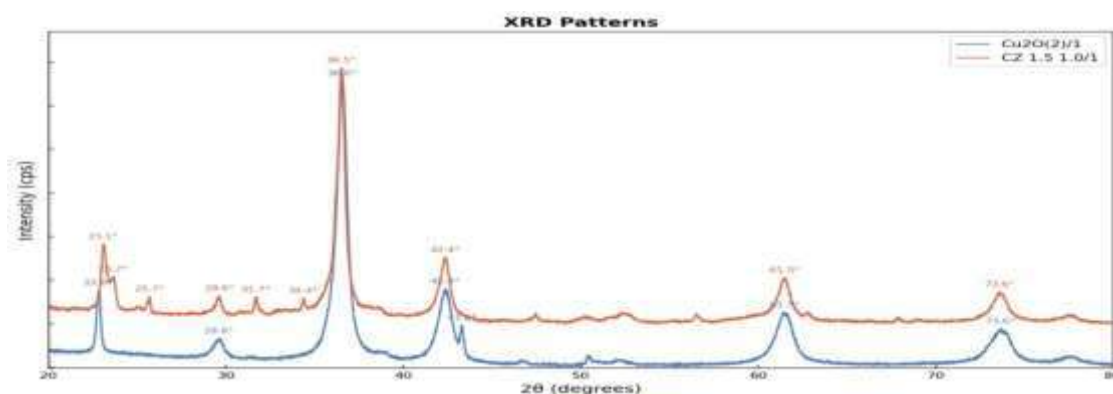


Figure 1. XRD patterns of Cu_2O and $\text{Cu}_2\text{O}/\text{ZnFe}_2\text{O}_4$ composite.

3.2 FTIR Spectroscopy Analysis

The FTIR spectrum of Cu_2O (Figure 2) showed broad bands at $3700\text{--}3900\text{ cm}^{-1}$ (O–H stretching), peaks at 3085 , 3028 , and 2811 cm^{-1} (organic residues), and Cu–O vibrations at $1339\text{--}924\text{ cm}^{-1}$, consistent with Kumar et al. (2014) and Ho and Huang (2009). ZnFe_2O_4 (Figure 3) exhibited bands at $3200\text{--}3600\text{ cm}^{-1}$ (O–H stretching), 1540 cm^{-1} (H–O–H bending), 1406 cm^{-1} (carbonate species), and a prominent Fe–O stretching at 699 cm^{-1} , confirming spinel formation (Raja et al., 2017). The composite (Figure 4) showed combined features at 3906 , 3755 , 3469 , 2814 , 1712 ($\text{C}=\text{O}$ stretching), 1124 ($\text{C}-\text{O}$ stretching), and 686 cm^{-1} (metal–oxygen vibrations), confirming successful integration.

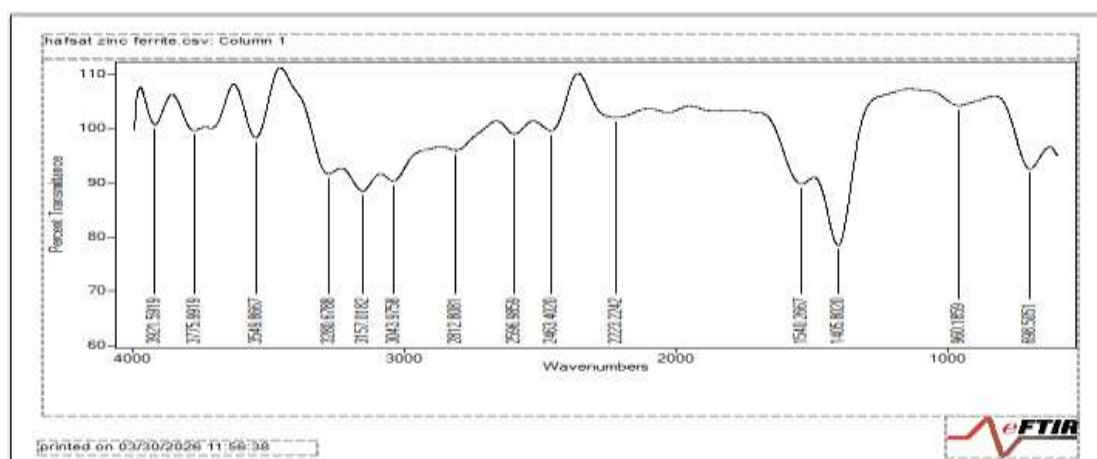


Figure 2. FTIR spectrum of Cu_2O .

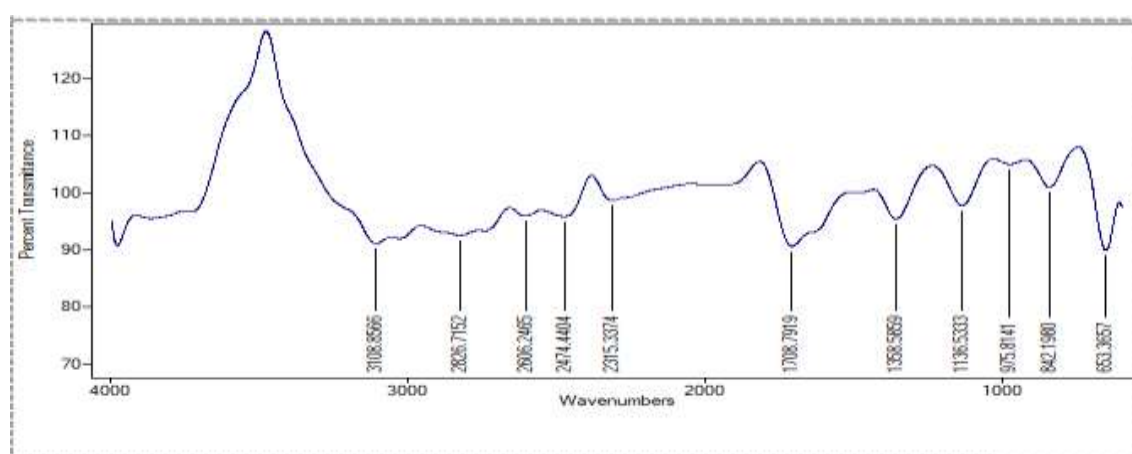


Figure 3. FTIR spectrum of ZnFe_2O_4 .

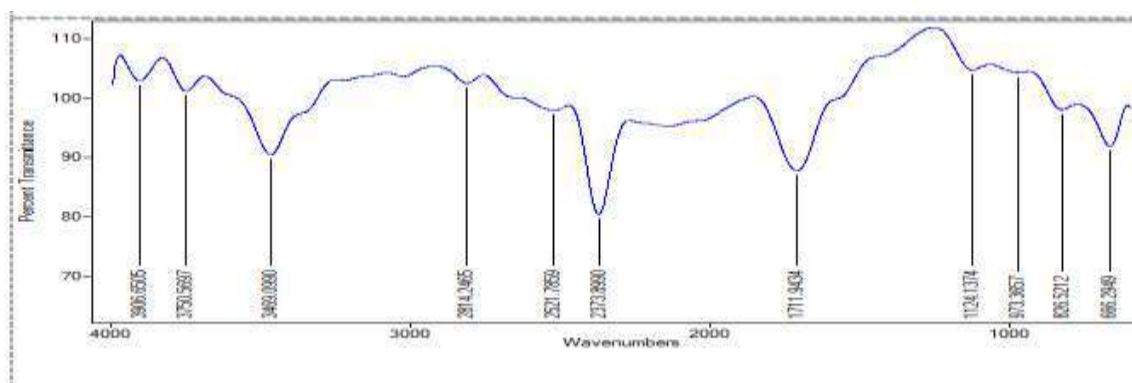


Figure 4. FTIR spectrum of $\text{Cu}_2\text{O}/\text{ZnFe}_2\text{O}_4$ composite.

3.3 FESEM Morphological Analysis

FESEM micrographs (Figure 5) revealed agglomerated nanoparticles with rough, porous morphology. Larger polyhedral particles (Cu_2O) were embedded within a fine nanoparticle matrix (ZnFe_2O_4), indicating intimate interfacial contact. Primary particles were less than 100 nm, forming interconnected porous clusters. This morphology provides high surface area and abundant active sites while facilitating charge transfer at heterojunction interfaces (Wang *et al.*, 2024).

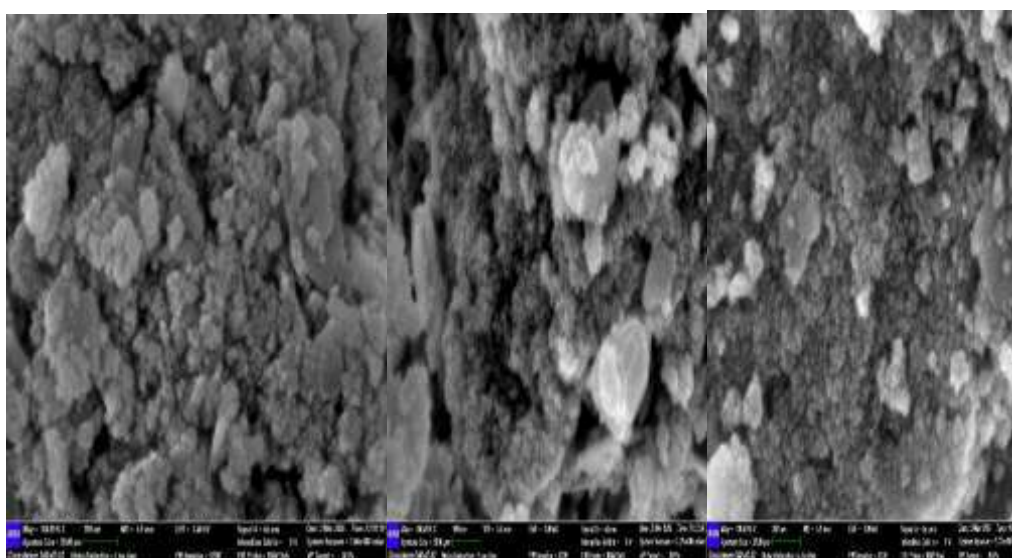


Figure 5. FESEM micrographs of $\text{Cu}_2\text{O}/\text{ZnFe}_2\text{O}_4$ composite.

3.4 Surface Area and Porosity Analysis

Nitrogen adsorption–desorption results are summarized in Table 1. The composite exhibited a BET surface area of $36.37 \text{ m}^2/\text{g}$, significantly higher than pristine Cu_2O ($7.28 \text{ m}^2/\text{g}$). ZnFe_2O_4 showed the highest surface area ($101.90 \text{ m}^2/\text{g}$). Total pore volumes followed: ZnFe_2O_4 ($0.1224 \text{ cm}^3/\text{g}$) > composite ($0.0804 \text{ cm}^3/\text{g}$) > Cu_2O ($0.0369 \text{ cm}^3/\text{g}$). The composite showed a Type IV isotherm with an H3 hysteresis loop (Figure 6), characteristic of mesoporous materials with slit-shaped pores formed by platelet aggregation (Kumar *et al.*, 2017; Wang *et al.*, 2024). Average pore diameters were 22.31 nm (Cu_2O), 7.60 nm (ZnFe_2O_4), and 1.11 nm (composite). The low average pore diameter of the composite may reflect the presence of narrow pores within the aggregated structure and should be further verified against the BJH pore-size distribution.

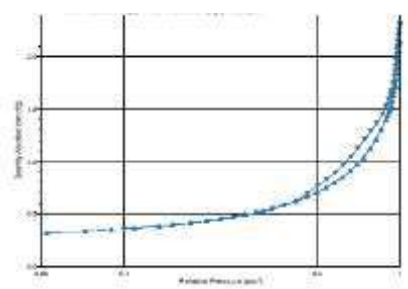


Figure 6a. Nitrogen adsorption–desorption isotherm of ZnFe_2O_4 .

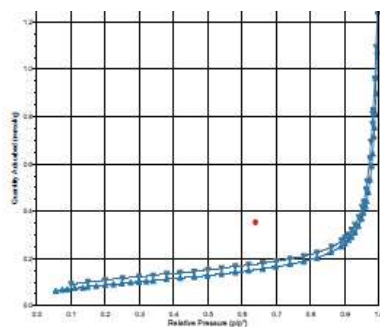


Figure 6b. BET linear plot for the composite.

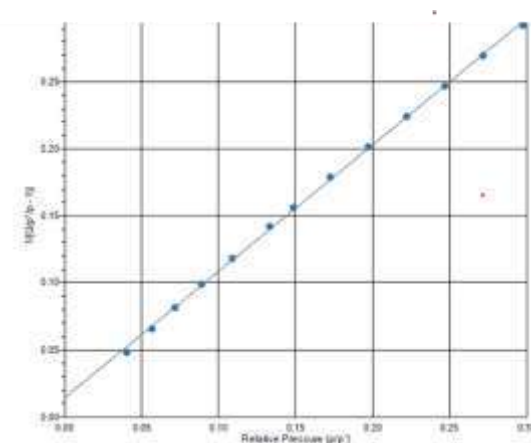


Figure 6c. Surface area plot for the composite.

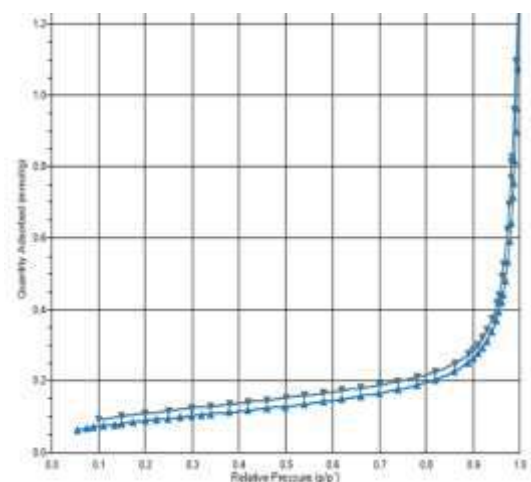


Figure 6d. Nitrogen adsorption–desorption isotherm of Cu_2O .

Table 1: Textural Properties of Synthesized Materials

Parameter	Cu_2O	ZnFe_2O_4	Composite
BET surface area (m^2/g)	7.28	101.90	36.37
Langmuir surface area (m^2/g)	16.65	294.62	106.24
Total pore volume (cm^3/g)	0.0369	0.1224	0.0804
Average pore diameter (nm)	22.31	7.60	1.11

3.5 Photoluminescence Analysis

PL spectra (Figure 7) showed significant quenching in the composite compared to pristine Cu_2O . Cu_2O exhibited strong emission bands at 520 and 540 nm (band-edge and defect-related recombination). The composite displayed broadened emission centered at 503 nm with significantly reduced intensity and a weak shoulder at 559 nm. The substantial PL quenching indicates efficient

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suppression of electron–hole recombination due to heterojunction formation, facilitating interfacial charge transfer (Wang *et al.*, 2024; Zhang *et al.*, 2025).

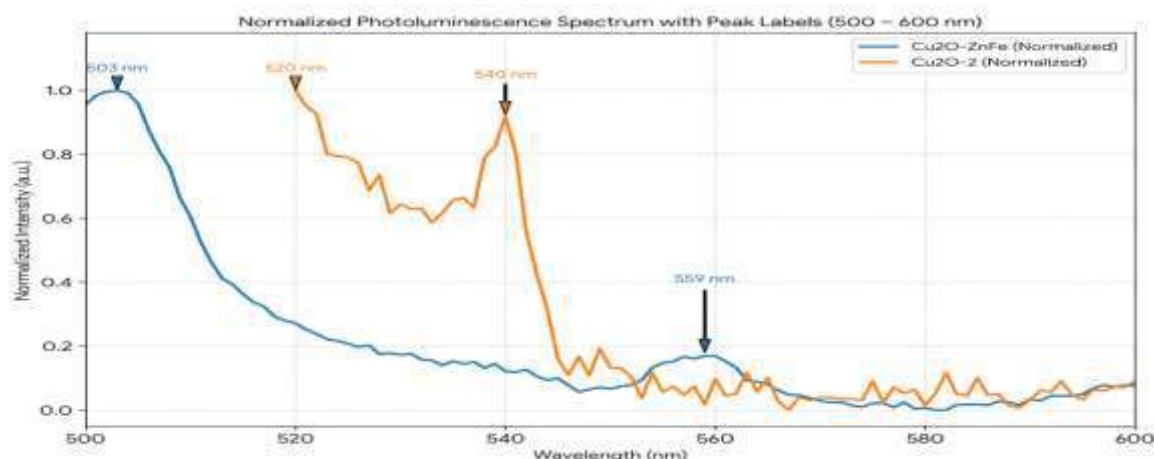


Figure 7. PL spectra of Cu_2O and $\text{Cu}_2\text{O}/\text{ZnFe}_2\text{O}_4$ composite.

3.6 UV–Vis–NIR Analysis

The optical band gap estimated from the Tauc plot was approximately 2.6 eV, confirming the semiconducting nature and visible light absorption capability. The narrow band gap enhances visible-light harvesting and photogenerated charge carrier generation.

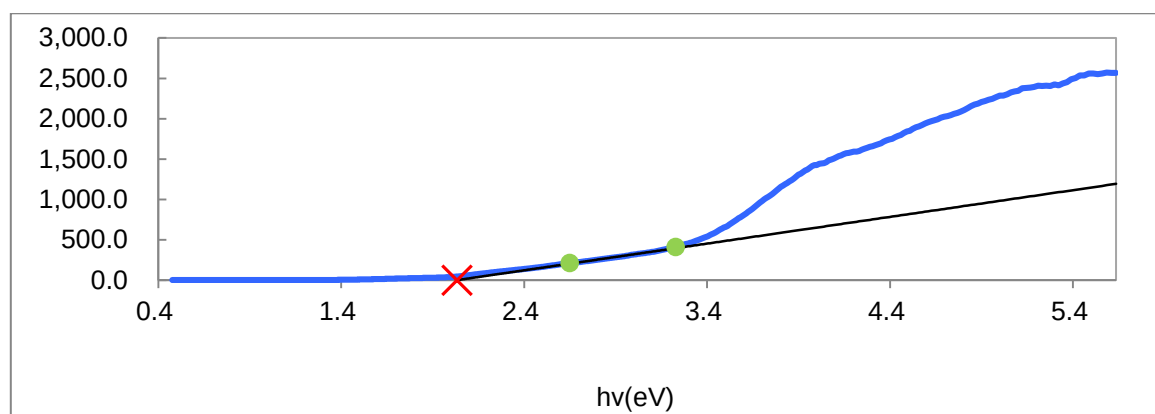


Figure 8. UV–Vis–NIR Tauc plot of $\text{Cu}_2\text{O}/\text{ZnFe}_2\text{O}_4$ composite.

4. CONCLUSION

The $\text{Cu}_2\text{O}/\text{ZnFe}_2\text{O}_4$ heterojunction nanocomposite was successfully synthesized via a hydrothermal method followed by ball milling. Comprehensive characterization confirmed:

1. Formation of pure crystalline phases with no impurities.
2. Cubic cuprite (Cu_2O) and cubic spinel (ZnFe_2O_4) structures.
3. Enhanced surface area ($36.37 \text{ m}^2/\text{g}$) with a mesoporous structure.
4. Intimate interfacial contact between semiconductor components.
5. Significant PL quenching indicating suppressed charge recombination.
6. Optical band gap of 2.6 eV suitable for visible light photocatalysis.

These properties establish the $\text{Cu}_2\text{O}/\text{ZnFe}_2\text{O}_4$ composite as a promising photocatalyst for wastewater treatment applications.

5. ACKNOWLEDGMENT

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