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Photocatalytic activity of BiFeO₃/ZnFe₂O₄ nanocomposites under visible light irradiation†

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Herein, BiFeO₃/ZnFe₂O₄ nanocomposites were synthesized *via* a glyoxylate precursor method using a two-pot approach. Phase evolution is investigated by X-ray diffraction and Raman spectroscopy, which confirm that no impurity phases are formed between BiFeO₃ and ZnFe₂O₄ following calcination at 600 °C. The specific surface area characterized by N₂ adsorption–desorption isotherms decreases from 30.56 to 13.13 m² g⁻¹ with the addition of zinc ferrite. In contrast, the magnetization increases from 0.28 to 1.8 emu g⁻¹ with an increase in the amount of ZnFe₂O₄. The composites show strong absorption in the visible region with the optical band gap calculated from the Tauc's plot in the range from 2.17 to 2.22 eV, as measured by diffuse reflectance spectroscopy. Furthermore, the maximum efficiency for the photodegradation of methylene blue under visible light is displayed by the composite containing 25 wt% ZnFe₂O₄ due to the synergic effect between BiFeO₃ and ZnFe₂O₄, as confirmed by photoluminescence spectroscopy.

1. Introduction

In recent years, scientific research has been focused on new visible light photocatalysts based on semiconductors to address the increasing environmental pollution and energy demands by efficient utilization of solar energy.^{1,2} To date, various metal oxides (ZnO³ and TiO₂⁴) and metal sulfides (ZnS⁵) have been studied to efficiently degrade harmful organic pollutants and for hydrogen production through water splitting under UV light irradiation.⁴ However, the UV region spans only 5% of the entire solar spectrum, restricting their applications. As a result of band gap engineering improvement, composites can be fabricated by coupling two narrow band gap semiconductors, which have attracted considerable attention for the development of efficient visible light photocatalysts.^{6–8}

Bismuth ferrite (BiFeO₃), which has potential applications in sensors, actuators, and digital memory, is a well-known multi-ferroic material simultaneously possessing ferroelectric and ferromagnetic ordering at room temperature.^{9,10} Furthermore, BiFeO₃ displays a distinct photovoltaic effect with an open circuit voltage of 0.8–0.9 V as a working solar device, which represents a new potential application.^{11,12} Due to its relatively narrow band gap of 2.2 eV, BiFeO₃ has been considered as a possible visible light photocatalyst under solar light irradiation for the photodegradation of organic contaminants.^{13,14} However, its quantum yield is poor due to the rapid recombination of the photogenerated electron–hole pairs that limits its

practical use in photocatalytic applications.^{15,16} Therefore, many strategies have been developed to enhance the photocatalytic efficiency of BiFeO₃ by modifying the size and morphology of its particles, cation doping, and coupling with other semiconductors.^{17–19} For instance, several semiconductors such as g-C₃N₄, carbon nanofiber, graphene, CuO and ZnO have been coupled with BiFeO₃ to improve its photogenerated electron–hole separation, thus enhancing its interfacial charge transfer the efficiency.^{6,20–27}

Spinel magnetic zinc ferrite (ZnFe₂O₄) with a narrow band gap of 1.92 eV exhibits a significant photoresponse in the visible light region and has been utilized in gas sensors, catalysts and semiconductor photocatalysts.¹ Furthermore, the magnetic properties of ZnFe₂O₄ can be used to recycle photocatalysts by the application of a magnetic field, making it an interesting product in the industrial photodegradation of organic pollutants.^{7,28} To the best of our knowledge, there are no reports on the synthesis and application of BiFeO₃/ZnFe₂O₄ nanocomposites for pollutant degradation under visible light irradiation. Uniyal and Yadav only reported the dielectric and magnetic properties of BiFeO₃/ZnFe₂O₄ composites synthesized *via* the sol–gel method as a function of annealing temperature.²⁹

Herein, we report the structure, microstructure, magnetic properties and photocatalytic performances of BiFeO₃/ZnFe₂O₄ composites synthesized *via* the glyoxylate precursor method. The optimum amount of ZnFe₂O₄ is determined to maximize the photocatalytic activity of BiFeO₃ powder.

2. Experimental procedure

Starting materials of Fe(NO₃)₃·9H₂O (>99%), Bi(NO₃)₂·5H₂O (>99%), Zn(NO₃)₂·6H₂O (>99%), 1,2-ethanediol (OH(CH₂)₂OH)

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and nitric acid (HNO₃, 68 wt%) of analytical grade were provided by Merck & Co.

BiFeO₃ powder was prepared *via* the glyoxylate precursor method in which the required amount of Fe(NO₃)₃·9H₂O was dissolved in 1,2-ethanediol (ethylene glycol) and then added to 15 mL of 3 mol L⁻¹ nitric acid solution containing Bi(NO₃)₃·5H₂O under magnetic stirring at 100 °C. The ethylene glycol : NO₃⁻ (EG/NO₃) molar ratio was set to 2.5 : 1. Evolving bubbles of brown nitrogen oxide (NO_x) indicated the initiation of the redox reaction between the NO₃⁻ anions and OH groups of diol. After drying at 130 °C, the precursor was calcined at 600 °C for 1 h in ambient air.³⁰ ZnFe₂O₄ powder was produced by dissolving Zn(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O in ethylene glycol under magnetic stirring at 100 °C. Once the NO_x bubbles disappeared, the solution precursor was dried at 130 °C and then calcined at 600 °C for 1 h in air. BiFeO₃/ZnFe₂O₄ composites were synthesized *via* a two-pot approach in which the required amount of previously synthesized BiFeO₃ powder was added to the solution precursor of zinc ferrite, where the dried precursor was calcined at 600 °C for 1 hour.

Phase evolution was investigated using a PANalytical X'pert X-ray diffractometer (XRD) with monochromatic CuKα radiation. Raman analysis was performed on the powders using a WiTec Alpha 300R instrument (Nd:YAG laser source: λ = 532 nm and 0.7 MW power, and range: 100–900 cm⁻¹). The morphology and microstructure of the powders were observed using a TESCAN Vega II scanning electron microscope (SEM). The specific surface areas of the as-prepared powders were determined according to the Brunauer–Emmett–Teller (BET) method with nitrogen adsorption at 77 K using a PHS-1020 instrument after degassing at 250 °C for 5 h. The Barrett–Joyner–Halenda (BJH) cumulative pore volume was calculated from the adsorption branch of the isotherms. The equivalent particle size was calculated based on the BET surface area as follows:

$$D_{\text{BET}} = \frac{6000}{\rho S_{\text{BET}}} \quad (1)$$

where, D_{BET} is the equivalent particle size (nm), ρ is the theoretical density and S_{BET} stands for the BET surface area (m² g⁻¹). A vibrating sample magnetometer (Meghnatis Daghigh Kavir Kashan Co., Iran) with a maximum field of 10 kOe was employed to measure the magnetic properties at room temperature. UV-vis absorption spectra were recorded on a Shimadzu UV-vis-52550 spectrophotometer in the wavelength range of 300–800 nm. Room temperature photoluminescence spectra (PL) were obtained on a fluorescence spectrophotometer (F-4600, Hitachi, Japan) at an excitation wavelength of 210 nm.

The photocatalytic activity of the BiFeO₃/ZnFe₂O₄ nanocomposites was evaluated by the degradation of methylene blue (MB) in aqueous solution under visible light radiation. Two 100 W xenon lamps with a cutoff ultraviolet filter (λ = 420 nm) were introduced as the visible light source. In each experiment, 0.1 g of photocatalyst was added to 100 mL of methylene blue solution at a concentration of 15 mg L⁻¹. In addition, the solution pH was adjusted to 2 by adding HCl to obtain the maximum MB adsorption on the catalyst surface,¹⁴ as shown in

the ESI.† The suspension was stirred in the dark for 60 min to establish the adsorption/desorption equilibrium, then the solution was irradiated under visible light. At appropriate time intervals, about 5 mL of suspension was sampled, where the solid phase was separated from the solution *via* centrifugation at 4000 rpm for 20 min. The concentration of each degraded solution was monitored on a PG Instruments Ltd T80-UV/vis spectrophotometer.

3. Results and discussion

Fig. 1 shows the XRD patterns of the pure BiFeO₃, pure ZnFe₂O₄ and the BiFeO₃-xZnFe₂O₄ composites. The indexed diffraction peaks of ZnFe₂O₄ are (220), (311), (400), (422), (511), (440) and (533) which match well with the cubic spinel structure having the $Fd\bar{3}m$ space group and are in good agreement with the standard JCPDS card no. 22-1012. Pure BiFeO₃ shows indexed diffraction peaks corresponding to a rhombohedral phase with the $R3c$ space group (JCPDS no. 86-1518), which indicates well crystallized BiFeO₃ nanoparticles were produced by the glyoxylate precursor method. However, some impurity Bi₂Fe₄O₉ phases (JCPDS card no. 42-0181) were also observed with BiFeO₃. The chemical synthesis of BiFeO₃ typically leads to the formation of impurities, may be due to its chemical kinetics.³¹ After compositing with 25 wt% ZnFe₂O₄, a weak diffraction peak at $2\theta = 35.32^\circ$ corresponding to the (311) reflection peak of ZnFe₂O₄ appeared. With an increase in the zinc ferrite content, the diffraction peaks of ZnFe₂O₄ became clearer and stronger, and the impurity peak disappeared. Furthermore, no impurity species were formed between BiFeO₃ and ZnFe₂O₄ during the calcination process, which indicates that ZnFe₂O₄ was successfully loaded on the BiFeO₃ particles without destroying its crystal structure. The amount of BiFeO₃ and ZnFe₂O₄ phases

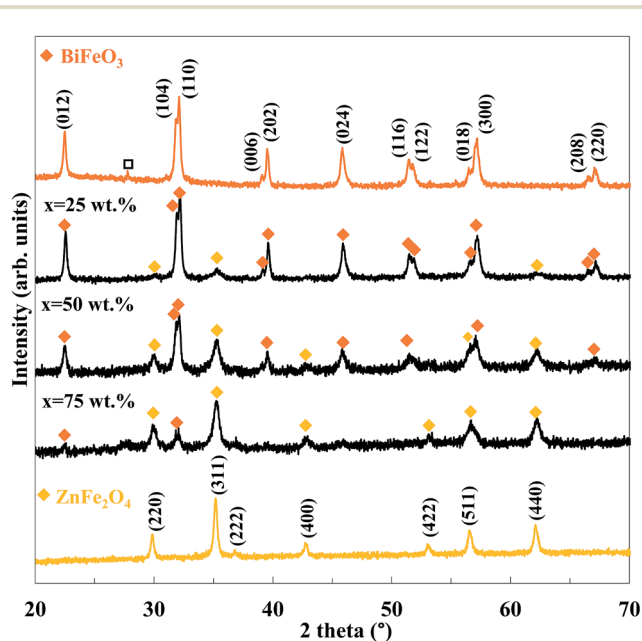


Fig. 1 XRD patterns of the BiFeO₃-xZnFe₂O₄ composites as a function of ZnFe₂O₄ content (x) (Bi₂Fe₄O₉).



in the composites was calculated by Rietveld refinement, which is in agreement with the nominal values, as typically shown in the ESI.†

The Raman spectra of pure BiFeO₃, pure ZnFe₂O₄ and BiFeO₃-*x*ZnFe₂O₄ composites are presented in Fig. 2. In the spectrum of pure BiFeO₃, the Raman active modes with A₁ and E symmetry can be summarized using the following irreducible representation $\Gamma = 4A_1 + 9E$.³² The two peaks at 173 and 220 cm⁻¹ are assigned as A₁ modes, and the peaks at 286, 361 and 481 cm⁻¹ correspond to the E modes. Pure ZnFe₂O₄ exhibited four peaks at 246, 327, 471 and 648 cm⁻¹, which are assigned as the T_{2g}(1), E_g, T_{2g}(2) and A_{1g} modes for a cubic spinel structure, respectively.³³ The A_{1g} mode of ZnFe₂O₄ appears after 25 wt% ZnFe₂O₄ was loaded, while the other modes were dominant at higher zinc ferrite contents. Moreover, the purity of the BiFeO₃-*x*ZnFe₂O₄ composites is confirmed by the absence of Raman modes of impurity phases.

The SEM images of pure BiFeO₃, BiFeO₃-25 wt% ZnFe₂O₄, BiFeO₃-75 wt% ZnFe₂O₄ and pure ZnFe₂O₄ powders are displayed in Fig. 3. The quasi-spherical particles of BiFeO₃ (210 nm) are larger than the ZnFe₂O₄ particles (80 nm). However, the BiFeO₃-25 wt% ZnFe₂O₄ composite is composed of plate-like particles. Furthermore, the average particle size decreases while the particle size distribution becomes rather uniform with an increase in ZnFe₂O₄ content.

The N₂ adsorption-desorption isotherms of the BiFeO₃-50 wt% ZnFe₂O₄ composite are shown in Fig. 4. Table 1 also presents the specific surface area (*S*_{BET}), equivalent particle size (*D*_{BET}) and pore volume. The particle agglomerations show a typical type II isotherm according to the International Union of Pure and Applied Chemistry (IUPAC) classification.³⁴ The surface area of pure BiFeO₃ is 30.56 m² g⁻¹ and 13.13 m² g⁻¹ for pure ZnFe₂O₄. The higher specific surface area of pure BiFeO₃ is attributed to more gaseous products being formed during its synthesis,³⁵ as confirmed by its higher pore volume

(0.089 cm³ g⁻¹). The BJH pore size distribution is also depicted in the inset of Fig. 4. The pore size distribution of the BiFeO₃-50 wt% ZnFe₂O₄ composite powder exhibits a mesopore spreading of about 3–4 nm.

Fig. 5 illustrates the magnetization curves of the BiFeO₃-*x*ZnFe₂O₄ composites as well as the pure BiFeO₃ and ZnFe₂O₄ powders. The pure BiFeO₃ nanoparticles exhibit a ferrimagnetic response with the magnetization of 0.28 emu g⁻¹ at 10 kOe. However, the magnetization increases with an increase in zinc ferrite content since pure ZnFe₂O₄ has a magnetization of 1.8 emu g⁻¹. Bulk BiFeO₃ is known to show a G-type antiferromagnetic ordering with a linear field-dependence of magnetization, while the BiFeO₃ nanoparticles exhibit weak ferrimagnetism due to the interruption of the long-range antiferromagnetic order at the particle surface.³⁶ The bulk ZnFe₂O₄ also has a normal spinel structure with antiferromagnetic behavior, while the ZnFe₂O₄ nanoparticles exhibit a partially inverse spinel structure with some magnetic moment at room temperature.³⁷ A high surface-to-volume ratio in nanoparticles leads to more uncompensated spins from the surface, inducing an enhancement in magnetization. The BiFeO₃-*x*ZnFe₂O₄ composites show higher saturation magnetization than pure bismuth ferrite as a result of the higher magnetization in the zinc ferrite phase. This ferrimagnetism behavior can be exploited for the magnetic recovery of the photocatalyst after degradation.

The optical properties of the BiFeO₃-*x*ZnFe₂O₄ composites, as well as the pure BiFeO₃ and ZnFe₂O₄ powders were investigated *via* UV-vis diffuse reflectance spectroscopy, which are presented in Fig. 6. The absorption spectra show that the samples absorb a considerable amount of visible light. The direct optical band gap, *E*_g, was determined using the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$, where, *hν* is the photon energy in eV, α is the absorption coefficient and *A* is a material constant,³⁸ as shown in the inset of Fig. 6. According to the Tauc plots, the band gaps for *x* = 0, 25, 50, 75 and 100 wt% were calculated to be 2.17, 2.03, 2.14, 2.15 and 2.22 eV, respectively. The absorption band of BiFeO₃ and ZnFe₂O₄ is attributed to the electronic transition from the valence band (O 2p orbital) to the conduction band (Fe 3d orbital) (O_{2p}²⁻ → Fe_{3d}³⁺).^{39,40} Clearly, the band gap of the BiFeO₃-*x*ZnFe₂O₄ photocatalysts gradually decreases with an increase in BiFeO₃. In other words, by introducing ZnFe₂O₄ into BiFeO₃, the photocatalyst could absorb more visible light for the production of electron-hole pairs, which are favorable for photocatalytic reactions.

Fig. 7a shows the UV-vis spectra of the MB solution after different irradiation times in the presence of the BiFeO₃-25 wt% ZnFe₂O₄ composite. The main absorption peaks of MB molecules at 664 nm almost completely disappeared after about 120 min, which suggests the excellent photocatalytic activity of the BiFeO₃-25 wt% ZnFe₂O₄ composite. The photodegradation efficiency of MB dye by pure BiFeO₃, pure ZnFe₂O₄ and BiFeO₃-*x*ZnFe₂O₄ composites as a function of irradiation time are summarized in Fig. 7b.

Methylene blue was hardly degraded (~3%) by pure ZnFe₂O₄ which exhibited very limited photolysis of MB under visible light irradiation. The low photocatalytic efficiency of pure

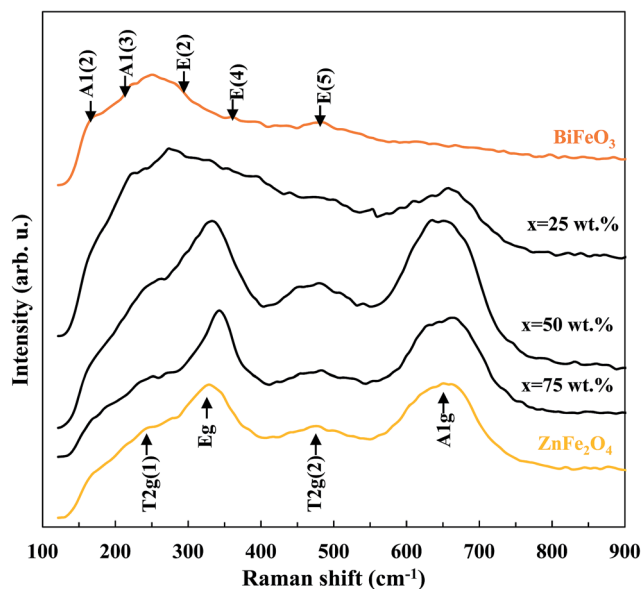


Fig. 2 Raman spectra of the BiFeO₃-*x*ZnFe₂O₄ composites.



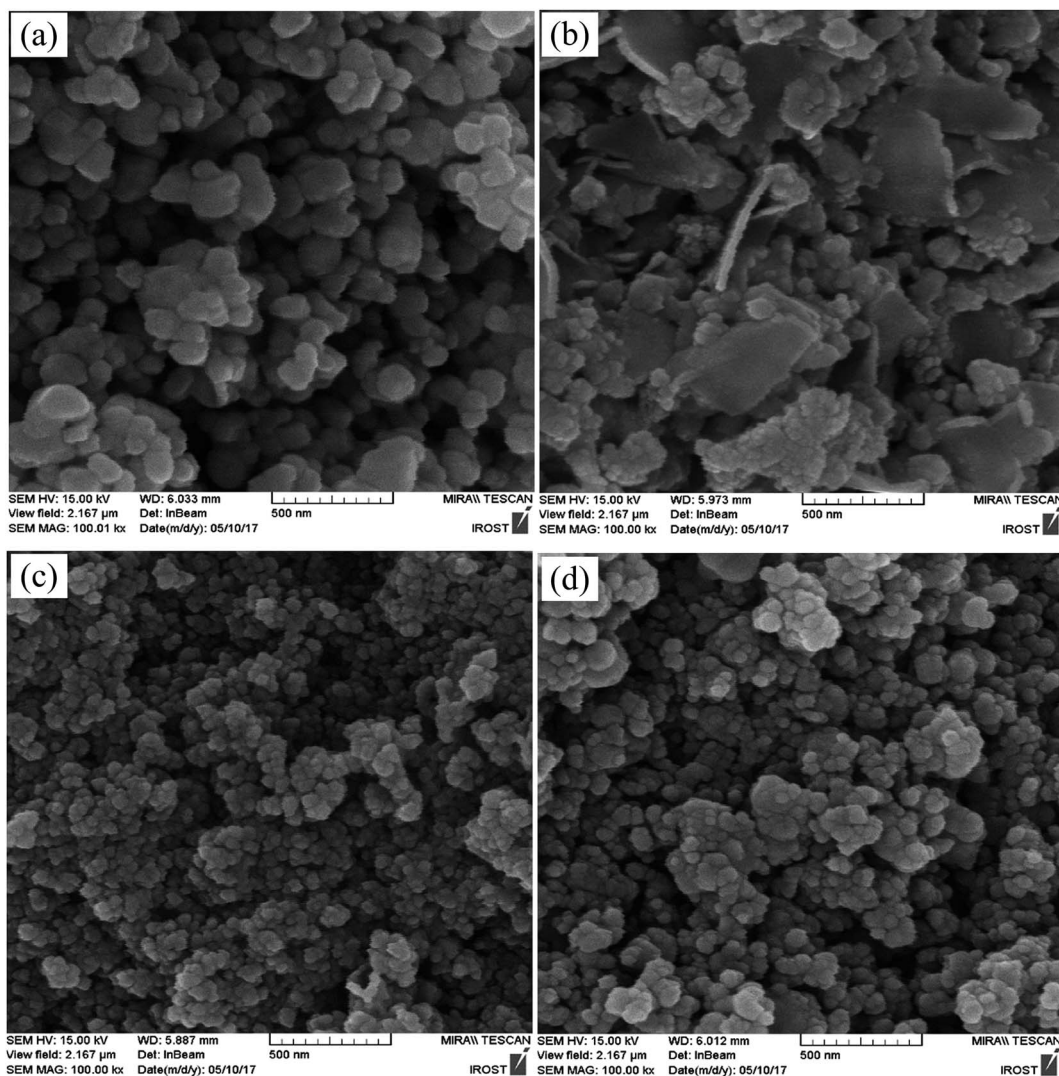


Fig. 3 SEM images of (a) pure BiFeO_3 , (b) BiFeO_3 -25 wt% ZnFe_2O_4 , (c) BiFeO_3 -75 wt% ZnFe_2O_4 , and (d) pure ZnFe_2O_4 powders.

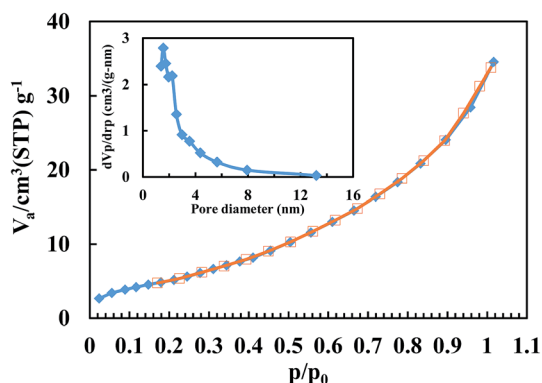


Fig. 4 Adsorption (filled symbol)–desorption (open symbol) isotherms of the BiFeO_3 -50 wt% ZnFe_2O_4 composite (the inset shows the pore size distribution).

ZnFe_2O_4 can be attributed to its low valence band potential and poor photoelectric conversion.^{7,41} However, pure BiFeO_3 can degrade 94.5% of MB after 2 hours of irradiation. The

Table 1 Dependence of specific surface area, S_{BET} , pore volume and equivalent particle size, D_{BET} , on ZnFe_2O_4 content (x)

x	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	D_{BET} (nm)
BiFeO_3	30.56	0.089	23.6
25 wt%	28.42	0.086	27.9
50 wt%	19.75	0.072	44.8
75 wt%	18.97	0.069	52.6
ZnFe_2O_4	13.13	0.053	87.1

maximum MB photodegradation of $\sim 97\%$ was observed for the BiFeO_3 -25 wt% ZnFe_2O_4 composite after 30 minutes of irradiation. The extraordinary photocatalytic efficiency of the BiFeO_3 -25 wt% ZnFe_2O_4 composite may be attributed to the formation of BiFeO_3 - ZnFe_2O_4 heterojunctions, which promote the separation of photogenerated electron–hole pairs, thus enhancing the photocatalytic activity. However, the number of effective heterojunctions and thus separation efficiency strongly depend



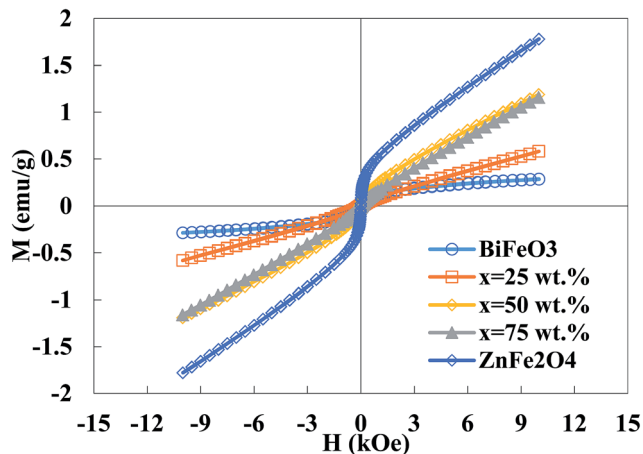


Fig. 5 Magnetization curves of the BiFeO_3 - $x\text{ZnFe}_2\text{O}_4$ composites.

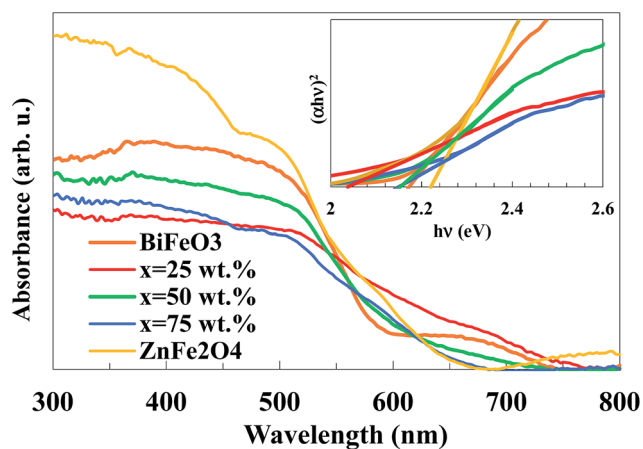


Fig. 6 UV-vis absorption spectra of the BiFeO_3 - $x\text{ZnFe}_2\text{O}_4$ composites (the inset shows the Tauc plots).

on the content of the two components in the composite.^{20–22,42} For the optimal content of 25 wt% ZnFe_2O_4 , the most appropriate $\text{BiFeO}_3/\text{ZnFe}_2\text{O}_4$ heterojunctions might be formed, which benefit the transfer and separation of photogenerated electrons and holes, as can be inferred from the PL spectra.

The suppression of charge recombination in BiFeO_3 by pairing with ZnFe_2O_4 can be confirmed by photoluminescence (PL) emission spectra, as presented in Fig. 8. As is known, the recombination of excited electrons and holes leads to PL emission, where a lower emission intensity indicates a decrease in recombination probability. Fig. 8 shows the PL emission spectra of the pure BiFeO_3 and BiFeO_3 -25 wt% ZnFe_2O_4 photocatalysts at an excitation wavelength of 210 nm. The irradiative recombination process of self-trapped excitations results in an emission band at about 423 nm for pure BiFeO_3 .⁴³ Clearly, the PL emission intensity decreases when zinc ferrite was added, which confirms that the coupling of BiFeO_3 with ZnFe_2O_4 results in an enhanced ability to capture photoinduced electrons in comparison with pure BiFeO_3 and pure ZnFe_2O_4 . The lower PL emission intensity of the BiFeO_3 -25 wt% ZnFe_2O_4

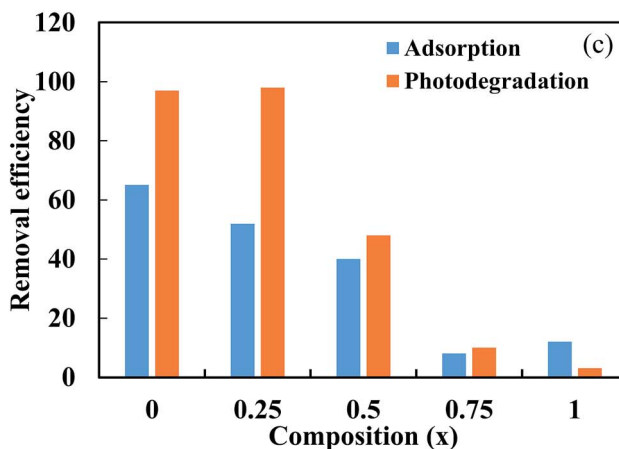
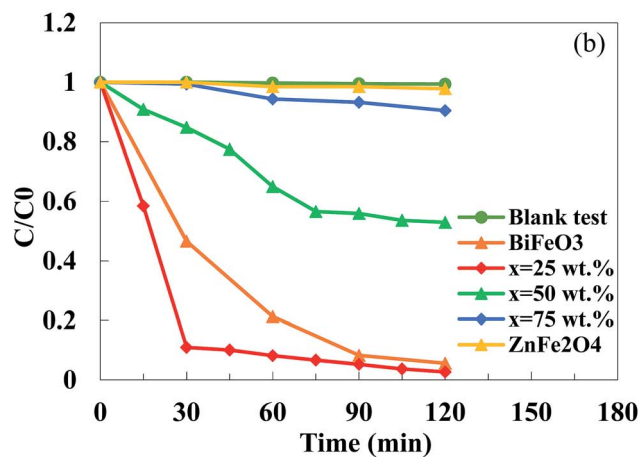
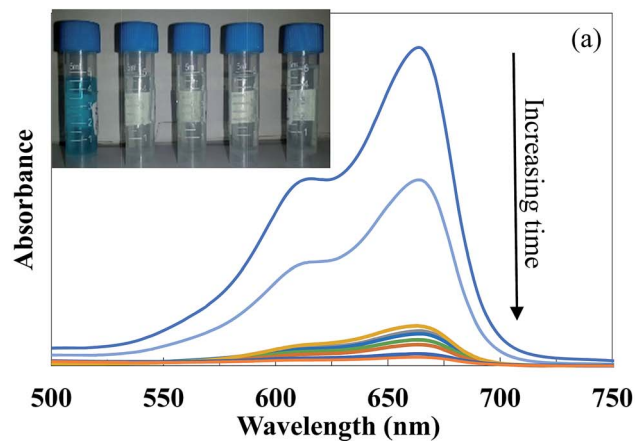


Fig. 7 (a) UV-vis spectra of MB solution in the presence of the BiFeO_3 -25 wt% ZnFe_2O_4 composite (the inset shows the photodegradation of MB), (b) C/C_0 versus irradiation time for the photodegradation of MB dye under visible light irradiation by the BiFeO_3 - $x\text{ZnFe}_2\text{O}_4$ nano-composites and (c) the removal efficiency of MB dye by adsorption and photodegradation.

photocatalyst benefits a delay in the recombination rate and, thus, higher photocatalytic activity.^{44–47} In addition to the lower recombination rate of electron–hole pairs in the BiFeO_3 -25 wt% ZnFe_2O_4 catalyst, its higher specific surface area can also adsorb more MB dye on the exterior of its particles, as shown in Fig. 7c, hence facilitating the photodegradation of MB dye.



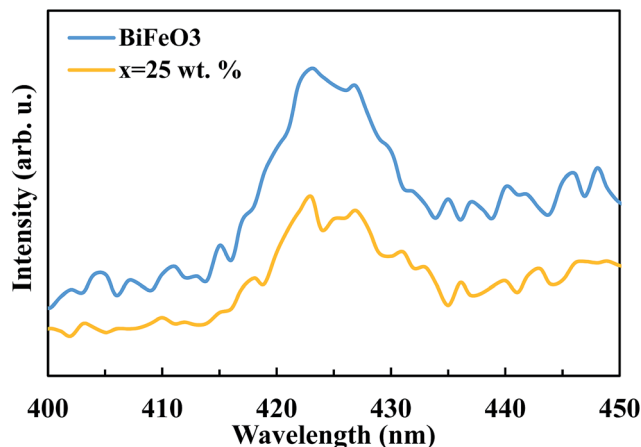


Fig. 8 Comparison of the PL spectra of pure BiFeO₃ and BiFeO₃-25 wt% ZnFe₂O₄ composite.

Based on the above structural characterizations and visible light photocatalytic tests, a possible mechanism for the photodegradation of MB by the BiFeO₃/ZnFe₂O₄ photocatalyst under visible light irradiation is proposed. Fig. 9 shows the band positions and transfer path of the photogenerated electron-hole pairs between BiFeO₃ and ZnFe₂O₄. The conduction (CB) and valence (VB) band positions of BiFeO₃ and ZnFe₂O₄ at the point of zero charge were obtained from previous reports.^{15,48} According to the general p-n heterojunction formation process,⁸ the entire energy band of BiFeO₃ increases while that of ZnFe₂O₄ decreases to achieve an equilibrium state of the Fermi energy level of BiFeO₃ and ZnFe₂O₄. In this case, the conduction band and valence band of ZnFe₂O₄ become higher than that of BiFeO₃.

Under visible light irradiation, a high energy photon excites an electron from the valence band (VB) to the conduction band (CB) of BiFeO₃ and ZnFe₂O₄. The photoinduced electrons in ZnFe₂O₄ can easily transfer to BiFeO₃, while the holes can

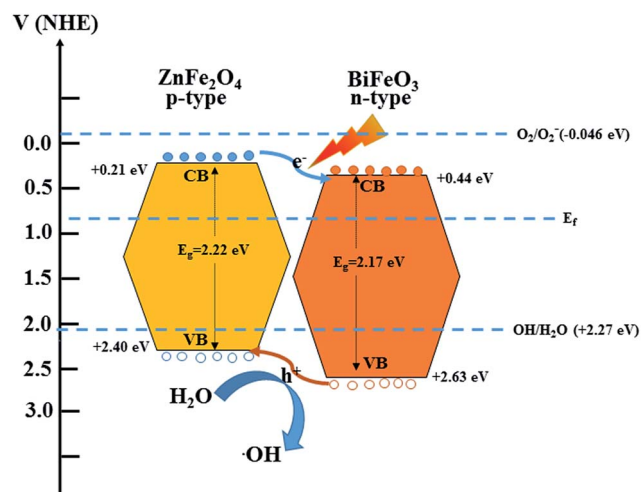


Fig. 9 Schematic for electron-hole transport at the interface of the BiFeO₃-ZnFe₂O₄ composite.

transfer to the VB of ZnFe₂O₄ from the VB of BiFeO₃ conveniently with the help of the internal electric field formed at the interface between BiFeO₃ and ZnFe₂O₄.²⁰ Therefore, the photogenerated electrons and holes are efficiently separated between BiFeO₃ and ZnFe₂O₄ reducing the electron-hole recombination in the composite photocatalyst, thus improving the photo-oxidation efficiency. The separated holes when moving to the surface of the BiFeO₃/ZnFe₂O₄ composite could react with H₂O to form hydroxyl radicals, ·OH, which are powerful oxidative species for the direct oxidation of MB, leading to its decomposition.^{49,50} However, the single electron reduction potential of O₂ ($E_0(\text{O}_2/\text{O}_2^-) = -0.046$ eV) is less negative than the CB potentials, which confirms that the photoinduced electrons on the surfaces of BiFeO₃/ZnFe₂O₄ could not reduce O₂ to yield O₂⁻ and could not take part in the photodegradation process.^{50,51} The suitable ZnFe₂O₄ content causes good dispersion in the catalyst, which benefits the formation of heterojunctions between the BiFeO₃ and ZnFe₂O₄ particles. Therefore, the high separation of charge carriers leads to the high photocatalytic activity of the BiFeO₃-25 wt% ZnFe₂O₄ photocatalyst.

4. Conclusions

A two-pot approach was used for the synthesis of BiFeO₃/ZnFe₂O₄ composites without any impurity species formed between BiFeO₃ and ZnFe₂O₄. The particle size decreased from 210 nm for pure BiFeO₃ to 80 nm for pure ZnFe₂O₄. The pure BiFeO₃ nanoparticles exhibited a higher specific surface area than the pure ZnFe₂O₄ nanoparticles, which may be due to the greater amount of released gaseous products. The magnetization of the BiFeO₃/ZnFe₂O₄ composites increased from 0.28 to 1.8 emu g⁻¹ with an increase in the ZnFe₂O₄ content. The optical band gaps of composites initially decreased from 2.17 to 2.03 eV and then increased to 2.22 eV as a function of the amount of zinc ferrite. The maximum efficiency (~97%) for the photodegradation of methylene blue under visible light was exhibited for BiFeO₃-25 wt% ZnFe₂O₄ after 30 minutes irradiation due to the synergic effect between BiFeO₃ and ZnFe₂O₄.

Conflicts of interest

There are no conflicts to declare.

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