


 Cite this: *RSC Adv.*, 2024, 14, 26066

Addition of silver nanoparticles to the zinc ferrite/polyaniline composition for boosting its visible photocatalytic degradation

 Safanah Sahib Jaafar,^a Rana Ismael Faeq,^a Amel Muhson Najji,^b Olfat A. Nief^a and Mustafa K. A. Mohammed *^c

Enhancing the photocatalytic activity of ZnFe₂O₄ with a good energy band gap to degrade industrial waste under sunlight illumination can help to develop green environments. Here, to improve the photocatalytic efficiency of ZnFe₂O₄ ferrites, they were merged with polyaniline (PAni) and silver (Ag) nanoparticles to synthesize Ag@ZnFe₂O₄-PAni plasmonic nanostructures. The as-synthesized nanostructures were characterized using a series of advanced characterization techniques to confirm successful formation and investigate photocatalytic improvement origins. It was found that incorporating Ag NPs along with the PAni to ZnFe₂O₄ increases its absorption power and red-shifts its energy band gap, which increases the electron-hole production rate by exposure to light in ZnFe₂O₄. Contribution of the surface plasmon resonance effect of Ag NPs and conjugated double bonds of PAni to charge transfer mechanisms in Ag@ZnFe₂O₄-PAni material increased charge separation during photocatalytic process, boosting the photodegradation performance of ZnFe₂O₄.

 Received 14th July 2024
 Accepted 14th August 2024

DOI: 10.1039/d4ra05096g

rsc.li/rsc-advances

1 Introduction

With the increase in world population and the industrial development to meet human needs for food, clothing, electrical appliances, *etc.*, the increase in environmental pollution has become a critical challenge.^{1,2} This industrial waste affects the water quality of rivers and underground water, and subsequently negatively impact human health and the ecosystem.^{3,4} Heavy metal ions, phenols, dyes, polychlorinated biphenyls (PCBs), pharmaceutical drugs, haloacetic acids (HAAs), pesticides, disinfection byproducts (DBPs), and other synthetic chemicals are the main sources of water pollution.⁵⁻⁸ For years, the Environmental Protection Agency (EPA) and World Health Organization (WHO) have recommended that the world's industries do not discharge contaminated water into their surrounding environments. Various methodologies have been suggested to clean the water before discharging, including, precipitation, ozonation, adsorption, membrane separation, biodegradation, sonodegradation, solvent extraction, and ion exchange.⁹⁻¹³ These approaches have serious drawbacks, including toxic products, high operating costs, and low elimination rates. In contrast, advanced oxidation photocatalysis

offers an ultimate deterioration, cheap, and eco-friendly method to treat wastewater with considerable recyclability.^{14,15} The photocatalysis process is used to disinfect the wastewater and eliminate contaminants from water and air. The photocatalyst material promotes the elimination reaction rate of targeted waste from water with the assistance of a light illumination source. During the process, the irradiated light reacts with the photocatalyst material to generate electron-hole pairs. Next, these photo-generated electrons participate in reduction reactions to start the oxidation of holes.¹⁶⁻¹⁸

In recent years, nano-sized materials were introduced as a primary area of research to find advanced technologies for meeting the world's demands. Nano-sized materials have a considerable surface area, which increases their chemical reaction with other materials. In addition, tunable electrical conductivity and optical properties of nano-sized materials along with their mechanical strength, compared to their bulk counterparts, makes them interesting materials to design different advanced technologies. Nanotechnology suggests cost-effective and efficient materials to use in the remediation of dirty water.¹⁹⁻²³ As mentioned, industrial development and its conflict of interest with the green environment have led to an excessive increase in the pollution of natural water. Developing advanced nanomaterial photocatalysts has emerged as a promising technology to address this concern.²⁴ Spinel ferrites have attracted environmental research due to their unique features, such as chemical stability, high adsorption capacities, cost-effective preparations, and superparamagnetic capabilities, to employ them as photocatalyst material for water treatment to

^aDepartment of Chemistry, College of Science, Mustansiriyah University, P. O. BOX 14132, Baghdad, Iraq

^bDepartment of Optics Techniques, Dijlah University College, Al-Masafi Street, Baghdad, 00964, Iraq

^cCollege of Remote Sensing and Geophysics, Al-Karkh University of Science, Baghdad 10011, Iraq. E-mail: mustafa_kareem97@yahoo.com


remove pollutants *via* photodegradation mechanism.^{25–29} Zinc ferrite (ZnFe_2O_4), due to their small band gap, is more favorable for visible photocatalytic degradation of water pollution. However, the net zinc ferrites do not have strong photocatalytic efficiency due to weak charge separation.^{30–32}

Yu *et al.*³¹ to enhance catalytic activity of zinc ferrites substituted copper metal to ZnFe_2O_4 structure. They deduced that the increased catalytic activity of zinc-based ferrite ascribes to the dual active sites of Fe and Cu and oxygen vacancies after Cu substitution. Janani *et al.*³² decorated ZnFe_2O_4 with CdO material to boost the photocatalytic efficiency of ZnFe_2O_4 . They found that the CdO/ ZnFe_2O_4 with a high surface area offers more active sites to induce the photocatalysis performance of the system. In addition, they concluded that coupling of ZnFe_2O_4 and CdO improved the lifetime of charge carriers and promoted the reaction of photo-generated electrons and holes with dye molecules. Akshhaya *et al.*³³ decorated ZnFe_2O_4 with SnS_2 material to accelerate visible light photocatalysis of methylene blue. They observed that the formed interfacial contact in the $\text{ZnFe}_2\text{O}_4/\text{SnS}_2$ system suppresses charge recombination and retains better charge separation. These improvements with high visible-light absorbing ability offer an n- SnS_2/p - ZnFe_2O_4 hybrid system with improved photocatalytic activity. Kaushal *et al.*³⁴ developed a ZnFe_2O_4 @nitrogen-doped carbon dots hybrid material to decompose ciprofloxacin and norfloxacin materials under visible light irradiance. They observed that nitrogen-doped carbon dots hybridized with zinc ferrites, which enhanced photocurrent density and surface area. The ZnFe_2O_4 @nitrogen-doped carbon dots exhibited efficient transfer of charge carriers and can be used for environmental remediation through the photocatalytic degradation process. Modification of ZnFe_2O_4 with conjugated polymers such as polyaniline (PAni) with considerable carriers mobility and good optical properties can induce its photocatalytic activity.^{35–37} Photosensitizer behavior of PAni under visible light illumination establishes the electron donor phenomenon in it, resulting in enhanced catalytic performance in PAni-contained hybrid heterostructures.^{38,39} Developing plasmonic nanostructures based on ZnFe_2O_4 also can be used to increase the ZnFe_2O_4 catalyst activity. The surface plasmon resonance (SPR) effect observed in noble metals usually increases the light-harvesting ability of heterojunctions, resulting in considerable enhancement in the catalytic and photocatalytic activity.^{40–42}

The objective of the current study is to develop a ternary plasmonic nanostructures system based on ZnFe_2O_4 through its combination with PAni and Ag NPs. The $\text{Ag}@\text{ZnFe}_2\text{O}_4$ -PAni hybrid system was employed for the visible light photocatalytic application and recorded promising results. Results showed that the $\text{Ag}@\text{ZnFe}_2\text{O}_4$ -PAni nanocomposites have efficient charge transfer, higher surface area, and higher light-harvesting ability due to synergistic effects of Ag NPs and PAni, resulting in higher photodegradation behavior than the ZnFe_2O_4 and ZnFe_2O_4 -PAni materials. Moreover, the effect of the pH value of aqueous mediums, the initial concentration of dye, and the amount of photocatalyst were examined on the photocatalytic performance of the $\text{Ag}@\text{ZnFe}_2\text{O}_4$ -PAni.

2 Experimental

2.1 Materials

All solvents and materials that used in this study were purchased from Merck and used as received without any more purification steps.

2.2 Synthesis of zinc ferrite material

To synthesize ZnFe_2O_4 , 1.8 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 2 mmol of $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$ were dissolved in 10 mL of ethanol. In another vial, 10 mL of 2 mmol tetramethylammonium hydroxide pentahydrate (TMAH) solution in ethanol was prepared. Then, two solutions were added together and sonicated to obtain a dark red color solution. The obtained solution was exposed to microwave radiation at 180 °C for 45 min. The product was centrifuged and washed with ethanol. Finally, the brown precipitates were dried in a vacuum oven at 60 °C overnight, followed by calcination at 400 °C for 2 h to produce ZnFe_2O_4 NPs.

2.3 Synthesis of zinc ferrite-polyaniline material

To synthesize ZnFe_2O_4 -PAni nanocomposite, an *in situ* polymerization technique was employed. 4 g of aniline material was dissolved into 200 mL of 1 M HCl solution by stirring for 2 h at a temperature of 50 °C. Then, 1.2 g ZnFe_2O_4 NPs were added to the aniline solution, followed by sonication for about 30 min at room temperature to homogenize the scattered ZnFe_2O_4 NPs. In another vial, 100 mL of 1 M HCl was carefully mixed with ammonium persulfate (APS) to obtain a 0.2 M solution. Then, the precooled APS solution was dropped wise to the aniline- ZnFe_2O_4 solution, followed by stirring at a temperature of 2 °C for 12 h to complete polymerization. The obtained solution was kept in the freezer overnight. Finally, the solution was filtered and washed with deionized water and methanol, followed by drying in a vacuum oven for 24 h at a temperature of 60 °C.

2.4 Synthesis of zinc ferrite-polyaniline decorated with silver nanoparticles

The $\text{Ag}@\text{ZnFe}_2\text{O}_4$ -PAni plasmonic nanocomposites were synthesized through Ag^+ ions photoreduction in the ZnFe_2O_4 -PAni aqueous solution (see Fig. 1). 400 mg of ZnFe_2O_4 -PAni nanostructures were sonicated in 100 mL deionized water for 30 min to prepare a homogeneous suspension. Then, 40 mL of 2.5, 5, and 10 mM of AgNO_3 solution in deionized water were quickly added to ZnFe_2O_4 -PAni aqueous solution in dark conditions. The suspensions were stirred for 2 h at room temperature in dark conditions and then exposed to natural sunlight for 90 min. The black precipitates were centrifuged and washed with deionized water and methanol repeatedly to remove impurities. The washed products were dried overnight in an oven at 60 °C for 24 h. The obtained powders were marked as AZP1, AZP2, and AZP3, referring to samples prepared using 2.5, 5, and 10 mM AgNO_3 solutions, respectively.



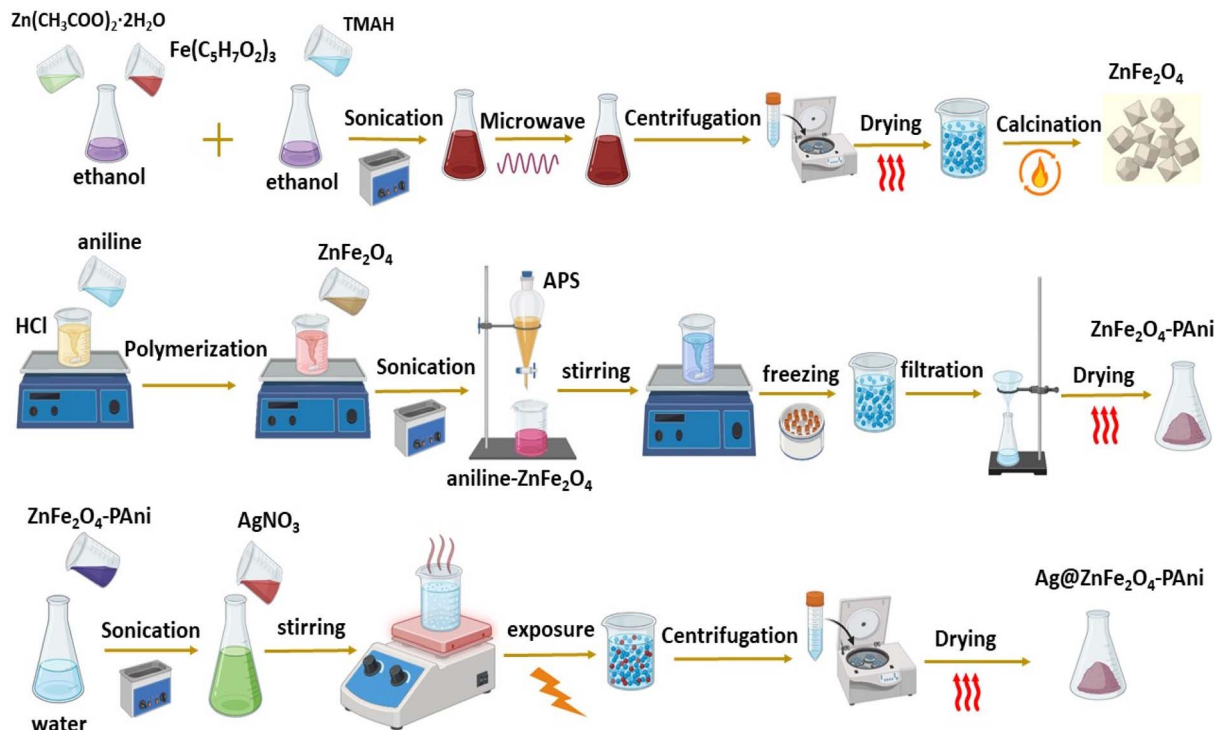


Fig. 1 Schematic diagram for preparation of Ag@ZnFe₂O₄-PANI nanocomposite.

2.5 Photocatalytic degradation investigation

The photocatalytic performance of the synthesized nanostructures for methylene blue (MB) or rhodamine B (RhB) dyes photodegradation was investigated by recording their UV-Vis spectra over reaction time under sunlight irradiance. For this test, 25 mg of MB or RhB dyes were dissolved into distilled water to obtain 25 ppm solutions. Then, 10 mg of photocatalyst materials (ZnFe₂O₄, ZnFe₂O₄-PANI, AZP1, AZP2, and AZP3) were dispersed into 100 mL dye solutions. The dye/photocatalyst material solutions were stirred under dark conditions for 30 min to establish an adsorption/desorption equilibrium between dye molecules and photocatalyst materials. Afterward, solutions were exposed to simulated sunlight illumination, and recorded their absorbance spectra. The same procedures were conducted to study the effects of pH and catalyst material concentration on the photodegradation performance of AZP2 material.

2.6 Characterizations

Crystalline structure of ZnFe₂O₄, ZnFe₂O₄-PANI, AZP1, AZP2, and AZP3 materials were measured by recording X-ray Diffraction (XRD) using a Rigaku Ultima IV XRD instrument. The morphology of the synthesized nanostructures were monitored using CM120 TEM and TESCAN Mira III FESEM. The FTIR spectra of materials were investigated using NICOLET-IS FTIR instrument. UV-vis spectra of samples were recorded using PerkinElmer Lambda Spectrometer. RAMAN spectra of materials were collected using a WiTec alpha 300 Raman spectrometer. The EIS response of samples were measured using

Gamry Interface 1000 Potentiostat. PL spectra of material was collected using FLS 1000, Edinburgh spectrometer. Specific surface area of samples were measured by recording their Bet response using a BELSORP Mini II device. The transient photocurrent response of samples were measured using a PGSTAT302 N electrochemical workstation with a 500 W xenon lamp as the light source.

3 Results and discussion

Fig. 2 shows XRD patterns of different samples to confirm their successful synthesis. As shown in Fig. 2a, there are six peaks

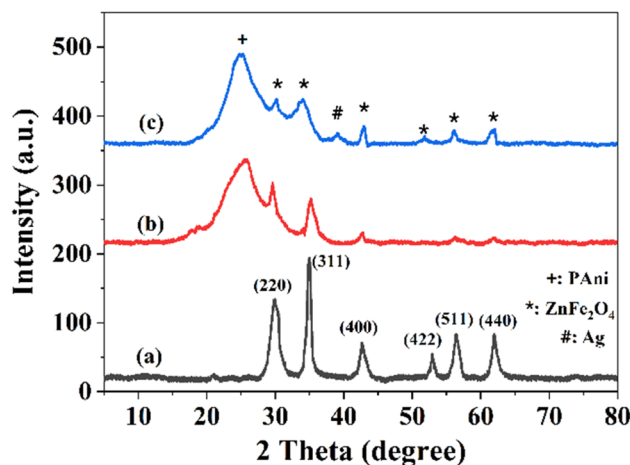


Fig. 2 XRD spectra of (a) ZnFe₂O₄, (b) ZnFe₂O₄-PANI, and (c) AZP2 nanostructures.



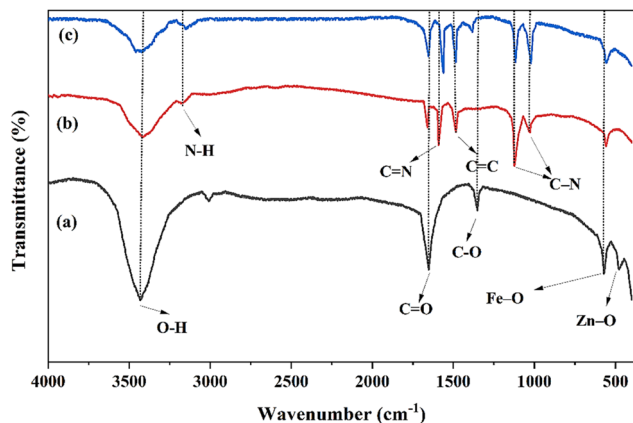


Fig. 3 FTIR spectra of (a) ZnFe_2O_4 , (b) ZnFe_2O_4 -PAni, and (c) AZP2 nanostructures.

positioned at 29.90° , 35° , 42.6° , 52.9° , 56.4° , and 62° , which are assigned to the (220), (311), (400), (422), (511), and (440) planes, respectively. These peaks align with the JCPDS file No. 00-022-1, confirming the formation of ZnFe_2O_4 NPs.⁴³ In the XRD pattern of ZnFe_2O_4 -PAni (Fig. 2b), a broad peak at 25.7° is observed, attributing to the amorphous nature of PAni with the crystalline plane of (200). Besides, six peaks, referring to (220), (311), (400), (422), (511), and (440) planes of ZnFe_2O_4 , are observed in the XRD pattern and prove the formation of ZnFe_2O_4 -PAni hybrid

structure. Fig. 2c shows XRD pattern of AZP2 material. In addition to the above-mentioned ZnFe_2O_4 and PAni phases, another peak is observed at 39.2° assigned to (111) Ag plane. It should be noted that the XRD peak of all the ZnFe_2O_4 NPs have minor shifts in AZP2, due to possible reaction of PAni and Ag with ZnFe_2O_4 material. These findings corroborate ternary $\text{Ag}@\text{ZnFe}_2\text{O}_4$ -PAni plasmonic nanocomposites formation.

The FTIR spectra of ZnFe_2O_4 , ZnFe_2O_4 -PAni, AZP2 nanostructures are depicted in Fig. 3. The ZnFe_2O_4 spectrum encompasses five major peaks at 478.3 and 571.7 cm^{-1} attributed to vibrations of Fe-O and Zn-O bonds at octahedral and tetrahedral sites, 1351.5 cm^{-1} attributed to C-O stretching from residual synthesis precursors, and 1649.5 and 3430.9 cm^{-1} attributed to the bending and stretching vibrations of adsorbed water. In FTIR spectrum of ZnFe_2O_4 -PAni (Fig. 2b), the characteristic peak of Fe-O in vanished, which can be caused by covering these bonds with the PAni molecules. In addition, five peaks at 1029.8 cm^{-1} assigned to secondary amine C-N stretching vibration, 1123.9 cm^{-1} assigned to vibration frequency of nitrogen quinone, 1484.2 cm^{-1} assigned to vibration for C=C bonds, 1593.1 cm^{-1} assigned to stretching mode of vibration for the C=N, and 3177.3 cm^{-1} assigned to the N-H stretching vibration. The AZP2 spectrum encompasses all peaks of ZnFe_2O_4 -PAni with no more peaks. Notably, the nitrogen bonds shifted from 1129.7 cm^{-1} to 1021.8 cm^{-1} and N-H bonds shifted from 3177.3 cm^{-1} to 3146.7 cm^{-1} , indicating successful incorporation of Ag NPs to ZnFe_2O_4 -PAni nanostructures.

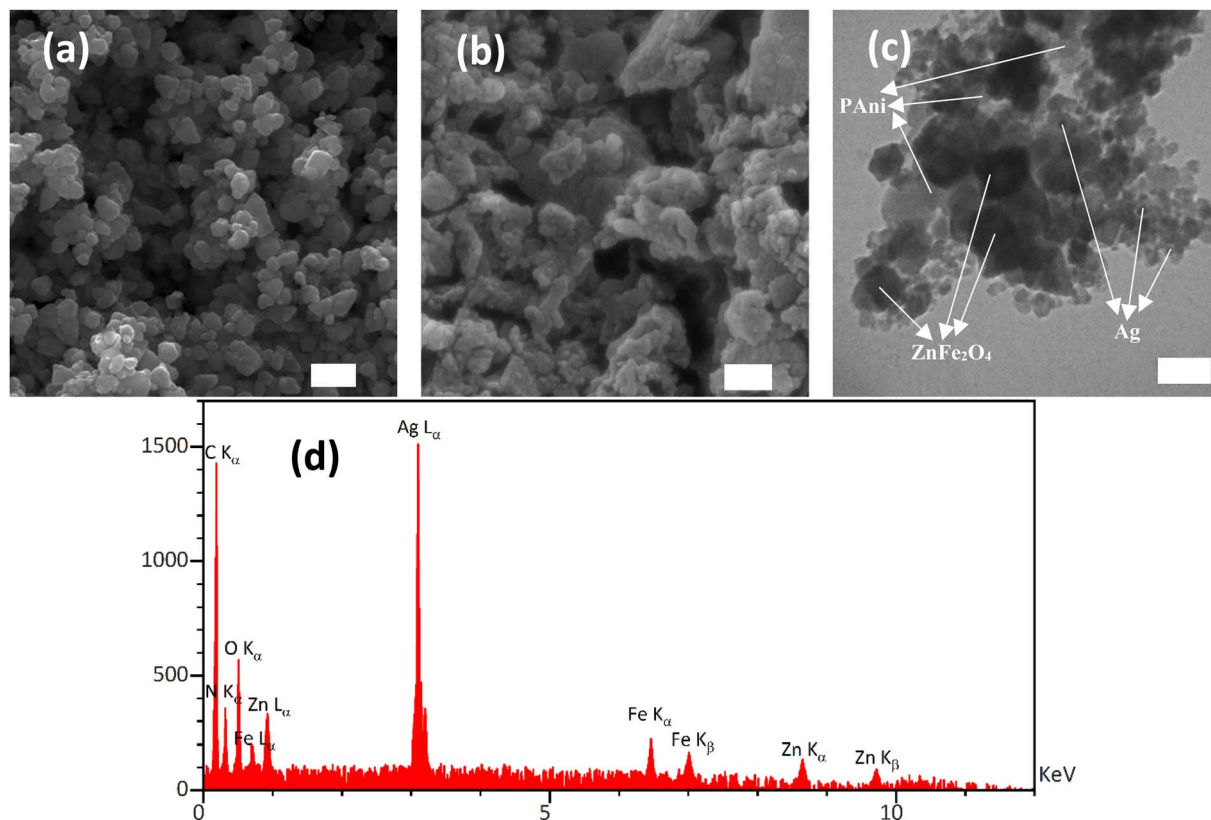


Fig. 4 FESEM image of (a) ZnFe_2O_4 and (b) AZP2. TEM image of (c) AZP2. (d) EDS elements mapping images of AZP2 composite. Scale bar of FESEM and TEM images are 200 nm and 80 nm, respectively.



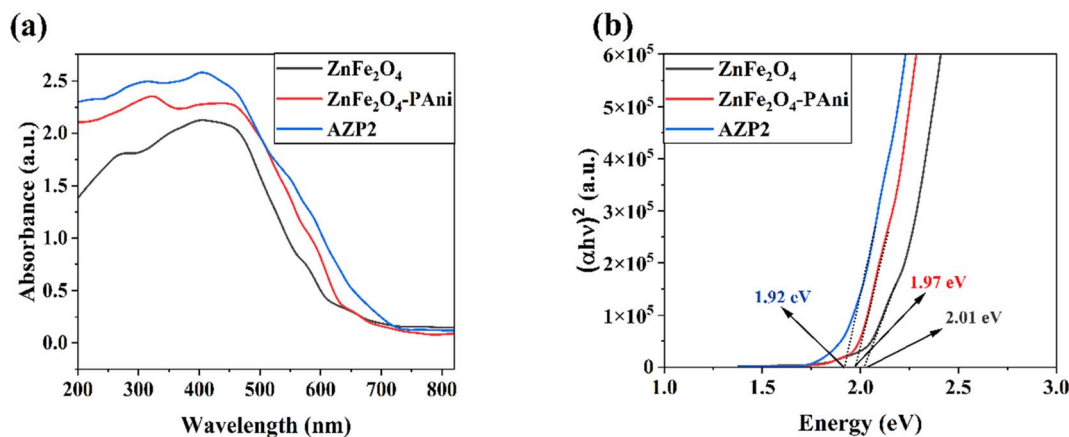


Fig. 5 (a) Absorbance spectra and (b) corresponding Tauc plots of ZnFe_2O_4 , $\text{ZnFe}_2\text{O}_4\text{-PANI}$, and AZP2 nanostructures.

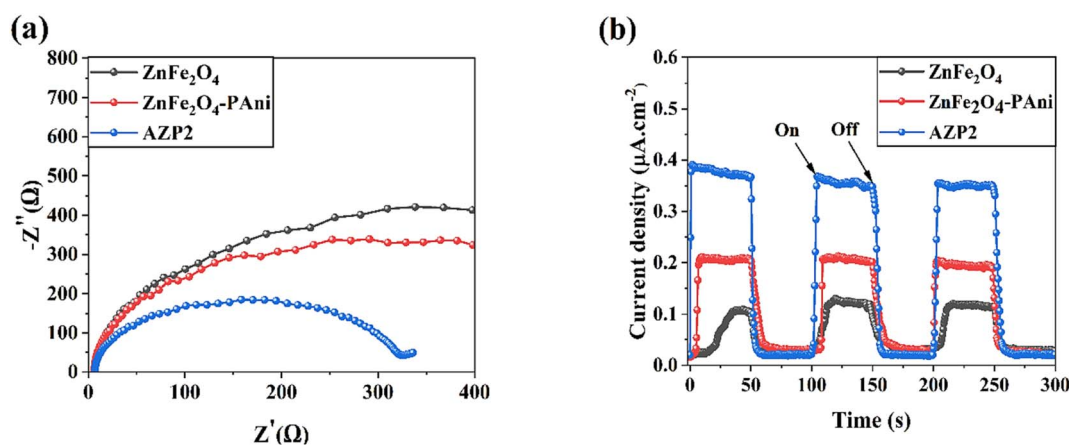


Fig. 6 (a) EIS spectra and (b) transient photocurrent response of ZnFe_2O_4 , $\text{ZnFe}_2\text{O}_4\text{-PANI}$, and AZP2 nanostructures.

The FESEM images of samples were taken to investigate the surface morphology of ZnFe_2O_4 and AZP2 photocatalysts (Fig. 4a and b). The nano-sized ZnFe_2O_4 particles were aggregated due to the magnetic attraction forces among ZnFe_2O_4 (Fig. 4a). In Fig. 4b, it is evident that particles are highly agglomerated, which is possibly due to the incorporation of Ag NPs. The successful incorporation of Ag NPs into the $\text{ZnFe}_2\text{O}_4\text{-PANI}$ nanostructures was evaluated by TEM (Fig. 3c). As can be seen, ZnFe_2O_4 NPs were capped with PANi molecules. Small Ag NPs attached on the ZnFe_2O_4 or PANi surfaces. Fig. 4d shows the EDS spectrum of the $\text{Ag@ZnFe}_2\text{O}_4\text{-PANI}$ nanostructure. As seen, six elements of C, N, O, Fe, Zn, and Ag were observed in the sample, consistent with existing elements in the $\text{Ag@ZnFe}_2\text{O}_4\text{-PANI}$ composite. It proves successful synthesis of the $\text{Ag@ZnFe}_2\text{O}_4\text{-PANI}$. Fig. 5a shows UV-Vis spectra of as-prepared photocatalyst materials. As can be seen, by incorporating Ag NPs into $\text{ZnFe}_2\text{O}_4\text{-PANI}$ nanostructure, its light-harvesting behavior is increased. This phenomenon increases the potential of ZnFe_2O_4 to absorb exposed light and generate electron-hole charges. Fig. 5b depicts the corresponding Tauc plot of samples to investigate their optical bandgap energy. The optical bandgap for ZnFe_2O_4 is 2.01 eV, aligning with the reported value

in literature.⁴⁴ Through the reaction of ZnFe_2O_4 with PANi materials, the optical bandgap is red-shifted to 1.97 eV and by the incorporation of Ag NPs to $\text{ZnFe}_2\text{O}_4\text{-PANI}$, it more reduced to 1.92 eV. It reveals that forming $\text{Ag@ZnFe}_2\text{O}_4\text{-PANI}$ nanostructures can minimize the optical band gap of net ZnFe_2O_4 and increase light utilization, improving the photodegradation performance of ZnFe_2O_4 under visible light illumination.

Nyquist plots of samples using EIS method were obtained under light illumination to investigate the interfacial charge transfer resistance (Fig. 6a). By fitting the EIS spectra with the equivalent electrical circuit, parameters including series resistance (R_s) and charge transport resistance (R_{Ch}) were obtained. The EIS arc radius of AZP2 on the Nyquist plot is smaller than that of ZnFe_2O_4 and $\text{ZnFe}_2\text{O}_4\text{-PANI}$, which implies the AZP2 nanostructures have the lowest R_{Ch} value (87.8 Ω). It indicates a fast interfacial charge carrier transfer with high photo-generated carriers separation efficiency, which both are responsible for the enhanced photocatalytic activity of ZnFe_2O_4 . It is due to the contribution of conjugated double bonds along the PANi structure and SPR effects of Ag NPs for the charge transfer mechanisms in AZP2 material. To get deeper insight on the photoelectrochemical properties of ZnFe_2O_4 NPs before and



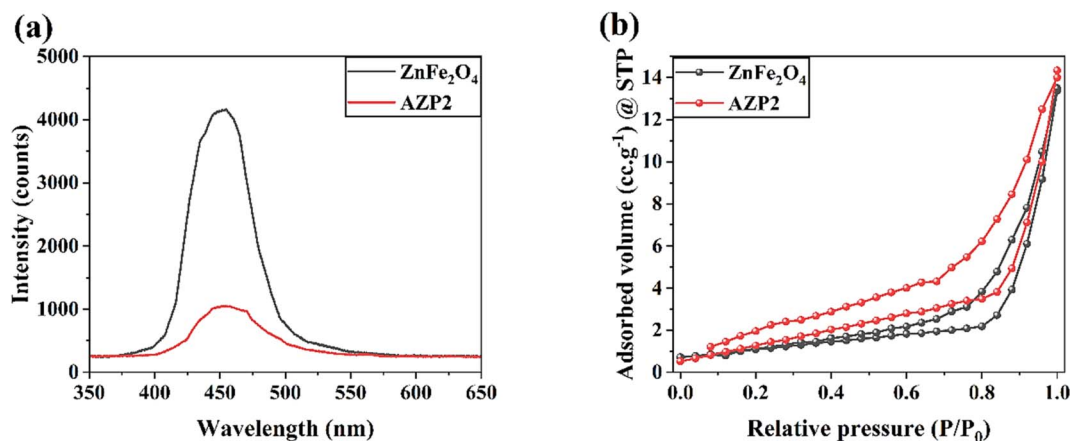


Fig. 7 (a) PL spectra and (b) BET curves of ZnFe₂O₄ and AZP2 nanostructures.

after modifications with PANi and Ag NPs, transient photocurrent response of ZnFe₂O₄ and ZnFe₂O₄-PANi, and AZP2 materials were investigated (Fig. 6b). As observed, the ZnFe₂O₄ sample implies a delayed photocurrent response upon the light is turned on and off. In contrast, the ZnFe₂O₄-PANi and AZP2 materials have rapid photocurrent responses. Moreover, results shows that the photocurrent of the ZnFe₂O₄-PANi electrode (0.213 mA cm⁻²) is 67.7% higher than that of ZnFe₂O₄ (0.126 mA cm⁻²), indicating the improved photoinduced electron-

hole pairs separation efficiency in ZnFe₂O₄-PANi due to unique interfacial charge transfer of heterojunction. AZP2 shows the highest photocurrent density (0.358 mA cm⁻²), indicating that the charge carrier separation in modified nanostructure of Ag@ZnFe₂O₄-PANi is further improved.

Fig. 7a shows PL spectra of ZnFe₂O₄ and AZP2 samples. The emission peak observed for both samples observed at 451 nm and indicates to the charge recombination.⁴⁵ As seen, the AZP2 has a weakened PL intensity than the pure ZnFe₂O₄, suggesting

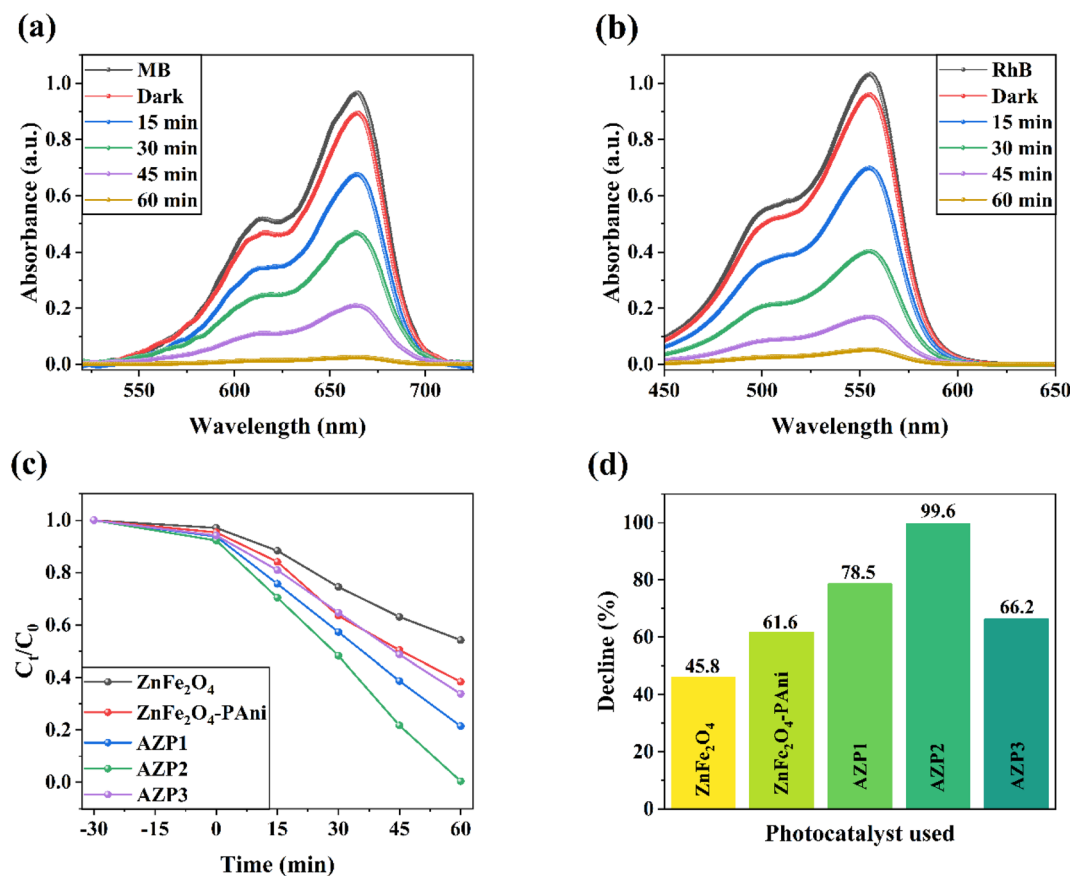


Fig. 8 Photocatalytic activity of AZP2 for (a) MB and (b) RhB dyes. (c) Kinetic plot versus illumination time for MB of ZnFe₂O₄, ZnFe₂O₄-PANi, AZP1, AZP2, and AZP3 nanostructures. (d) Comparison of MB degradation over different photocatalyst.



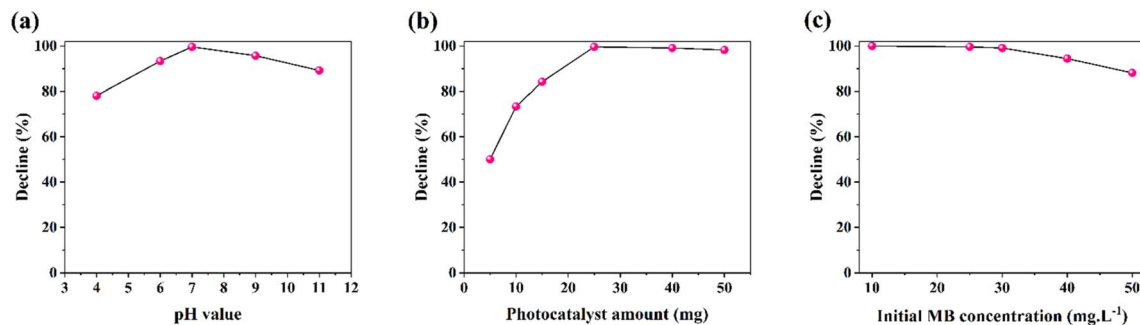


Fig. 9 (a) Effect of pH solution, (b) effect of photocatalyst amount and (c) effect of initial MB concentration on the photodegradation performance for AZP2.

reduced electron hole pair recombination rate in the AZP2 matrix.^{46,47} It supports the EIS and transient photocurrent findings. The specific surface area of synthesized ZnFe_2O_4 and AZP2 nanostructures are measured using N_2 adsorption-desorption isotherm BET studies and depicted in Fig. 7b. The AZP2 material has a specific surface area of $12.34 \text{ m}^2 \text{ g}^{-1}$, higher than the $7.41 \text{ m}^2 \text{ g}^{-1}$ obtained for pure ZnFe_2O_4 . Boosted surface area is an important factor in increasing the photocatalytic activity of nanomaterials. In other words, the boosted surface area in nanomaterials increases the adsorption capacity for the pollutants on the material surface and active photocatalytic sites number, enhancing pollutant decomposition.^{48,49} The photodegradation of MB and RhB dyes in aqueous medium was performed under simulated sunlight illumination for the AZP2 sample as the best photocatalyst was measured and depicted in Fig. 8a and b, respectively. The AZP2 plasmonic nanocomposites degraded 99.6% and 94.7% of MB and RhB molecules after exposure to light illumination for 60 min, respectively. Fig. 8c shows the degradation kinetics (C_t/C_0) for different photocatalysts to decompose MB dye during 60 min illumination. As shown, by increasing amounts of Ag NPs in $\text{Ag}@\text{ZnFe}_2\text{O}_4\text{-PANI}$ structure, its photocatalyst activity is reduced; indicating optimum amounts of AgNO_3 solution during synthesis process is 5 mM. As represented in Fig. 8d, the photocatalytic activity of photocatalysts are follows the trend of $\text{AZP2} > \text{AZP1} > \text{AZP3} > \text{ZnFe}_2\text{O}_4\text{-PANI} > \text{ZnFe}_2\text{O}_4$. It indicates that the employed method in here to advance photocatalytic performance of ZnFe_2O_4 has been very effective.

The solution pH value plays an important role in the photocatalytic-based reactions. The pH adjusting alters the interaction between the photocatalyst and dye molecules. Here, the photocatalytic activity of AZP2 nanostructures enhances from 78.1% to 99.6% as the pH value increases from 4 to 7 (Fig. 9a). By increasing the pH value to non-acidic conditions, the photocatalytic efficiency reduces to 89.2 (pH 11). Under acidic conditions (pH < 7), both $\text{Ag}@\text{ZnFe}_2\text{O}_4\text{-PANI}$ and MB are positively charged, which results in a repulsive interaction in the solution and reduces photocatalytic activity. In neutral conditions, appropriate interactions between positively charged photocatalysts and MB enhance the photocatalytic activity. Under alkaline conditions, a slight reduction in the photocatalytic efficiency is observed, which is due to the interactions

between anionic MB negatively charged photocatalysts. Next, effect of the initial AZP2 amount on the photocatalytic activity was investigated (Fig. 9b). For this aim, 5, 10, 15, 25, 40, and 50 mg of AZP2 nanostructures were dispersed in 100 mL of 25 ppm MB aqueous solution and their photocatalytic activities over 60 min light illumination were monitored. By enhancing the AZP2 amount, the MB photodegradation efficiency increased. The MB photodegradation efficiency started declining by raising the AZP2 amount to >40 mg, possibly due to the photocatalysts aggregation or more light scattering from photocatalyst nanoparticles.

Furthermore, effect of the initial MB concentration on the AZP2 photocatalytic performance was studied by varying MB concentration from 10 to 50 mg L^{-1} and probing their degradation efficiency. As shown in Fig. 9c, the photodegradation performance reduced from 100% (for 10 mg L^{-1}) to 88.1% (50 mg L^{-1}). The observed decline in performance is possibly due to the saturation of photocatalytic sites of AZP2 in high amounts of MB.

Reusability experiments were conducted for six successive runs (Fig. 10). After each photodegradation run, the AZP2-contained solution was centrifuged at 4000 rpm for 6 min. The collected AZP2 was washed with deionized water and methanol, followed by drying for 6 h at 75 °C. The dried AZP2

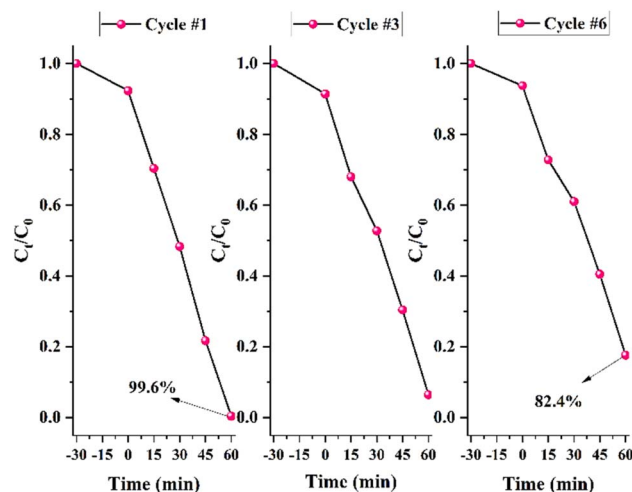


Fig. 10 Stability test of photodegradation of MB for AZP2.



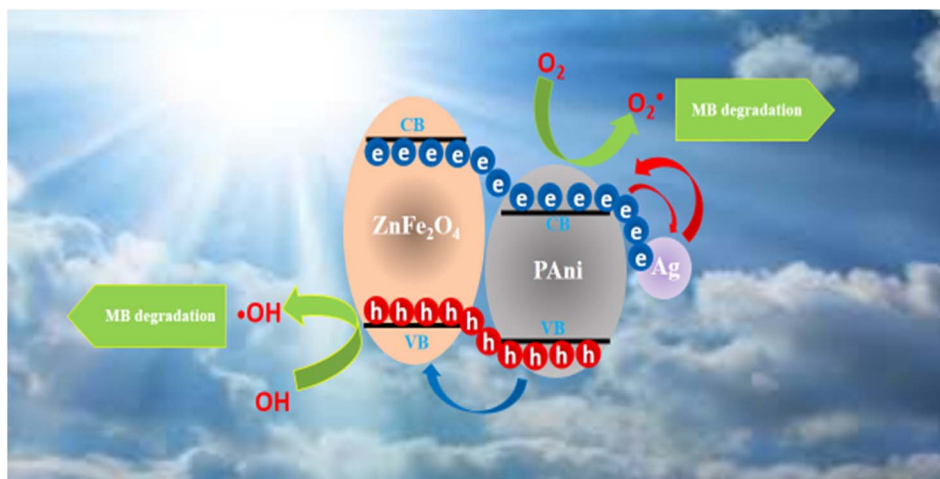


Fig. 11 Schematic view for possible photocatalytic mechanism behind Ag@ZnFe₂O₄-PANI nanocomposites for photo-degradation of dye molecules.

Table 1 Compare the obtained kinetic rate for MB degradation with literature

Photocatalyst	Kinetic rate (min ⁻¹)	Photocatalyst	Kinetic rate (min ⁻¹)
CeO ₂ /GO/PAM ⁵⁰	0.0259	ZnO ⁵¹	0.0300
MnTiO ₃ /TiO ₂ (ref. 52)	0.0059	Bi ₂ O ₃ /MoSe ₂ (ref. 53)	0.0455
NiO/Ag/TiO ₂ (ref. 54)	0.0312	rGO/WO ₃ (ref. 55)	0.0073
Ag ₂ O ⁵⁶	0.0319	g-C ₃ N ₄ /CoFe ₂ O ₄ (ref. 57)	0.0190
CdSe ⁵⁸	0.0380	This study	0.0406

was again used for reusability test. As can be seen, a photocatalytic performance of 99.6% and 96.6% was recorded for the first and second cycles; however, in total a ~17% decline in photocatalytic performance was observed after six runs. The reusability test implies that the Ag@ZnFe₂O₄-PANI plasmonic nanocomposites can be used for photodegradation of industrial aqueous wastes.

The possible photodegradation mechanism of the Ag@ZnFe₂O₄-PANI system is depicted in Fig. 11. By exposing sunlight illumination to the Ag@ZnFe₂O₄-PANI/dye aqueous solution, the ZnFe₂O₄ valence band (VB) electrons absorb light energy and generate hot electrons. Next, these hot electrons inject into the conduction band of PANI polymer, then moved to Ag NPs surface. These hot electrons react with surrounding O₂ and form superoxide radicals (O₂^{•-}). The O₂^{•-} radicals assist to form the hydroxyl radicals (•OH). In addition, the holes from the PANI molecules transfer to the VB of ZnFe₂O₄, which contribute to the •OH radicals formation. Then, the •OH and O₂^{•-} radicals decompose the dye molecules.

Table 1 summarizes the kinetic rate values provided for several types of nanocomposites and compares them with the values acquired in this work.

4 Conclusions

In the current study, ZnFe₂O₄ photocatalytic activity was increased by developing Ag@ZnFe₂O₄-PANI plasmonic nanostructures. The synthesized Ag@ZnFe₂O₄-PANI nanostructures

was employed to photodegradation of MB and RhB dyes under simulated sunlight illumination. Results showed the ternary nanostructures exhibit higher photocatalytic efficiency than that of the pure ZnFe₂O₄ ferrites. After 60 min light illumination, Ag@ZnFe₂O₄-PANI plasmonic nanostructures decomposed 99.6% of MB dye. Incorporating Ag NPs into ZnFe₂O₄-PANI nanocomposites boosted light-harvesting photocatalyst and reduced energy bandgap from 2.01 eV to 1.92 eV. These phenomena increased the electron-hole production rate in ZnFe₂O₄ by exposure to light. Moreover, contribution Ag NPs and PANI to charge transfer mechanisms boosted charge separation during photocatalytic process. The Ag@ZnFe₂O₄-PANI plasmonic nanostructures offered larger surface area and photocatalytic sites than the pure ZnFe₂O₄. Overall, enlarged surface area, increased electron-hole production rate, and boosted charge separation are the origins of photocatalytic improvement of ZnFe₂O₄. Furthermore, the Ag@ZnFe₂O₄-PANI photocatalyst with its considerable reusability can be used in industries to photodegrade their aqueous wastes. In addition, the obtained results show that by modification ZnFe₂O₄ materials with metallic dopants and by developing ZnFe₂O₄-polymer hybrid systems can design efficient photocatalyst materials to waste water treatments.

Data availability

The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.



Author contributions

Conceptualization, methodology, formal analysis, investigation, data curation, validation; visualization, original draft preparation, writing–review and editing M. K. A. M., A. M. N., S. S. J., R. I. F., O. A. N. All authors reviewed the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

References

- H. M. Al-Attar, H. T. Hussein, R. S. Zamel, A. J. Addie and M. K. Mohammed, Methylene blue degradation using ZnO: CuO: Al₂O₃ nanocomposite synthesized by liquid laser ablation, *Opt. Quantum Electron.*, 2023, **55**, 309.
- R. I. Faeq, S. S. Jaafar, A. M. Najji, M. K. Mohammed and O. A. Nief, Increasing the photocatalytic degradation rate of a rGO/PVA nanocomposite decorated with ZnO nanoparticles, *New J. Chem.*, 2023, **47**, 13661–13670.
- A. M. Najji, I. Y. Mohammed, S. H. Mohammed, M. K. Mohammed, D. S. Ahmed, M. S. Jabir and A. M. Rheima, Photocatalytic degradation of methylene blue dye using F doped ZnO/polyvinyl alcohol nanocomposites, *Mater. Lett.*, 2022, **322**, 132473.
- R. I. Faeq, S. S. Jaafar, A. M. Najji, M. K. Mohammed and O. A. Nief, Investigation of the visible-light-driven catalytic activity of nickel oxide-doped carbon nanotubes/polyvinylpyrrolidone nanocomposites towards methylene blue dye, *Inorg. Chem. Commun.*, 2023, **157**, 111390.
- J. Karpińska and U. Kotowska, *Removal of Organic Pollution in the Water Environment*, MDPI, 2019, p. 2017.
- D. Han and M. J. Currell, Persistent organic pollutants in China's surface water systems, *Sci. Total Environ.*, 2017, **580**, 602–625.
- A. G. Heath, *Water Pollution and Fish Physiology*, CRC press, 2018.
- E. Molahosseini, M. Molaei, H. Zare and F. Farahmandzadeh, A novel dark catalyst material based on Fe₃O₄/MWCNT/SiO₂ magnetic nanocomposite for simple and ultrafast degradation of methylene blue, *Mater. Res. Bull.*, 2024, **170**, 112571.
- A. Ahmadpour, Using of activated carbon adsorption in wastewater industries, *J. Chem. Lett.*, 2022, **3**, 2–9.
- J. Kim, S. Yoon, M. Choi, K. J. Min, K. Y. Park, K. Chon and S. Bae, Metal ion recovery from electro dialysis-concentrated plating wastewater via pilot-scale sequential electrowinning/chemical precipitation, *J. Cleaner Prod.*, 2022, **330**, 129879.
- A. George, A. D. Raj, A. A. Irudayaraj, R. Josephine, X. Venci, S. J. Sundaram, R. Rajakrishnan, P. Kuppusamy and K. Kaviyarasu, Regeneration study of MB in recycling runs over nickel vanadium oxide by solvent extraction for photocatalytic performance for wastewater treatments, *Environ. Res.*, 2022, **211**, 112970.
- K. Hussain, N. A. Khan, V. Vambol, S. Vambol, S. Yeremenko and V. Sydorenko, Advancement in Ozone base wastewater treatment technologies: Brief review, *Ecol. Quest.*, 2022, **33**, 7–19.
- S. Lahiri, C. Zhang, M. Sillanpää and L. Liu, Nanoporous NiO@ SiO₂ photo-catalyst prepared by ion-exchange method for fast elimination of reactive dyes from wastewater, *Mater. Today Chem.*, 2022, **23**, 100677.
- Y. Wu, X. He, X. Wang, J. Xv, M. Muddassir, I. A. Ansari and A. Zhong, Synergistic efficacy unleashed: Co/Ni-based catalysts as a versatile powerhouse for photocatalytic degradation of ornidazole, *Inorg. Chim. Acta*, 2024, **568**, 122115.
- I. Ahmad, M. A. Aftab, A. Fatima, S. D. Mekkey, S. Melhi and S. Ikram, A comprehensive review on the advancement of transition metals incorporated on functional magnetic nanocomposites for the catalytic reduction and photocatalytic degradation of organic pollutants, *Coord. Chem. Rev.*, 2024, **514**, 215904.
- W. Guo, T. Guo, Y. Zhang, L. Yin and Y. Dai, Progress on simultaneous photocatalytic degradation of pollutants and production of clean energy: A review, *Chemosphere*, 2023, 139486.
- X. Lu, K. Xu, P. Chen, K. Jia, S. Liu and C. Wu, Facile one step method realizing scalable production of gC₃N₄ nanosheets and study of their photocatalytic H₂ evolution activity, *J. Mater. Chem. A*, 2014, **2**, 18924–18928.
- E. Y. Salih, Z. Abbas, S. H. H. Al Ali and M. Z. Hussein, Dielectric Behaviour of Zn/Al-NO₃ LDHs Filled with Polyvinyl Chloride Composite at Low Microwave Frequencies, *Adv. Mater. Sci. Eng.*, 2014, **2014**, 647120.
- M. Dehghanipour, M. Khanzadeh, M. Karimipour and M. Molaei, Dependence of nonlinear optical properties of Ag₂S@ ZnS core-shells on Zinc precursor and capping agent, *Opt Laser. Technol.*, 2018, **100**, 286–293.
- S. Perumal, M. K. Mohammed, M. Govindasamy, A. A. Alothman, M. Ouladsmene and R. Ganesan, An ultra-high electrochemical performance of surface-rich boron induced multi-metal centered heterocatalyst for overall water splitting, *Int. J. Hydrogen Energy*, 2024, **54**, 652–664.
- S. O. Abdulghani, E. Y. Salih and A. S. Mohammed, Fabrication and photo-responsive characteristics of GeO₂ doped SnO₂/porous Si film for ultraviolet photodetector application, *Mater. Chem. Phys.*, 2023, **303**, 127859.
- O. Aldaghri, E. Y. Salih, A. Ramizy, A. S. Mohammed, K. H. Ibnaouf and M. H. Eisa, Rapid fabrication of fast response CdS/Si visible light photodetector: Influence of laser energy, *Res. Phys.*, 2023, **54**, 107112.
- M. B. A. Bashir, S. M. Said, M. F. M. Sabri, Y. Miyazaki, D. A. Shnawah, M. Shimada, M. F. M. Salleh, M. S. Mahmood, E. Y. Salih and F. Fitriani, In-filled La_{0.5}Co₄Sb₁₂ skutterudite system with high thermoelectric figure of merit, *J. Electron. Mater.*, 2018, **47**, 2429–2438.
- X. Qiu, Y. Zhang, Y. Zhu, C. Long, L. Su, S. Liu and Z. Tang, Applications of nanomaterials in asymmetric photocatalysis: recent progress, challenges, and opportunities, *Adv. Mater.*, 2021, **33**, 2001731.



- 25 A. Arimi, L. Megatiff, L. I. Granone, R. Dillert and D. W. Bahnemann, Visible-light photocatalytic activity of zinc ferrites, *J. Photochem. Photobiol., A*, 2018, **366**, 118–126.
- 26 O. K. Mmesesi, N. Masunga, A. Kuvarega, T. T. Nkambule, B. B. Mamba and K. K. Kefeni, Cobalt ferrite nanoparticles and nanocomposites: Photocatalytic, antimicrobial activity and toxicity in water treatment, *Mater. Sci. Semicond. Process.*, 2021, **123**, 105523.
- 27 Q. Zhang, Z. Li, X. Li, L. Yu, Z. Zhang and Z. Wu, Preparation of cobalt ferrite nanoparticle-decorated boron nitride nanosheet flame retardant and its flame retardancy in epoxy resin, *Nano*, 2019, **14**, 1950063.
- 28 P. Thakur, S. Taneja, D. Chahar, B. Ravelo and A. Thakur, Recent advances on synthesis, characterization and high frequency applications of Ni-Zn ferrite nanoparticles, *J. Magn. Magn. Mater.*, 2021, **530**, 167925.
- 29 N. Yadav, L. Chaudhary, P. Sakhare, T. Dongale, P. Patil and A. Sheikh, Impact of collected sunlight on ZnFe₂O₄ nanoparticles for photocatalytic application, *J. Colloid Interface Sci.*, 2018, **527**, 289–297.
- 30 G. Fan, J. Tong and F. Li, Visible-light-induced photocatalyst based on cobalt-doped zinc ferrite nanocrystals, *Ind. Eng. Chem. Res.*, 2012, **51**, 13639–13647.
- 31 R. Yu, J. Zhao, Z. Zhao and F. Cui, Copper substituted zinc ferrite with abundant oxygen vacancies for enhanced ciprofloxacin degradation via peroxymonosulfate activation, *J. Hazard. Mater.*, 2020, **390**, 121998.
- 32 B. Janani, A. Syed, L. Sruthi, P. Sivaranjani, A. M. Elgorban, A. H. Bahkali, N. S. Zaghoul, M. M. Badawy, A. Das and S. S. Khan, Visible light driven photocatalytic activity and efficient antibacterial activity of ZnFe₂O₄ decorated CdO nanohybrid heterostructures synthesized by ultrasonic-assisted method, *Colloids Surf., A*, 2021, **628**, 127307.
- 33 C. Akshayya, M. K. Okla, A. M. Thomas, A. A. AL-ghamdi, M. A. Abdel-Maksoud, B. Almunqedhi, H. AbdElgawad, L. L. Raju and S. S. Khan, Insights into photocatalytic mechanism for the rational design of pn heterojunction by decorating mesoporous SnS₂ over ZnFe₂O₄ nanocomposite for accelerated visible light photocatalysis, *Mater. Chem. Phys.*, 2022, **277**, 125464.
- 34 N. Kaushal, S. Sarraf, A. K. Basu, S. Mishra and A. Saha, Facile microwave synthesis of Zinc Ferrite@ NCDs for photocatalytic degradation of fluoroquinolone antibiotics, *Mater. Chem. Phys.*, 2024, **314**, 128823.
- 35 H. Mohseni, M. Dehghanipour, N. Dehghan, F. Tamaddon, M. Ahmadi, M. Sabet and A. Behjat, Enhancement of the photovoltaic performance and the stability of perovskite solar cells via the modification of electron transport layers with reduced graphene oxide/polyaniline composite, *Sol. Energy*, 2021, **213**, 59–66.
- 36 A. M. Najji, S. H. Kareem, A. H. Faris and M. K. Mohammed, Polyaniline polymer-modified ZnO electron transport material for high-performance planar perovskite solar cells, *Ceram. Int.*, 2021, **47**, 33390–33397.
- 37 Z. T. M. Noori, A. M. Najji, O. A. Nief, M. K. Mohammed, N. M. Ahmed and S. Singh, Polyaniline/Nickle oxide hole transport layers to increase stability and efficiency of regular perovskite solar cells, *Int. J. Energy Res.*, 2022, **46**, 17285–17294.
- 38 Q. Wang, J. Hui, J. Li, Y. Cai, S. Yin, F. Wang and B. Su, Photodegradation of methyl orange with PANI-modified BiOCl photocatalyst under visible light irradiation, *Appl. Surf. Sci.*, 2013, **283**, 577–583.
- 39 Q. Mo, S. Zeng, J. Yang, C. Wu and Y. Zhang, Polyaniline-ferrite nanocomposite as a new magnetically recyclable photocatalyst with enhanced photocatalytic activity, *J. Ceram. Soc. Jpn.*, 2020, **128**, 135–141.
- 40 S. Choudhary and S. Mohapatra, Boosting sunlight driven photocatalytic and catalytic performance of ZnFe₂O₄-ZnO nanohybrids by loading Ag nanoparticles, *J. Photochem. Photobiol., A*, 2024, 115797.
- 41 C. Karunakaran, I. JebaSing and P. Vinayagamoorthy, Synthesis of superparamagnetic ZnFe₂O₄-core/Ag-deposited ZnO-shell nanodiscs for application as visible light photocatalyst, *J. Nanosci. Nanotechnol.*, 2019, **19**, 4064–4071.
- 42 S. Choudhary, A. Bisht, B. Satpati and S. Mohapatra, Facile synthesis of Ce-doped ZnO nanospindles for photocatalytic applications, *Appl. Phys. A: Mater. Sci. Process.*, 2021, **127**, 1–14.
- 43 P. Dolcet, K. Kirchberg, A. Antonello, C. Suchomski, R. Marschall, S. Diodati, R. Muñoz-Espí, K. Landfester and S. Gross, Exploring wet chemistry approaches to ZnFe₂O₄ spinel ferrite nanoparticles with different inversion degrees: a comparative study, *Inorg. Chem. Front.*, 2019, **6**, 1527–1534.
- 44 S. Sasikumar and A. Rajaram, The synergetic effect of cobalt-doped zinc ferrite and hexagonal boron nitride photocatalyst for wastewater treatment, *Diamond Relat. Mater.*, 2024, 111270.
- 45 M. Shakil, U. Inayat, M. Ashraf, M. Tanveer, S. Gillani and A. Dahshan, Photocatalytic performance of novel zinc ferrite/copper sulfide composites for the degradation of Rhodamine B dye from wastewater using visible spectrum, *Optik*, 2023, **272**, 170353.
- 46 N. Khadgi, A. R. Upreti and Y. Li, Simultaneous bacterial inactivation and degradation of an emerging pollutant under visible light by ZnFe₂O₄ co-modified with Ag and rGO, *RSC Adv.*, 2017, **7**, 27007–27016.
- 47 A. Kar, P. Dagar, S. Kumar, I. S. Deo, G. V. Prakash and A. K. Ganguli, Photoluminescence and lifetime studies of C-dot decorated CdS/ZnFe₂O₄ composite designed for photoelectrochemical applications, *J. Photochem. Photobiol., A*, 2023, **439**, 114612.
- 48 A. Singh, F. Wan, K. Yadav, S. Kharbanda, P. Thakur and A. Thakur, A novel magnetic NiFe₂O₄-Ag-ZnO hybrid nanocomposite for the escalated photocatalytic dye degradation and antibacterial activities, *Mater. Sci. Eng., B*, 2024, **299**, 116935.
- 49 M. M. J. Sadiq, U. S. Shenoy and D. K. Bhat, NiWO₄-ZnO-NRGO ternary nanocomposite as an efficient photocatalyst for degradation of methylene blue and reduction of 4-nitro phenol, *J. Phys. Chem. Solids*, 2017, **109**, 124–133.



- 50 Z. Kalaycıoğlu, B. Özüğür Uysal, O. N. Pekcan and F. B. Erim, Efficient photocatalytic degradation of methylene blue dye from aqueous solution with cerium oxide nanoparticles and graphene oxide-doped polyacrylamide, *ACS Omega*, 2023, **8**, 13004–13015.
- 51 R. H. Waghchaure, V. A. Adole and B. S. Jagdale, Photocatalytic degradation of methylene blue, rhodamine B, methyl orange and Eriochrome black T dyes by modified ZnO nanocatalysts: A concise review, *Inorg. Chem. Commun.*, 2022, **143**, 109764.
- 52 S. Alkaykh, A. Mbarek and E. E. Ali-Shattle, Photocatalytic degradation of methylene blue dye in aqueous solution by MnTiO₃ nanoparticles under sunlight irradiation, *Heliyon*, 2020, **6**(4), e03663.
- 53 M. Alahmadi, W. H. Alsaedi, W. Mohamed, H. M. Hassan, M. Ezzeldien and A. M. Abu-Dief, Development of Bi₂O₃/MoSe₂ mixed nanostructures for photocatalytic degradation of methylene blue dye, *J. Taibah Univ. Sci.*, 2023, **17**, 2161333.
- 54 W. Mohammed, M. Matalkeh, R. M. Al Soubaihi, A. Elzatahry and K. M. Saoud, Visible light photocatalytic degradation of methylene blue dye and pharmaceutical wastes over ternary NiO/Ag/TiO₂ heterojunction, *ACS Omega*, 2023, **8**, 40063–40077.
- 55 V. Ramar and K. Balasubramanian, Reduced graphene oxide/WO₃ nanorod composites for photocatalytic degradation of methylene blue under sunlight irradiation, *ACS Appl. Nano Mater.*, 2021, **4**, 5512–5521.
- 56 S. Sagadevan, S. F. Alshahateet, J. A. Lett, I. Fatimah, R. P. Sivasankaran, A. K. Sibhatu, E. Leonard, M.-V. Le and T. Soga, Highly efficient photocatalytic degradation of methylene blue dye over Ag₂O nanoparticles under solar light irradiation, *Inorg. Chem. Commun.*, 2023, **148**, 110288.
- 57 H. D. Weldekirstos, T. Mengist, N. Belachew and M. L. Mekonnen, Enhanced photocatalytic degradation of methylene blue dye using facilely synthesized g-C₃N₄/CoFe₂O₄ composite under sun light irradiation, *Res. Chem.*, 2024, **7**, 101306.
- 58 P. Gharbani, A. Mehrizad and S. A. Mosavi, Optimization, kinetics and thermodynamics studies for photocatalytic degradation of Methylene Blue using cadmium selenide nanoparticles, *npj Clean Water*, 2022, **5**, 34.

