

Original Research

Structural, Morphological, Optical and Dielectric Study along with Efficient Photocatalytic Activity of Dy³⁺ doped ZnFe₂O₄/g-C₃N₄ Composites for RhB Dye Degradation

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Abstract: Dye pollution harms the environment, but photocatalysis provides an eco-friendly remedy. Dy³⁺-doped ZnFe₂O₄ with different weight ratios of g-C₃N₄ were synthesized via co-precipitation for RhB dye degradation. XRD confirmed a cubic structure with crystallite sizes of 20–30 nm, while SEM showed grain sizes of 8–24.5 nm. FTIR (650–4000 cm⁻¹) confirmed O–H, C–N, and C=N groups; UV–Vis showed band gaps of 1.98–1.74 eV. The dielectric constant peaked at low frequencies (31.6–3162 Hz), and AC conductivity reached $1.4 \times 10^{-6}(\Omega\text{m})^{-1}$. Optimal photocatalytic performance was achieved at pH 8, 40 mg/100 mL catalyst dose, and 8 mM H₂O₂ using Dy³⁺-doped ZnFe₂O₄ with composite g-C₃N₄ (0.4g), attaining ≈96.5% RhB degradation within 75 min. This composite showed good reusability over five cycles, confirming its high efficiency for water contaminant removal.

Keywords: co-precipitation; semiconductor materials; heterogeneous photocatalysis; wastewater treatment

1. Introduction

Clean water is essential for human survival. However, the rapid increase in organic pollutants has become a primary cause of global water contamination. Currently, nearly two billion people rely on polluted water sources, posing severe risks to public health. Herbicides, pesticides (such as chlordane and aldrin), and various industrial chemicals are major contributors to water pollution. Even at very low concentrations, these contaminants can cause serious health hazards, including carcinogenic and mutagenic effects [1–3].

Among organic pollutants, synthetic dyes are extensively used as colorants in numerous industrial applications, including textiles, paper, cosmetics, food additives, and laser printing. The uncontrolled discharge of these dyes into aquatic environments creates severe ecological problems, adversely affecting aquatic organisms and human health [4]. Rhodamine B (RhB) is a widely used xanthene dye in textile and food industries and is recognized for its high toxicity, non-biodegradability, and long-term persistence in water bodies. RhB obstructs light penetration in water, disrupts photosynthetic processes, and interferes with natural purification mechanisms, posing a significant threat to aquatic ecosystems and plant life [5,6]. Therefore, the complete removal of RhB from wastewater is critically important to mitigate its harmful environmental effects.

Various wastewater treatment methods, including ion exchange, membrane separation, evaporation, and advanced oxidation processes, have been explored for dye removal [7,8]. Among these, photocatalysis has attracted considerable attention due to its cost-effectiveness, operational

simplicity, and high degradation efficiency. Since the 1970s, hydroxyl-radical-based advanced oxidation processes (AOPs) have been widely employed for the degradation of non-biodegradable organic pollutants. In photocatalytic systems, a reusable semiconductor catalyst, light irradiation (preferably sunlight), and oxidizing agents such as oxygen or hydrogen peroxide are used to mineralize organic pollutants into harmless products [9,10].

Zinc-based semiconductors have been extensively investigated for photocatalytic applications. Zinc oxide (ZnO), for example, has shown promising performance in controlling water and air pollution, degrading organic contaminants, and enabling fuel generation from CO₂ and water [11,12]. Graphitic carbon nitride (g-C₃N₄) has also attracted significant interest due to its non-toxicity, suitable bandgap (~2.7 eV), chemical stability, and visible-light responsiveness. However, the practical application of pristine g-C₃N₄ is limited by its relatively low surface area and rapid recombination of photogenerated electron-hole pairs [13,14].

Another promising photocatalyst is zinc ferrite (ZnFe₂O₄), which exhibits low toxicity, visible-light absorption, structural stability, and magnetic recyclability [15]. Nevertheless, its photocatalytic performance is limited by rapid charge-carrier recombination. To overcome these limitations, rare-earth element doping has emerged as an effective strategy to tailor the electronic structure of photocatalysts. Rare-earth ions possess unique electronic configurations that can act as charge-trapping or mediating centers, thereby enhancing photocatalytic efficiency [16,17].

In this study, Dy³⁺-doped ZnFe₂O₄ coupled with g-C₃N₄ is developed as an efficient visible-light-driven photocatalyst, where Dy³⁺ ions function as electron mediators to facilitate interfacial charge transfer and suppress recombination. Dy³⁺-doped ZnFe₂O₄/g-C₃N₄ composites with different g-C₃N₄ weight ratios were synthesized via a co-precipitation method and applied for RhB dye degradation under solar irradiation. The synthesized materials were systematically characterized using XRD, SEM/EDX, FTIR, UV-Vis spectroscopy, and dielectric analysis to examine their structural, morphological, optical, and electrical properties. The results demonstrate that coupling Dy³⁺-doped ZnFe₂O₄ with g-C₃N₄ significantly enhances visible-light absorption and promotes efficient separation and transport of photogenerated charge carriers. The photocatalytic performance was evaluated under various operational parameters, including pH, catalyst dosage, H₂O₂ concentration, reaction time, and light exposure. The improved degradation efficiency of the optimized composite highlights the synergistic effect of rare-earth doping and heterojunction formation, offering a promising approach for sustainable wastewater treatment.

2. Materials and methods

2.1. Chemicals

All the chemicals were purchased from Sigma-Aldrich/Merck and used without additional purification. Zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O] (95.0%), Iron nitrate hexahydrate [Fe(NO₃)₂·6H₂O] (98.01%), Dysprosium nitrate [Dy(NO₃)₂·6H₂O] (99%), Ethanol, Sodium hydroxide [NaOH] (99.99%) and melamine were used as precursors and RhB dye was used for photocatalytic degradation process.

2.2. Synthesis of g-C₃N₄

The process of thermal polymerization was employed to make g-C₃N₄. 10 g of melamine was added to a crucible and heated to 550 °C for three hours. This heating process burned the melamine in the furnace, resulting in the production of yellow colored g-C₃N₄.

2.3. Synthesis of Dy-ZnFe₂O₄

A stoichiometric ratio of Zn_{1-x}Dy_xFe₂O₄ [x = 0.03], was used to dissolve zinc nitrate hexahydrate, dysprosium nitrate, and ferric nitrate in 50 ml of distilled water. Throughout the process of synthesis, solutions were constantly stirred to attain homogeneity and drops of the precipitating agent (NaOH) were added to reach and maintain pH 8. After that, the solution was heated to 80 °C for one hour.

The brown-colored precipitates were formed after undergoing two rounds of centrifugation (first with double-distilled water to remove impurities, followed by ethanol to remove nitrate ions). After being dried at 70 °C for 12 h, the resulting product was analyzed. The final product was ground into fine nanoparticles and the resulting powder was subsequently calcined in a muffle furnace at 500 °C for three hours.

2.4. Synthesis of Dy-ZnFe₂O₄/g-C₃N₄

The Co-precipitation method was used to produce the Dy-ZnFe₂O₄/g-C₃N₄ composites depicted in Figure 1. To attain homogeneous solutions, 0.2 g of Dy-ZnFe₂O₄ and 0.2 g of g-C₃N₄ were first separately dispersed in 50 mL of water. After 15 min of mixing and combining the solutions, the suspension was sonicated for another 15 min to make sure it was evenly distributed. After adding the g-C₃N₄ solution dropwise to the Dy-ZnFe₂O₄ solution, the mixture was allowed to stirred at room temperature for half an hour.

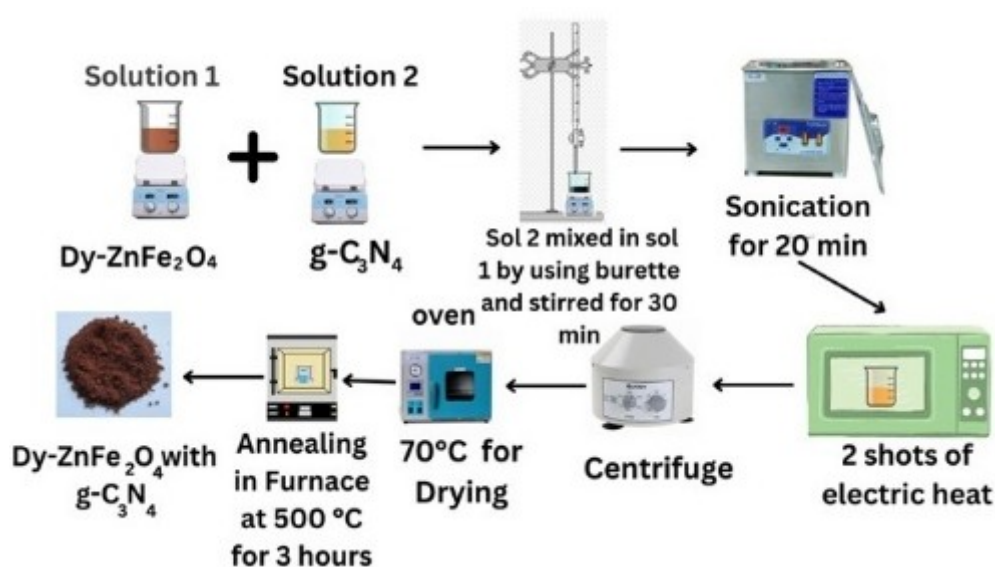


Figure 1. Schematic diagram for the synthesis of Dy³⁺ doped ZnFe₂O₄/g-C₃N₄.

The resultant solution was then sonicated for an additional 15 min. After that, the solution underwent centrifugation (5000 rpm) for 10 min and was washed three times with distilled water, followed by ethanol washing to remove residual nitrates. The gathered material was then dried in an oven at 70 °C overnight. The final product was converted into fine powder. The final product was ground into fine nanoparticles, and the resulting powder was subsequently calcined in a muffle furnace at 500 °C with heating rate of 5 °C min⁻¹, resulting in a brown-colored powder. By changing the weight ratios of g-C₃N₄-X (X = 0.2, 0.3, 0.4), the samples were named as DZG1, DZG2, and DZG3, respectively. Table 1 compares the co-precipitation conditions and parameters used in this work with those reported in previous studies.

Table 1. Comparison of current co-precipitation method conditions/parameters with literature.

Material/Composite	Synthesis Method	Temperature (°C)	Duration (h)	Crystallite size (nm)	SSA (m ² /g)	Ref
ZnFe ₂ O ₄ /Ag	Co-precipitation	80	2	10	64	[18]
ZnFe ₂ O ₄ /Ag/AgBr	Co-precipitation	90	3	30	48	[19]
ZnFe ₂ O ₄ /TiO ₂	Co-precipitation	75	3.5	22	45	[20]

ZnFe ₂ O ₄ /CNT	Co-precipitation	95	2	18	60	[21]
ZnFe ₂ O ₄ /SiO ₂	Co-precipitation	70	4	25	50	[22]
ZnFe ₂ O ₄ /MnO ₂	Co-precipitation	85	3	26	47	[9]
ZnFe ₂ O ₄ /NiO	Co-precipitation	90	3.5	29	61	[13]
Dy ³⁺ -ZnFe ₂ O ₄	Co-precipitation	80	2	18	62	[23]
Dy ³⁺ -ZnFe ₂ O ₄ /g-C ₃ N ₄	Co-precipitation	80	75 min	24.05	12.74	Present work

2.5. Photocatalytic activity

To assess the photocatalytic activity, 50 mL solution of RhB was prepared. To determine the equilibrium between desorption and adsorption of the photocatalyst and dye solution, 20 mg and 30 mg of the photocatalyst were separately added to 50 mL of RhB solution. Both samples were then kept in the dark for 30 min to allow equilibrium to be established. The pH was adjusted by using 1 M of NaOH and 0.1 M of HCl solutions. After 30 min in the dark, an oxidant (H₂O₂) solution was added. Then, the whole setup was exposed to sunlight irradiation between 11:00 and 14:00 h under strong sunlight. Using a LUX meter, the intensity of sunlight (1080 W m⁻²) was measured, with ambient temperatures ranging from 35 °C to 40 °C. After centrifuging for 15 min, 5 mL solution was taken and absorbance was determined from UV-Vis spectroscopy. The efficiency was determined by using Equation (1):

$$\text{Photocatalytic efficiency } (\eta) = \left(1 - \frac{C_t}{C_0}\right) \times 100 \quad (1)$$

The dye concentration is indicated by C_t after time 't' and C_0 indicates initial concentration.

3. Characterization

Diffraction patterns of the synthesized Dy³⁺ doped ZnFe₂O₄ with different contents of g-C₃N₄ were captured using the X-ray diffraction (XRD), which had a precise wavelength (λ) of 0.154 nm and covered a 2θ range from 20° to 80°. Morphological characterization was carried out using a JEOL-JSM 5910 scanning electron microscope (SEM) to examine the surface structure of the materials. The absorption bands were identified and checked using a [Perkin Elmer] FTIR spectrometer. A UV-visible spectrometer (PG Model T-80) was used to perform optical measurements in the wavelength range of 250–750 nm to examine the optical characteristics of the composites. Dielectric evaluations were taken at RT with a 3536 series LCR meter.

4. Results and discussions

4.1. XRD analysis

XRD investigation was utilized to estimate the phase and structural information of the synthesized Dy³⁺ doped ZnFe₂O₄ with g-C₃N₄ composites. Figure 2(a) shows the patterns of XRD of Dy³⁺-doped ZnFe₂O₄ with different content of g-C₃N₄. In XRD spectra, the diffraction peaks were seen at $2\theta = 29.69^\circ, 35.88^\circ, 43.19^\circ, 57.25^\circ, 62.91^\circ$ and indexed with (220), (311), (400), (511), (440) with the JCPDS card data 82–1012, which showed the cubic structure. The Dy³⁺ doped ZnFe₂O₄ with g-C₃N₄ structure is successfully obtained, as demonstrated by the strong interaction between g-C₃N₄ and ZnFe₂O₄. As the mass percentage of g-C₃N₄ increased, g-C₃N₄ diffraction peaks gradually increased. The crystallite size of a Dy³⁺ doped ZnFe₂O₄ with g-C₃N₄ composite is estimated using the Debye-Scherrer equation [24,25]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where D is the crystallite size, k represents the Scherrer constant (typically 0.9), λ is the wavelength of X-ray (1.54 Å), β is the full width at half maximum (FWHM) in radians and θ is the diffraction angle measured from the 2θ scale.

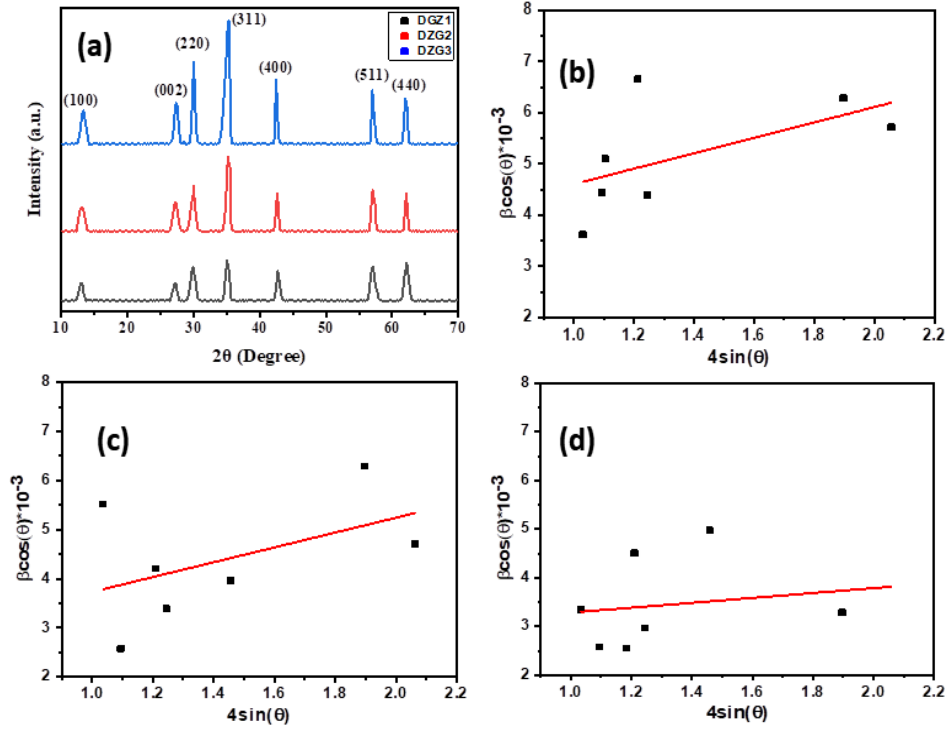


Figure 2. (a) XRD pattern, W-H plots of Dy^{3+} doped $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites; (b) DZG1; (c) DZG2; (d) DZG3.

The crystallite size decreases from 28.25 nm (DZG1) to 16.51 nm (DZG3), indicating that the addition of more amount of $\text{g-C}_3\text{N}_4$, leads to smaller crystalline domains. This may result from $\text{g-C}_3\text{N}_4$ acting as a growth inhibitor, limiting crystallite growth. This calculation also aided in determining the lattice parameters a , b and c , assuming cubic symmetry where $a = b = c$.

$$a = \frac{d}{\sqrt{(h^2 + k^2 + l^2)}} \quad (3)$$

where Miller indices, h , k and l indicate lattice parameters of a and d is the d spacing. The lattice parameter decreases from 8.41 Å (DZG1) to 8.28 Å (DZG3). Bragg's law can be used to calculate the d spacing (Equation (4)).

$$2d \sin \theta = n\lambda \quad (4)$$

The d -spacing decreases slightly from 2.60 Å (DZG1) to 2.53 Å (DZG3). Equation (5) is used to calculate the unit cell volume (V) for the cubic system based on the lattice parameter [26]:

$$V = a^3 \quad (5)$$

As the lattice parameter decreases, the unit cell volume drops from 594.8 Å³ (DZG1) to 567.7 Å³ (DZG3). As $\text{g-C}_3\text{N}_4$ alters the structural framework, this trend shows the packing of atoms into the crystal lattice. The following formula (Equation (6)) was employed to confirm the X-ray density (XRD) of the prepared samples:

$$\rho_{XRD} = \frac{N M_w}{N_A V} \quad (6)$$

Here, N indicates the quantity of atoms in the cubic lattice cell, Avogadro's number is represented by N_A , and the molecular weight of the prepared composites is indicated by M_w and V represents the volume of each unit cell.

The peaks in the XRD spectrum are indicative of an excessive nanocrystalline composition. The (M.I) is derived from the Full Width at Half Maximum (FWHM) of the XRD information. The morphological index (M.I) is determined by analyzing the full width at half maximum (FWHM) of peaks. The following equation (Equation (7)) is used to quantify the morphological index.

$$\text{Morphological Index} = \frac{FWHM_h}{FWHM_h + FWHM_p} \quad (7)$$

Here, $FWHM_h$ and $FWHM_p$ represent the full width at half maximum of the highest and specific peaks of crystalline, respectively. The morphological index for Dy^{3+} doped $ZnFe_2O_4$ with $g-C_3N_4$ is presented in Table 2. The morphological index (M.I.) is used as a qualitative comparative parameter to assess relative changes in particle morphology and surface irregularity among prepared samples. A higher M.I. value indicates increased peak broadening, which is generally associated with smaller crystallite size, greater surface irregularity, or higher defect density. Although M.I. is not a direct measure of surface area or porosity and does not substitute techniques such as BET analysis, it serves as a supplementary indicator for comparing relative morphological variations in samples synthesized under similar conditions. In this study, the observed variation in M.I. supports the SEM observations and helps explain trends in photocatalytic activity through its indirect relation to surface-active sites.

Micro-strain is determined using Equation (8) [27]:

$$\beta = 4 \times \varepsilon \times \tan \theta \quad (8)$$

For Williamson-Hall analysis, the detected peak broadening is the sum of Equation (2,8) and is expressed as:

$$\beta \cos \theta = \left(\frac{0.9 \lambda}{D} \right) + (4 \times \text{Strain} \times \sin \theta) \quad (9)$$

The relationship between $\beta \cos \theta$ and $4 \sin \theta$ shows the slope value, which is represented by the straight line. The W-H plots of Dy^{3+} doped $ZnFe_2O_4/g-C_3N_4$ nanocomposites (DZG1, DZG2, and DZG3) as depicted in Figure 2(b–d). It is noted that W-H plots exhibit a certain degree of data scattering. This behavior is attributed to the nanocrystalline nature of the Dy^{3+} doped $ZnFe_2O_4/g-C_3N_4$ nanocomposites and the simultaneous contribution of multiple peak-broadening factors, including crystallite size reduction, lattice strain, doping induced lattice distortion, and interfacial strain introduced by $g-C_3N_4$ coupling. Such non-ideal linearity in W-H plots is commonly observed in ferrite-based nanocomposite systems. Therefore, the W-H analysis is employed to estimate average effective crystallite size and to enable comparative evaluation among samples synthesized under similar conditions. The difference arises because the Scherrer equation, unlike the Williamson-Hall method, considers only size broadening. In contrast, the Williamson-Hall method includes both crystallite size and lattice strain. Figure 2(b–d) shows the micro-strain calculated from the slope values. The formula was used to calculate the SSA [28]:

$$SSA = \frac{6}{\rho_{XRD}} \times D \quad (10)$$

Dislocation density, which significantly impacts crystallographic properties, can be calculated from Equation (11) [29]:

$$\delta = \frac{1}{D^2} \quad (11)$$

Strain is calculated by Equation (12):

$$\varepsilon = \frac{1}{d^2} \quad (12)$$

The variation in XRD parameters for Dy³⁺ doped ZnFe₂O₄ with different contents of g-C₃N₄ nanocomposites is due to lattice distortions from Dy³⁺ doping, phase interactions with g-C₃N₄ and resulting changes. These factors can cause shifts in peak positions, changes in crystallite size and variations in peak intensity and broadening.

Table 2. Structural parameters calculated from XRD results.

Sample name	DZG1	DZG2	DZG3
<i>d</i> -spacing (Å)	2.60	2.54	2.53
D (nm) from Scherrer's equation	28.25	17.26	16.51
D (nm) from (W-H plot)	36.31	26.43	20.02
Lattice parameter (a = b = c)	8.41	8.34	8.28
V (Å ³)	594.8	580.1	567.7
Morphological Index (M.I)	1.55	1.3	1.24
X-ray density Q _{XRD} (g/cm ³)	1.33	1.35	1.36
SSA(m ² /g)	159.7	257.5	267.3
Dislocation density × 10 ⁴ (m ⁻²)	1.25	3.35	3.6
Strain ε	14.2	15.4	15.6

4.2. SEM analysis

The morphological analysis of Dy³⁺ doped ZnFe₂O₄ with g-C₃N₄ composites were determined through SEM. SEM analysis of Dy³⁺ doped ZnFe₂O₄ with g-C₃N₄ composites shows that Dy³⁺ doping alters surface morphology, affecting grain structures and particle sizes due to changes in growth kinetics. The incorporation of g-C₃N₄ in Dy³⁺ doped ZnFe₂O₄ enhanced surface area and improved particle dispersion, as shown in Figure 3(a-c). The size, shape, aggregation and overall distribution of particles have all changed due to g-C₃N₄ [30]. The increased presence of water and reducing agents among ferrite particles can be attributed to their agglomeration, likely caused by the magnetic attraction between the particles. The average grain sizes of the prepared composites were determined to be 8 nm, 13 nm, and 24.15 nm using ImageJ. It is observed that SEM-derived crystallite sizes are smaller than XRD-derived crystallite sizes due to particle aggregation, polycrystalline nature, and projection effects inherent to SEM imaging.

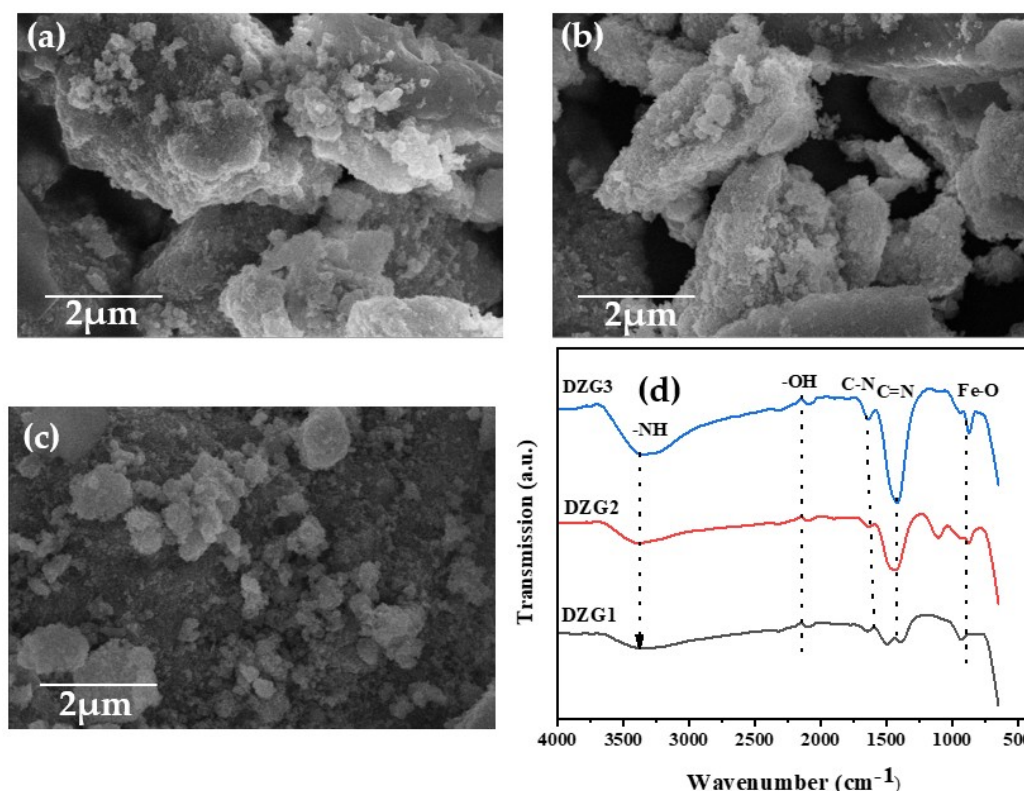


Figure 3. SEM micrographs of Dy³⁺ doped ZnFe₂O₄/g-C₃N₄ nanocomposites (a) DZG1; (b) DZG2; and (c) DZG3 ; (d) FTIR of Dy³⁺ doped ZnFe₂O₄/g-C₃N₄ nanocomposites DZG1, DZG2, DZG3.

4.3. FT-IR analysis

For identifying functional groups in prepared composites, FTIR is the most effective and dynamic method available. Figure 3(d) shows the FTIR characteristic peaks of Dy³⁺ doped ZnFe₂O₄ with g-C₃N₄ in the range of 650–4000 cm⁻¹ [31]. The FT-IR spectra reveal that the triazine units are responsible for the peak at 804 cm⁻¹, while the C–N and C=N are linked to the peaks at 1411 and 1645 cm⁻¹, respectively shown In Table 3. The absorptions of some bands at 590 cm⁻¹, are associated with the Fe–O, at 2620 cm⁻¹ demonstrating the OH groups' stretching vibration. The absorption band observed at 1630 cm⁻¹ and 3460 cm⁻¹, is attributed to the stretching and bending of the O–H bonds of the adsorbed H₂O molecules.

Table 3. Summarizing all FTIR peaks.

Wavenumber (cm ⁻¹)	Assignment	Reference
~804	Triazine ring breathing	[35]
~1411	C–N stretching	[35]
~1645	C=N stretching	[35]
~590	Fe–O vibration	[35]
~3460	O–H stretching	[35]

4.4. UV-visible spectroscopy analysis

The characteristics of the optical of semiconducting nanomaterials were examined using UV–visible spectra [32,33]. Figure 4(a) displays the band gap and absorption spectrum for the

synthesized Dy^{3+} doped ZnFe_2O_4 with $\text{g-C}_3\text{N}_4$ over the wavelength range of 300–800 nm. The optical bandgap (E_g) of material can be computed using a Tauc plot assuming an indirect allowed transition ($n = 2$), as shown in Figure 4(b–d). Equation (13) is utilized to determine the optical band gap [34].

$$\alpha h\nu = A(h\nu - E_g)^n \quad (13)$$

The (α) absorption coefficient was estimated in cm^{-1} , the characteristic parameter is represented by (A), Planck's constant denotes (h) and (n) are specified with the transition process.

The band gap values at different contents of $\text{g-C}_3\text{N}_4$ nanocomposites are determined as 1.98 eV, 1.86 eV and 1.74 eV, as shown in Figure 4(b–d), respectively. First, Dy^{3+} ions introduce localized 4f electronic states within the band structure, acting as shallow trapping centers and facilitating sub-bandgap electronic transitions. Second, the formation of a $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ heterojunction results in favorable band alignment, enabling efficient charge transfer at the interface and lowering the effective excitation energy. Third, Dy^{3+} substitution and interfacial interactions generate defect-related states, such as oxygen vacancies, which further contribute to band tailing and enhanced visible-light absorption. Overall, these effects improve photon utilization and enhance photocatalytic activity under solar irradiation.

The Tauc plots of Dy^{3+} -doped $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites exhibit two distinct linear regions, indicating the presence of multiple optical transitions. The higher-energy slope corresponds to the fundamental band-to-band transition, while the lower-energy slope originates from sub-bandgap transitions associated with Dy^{3+} 4f localized states, oxygen vacancies, and interfacial defect levels introduced by $\text{g-C}_3\text{N}_4$ coupling. These defect-related states contribute to enhanced visible-light absorption and improved photocatalytic activity. The reported band-gap values are extracted from the dominant absorption edge relevant to photocatalytic performance under solar irradiation [36,37].

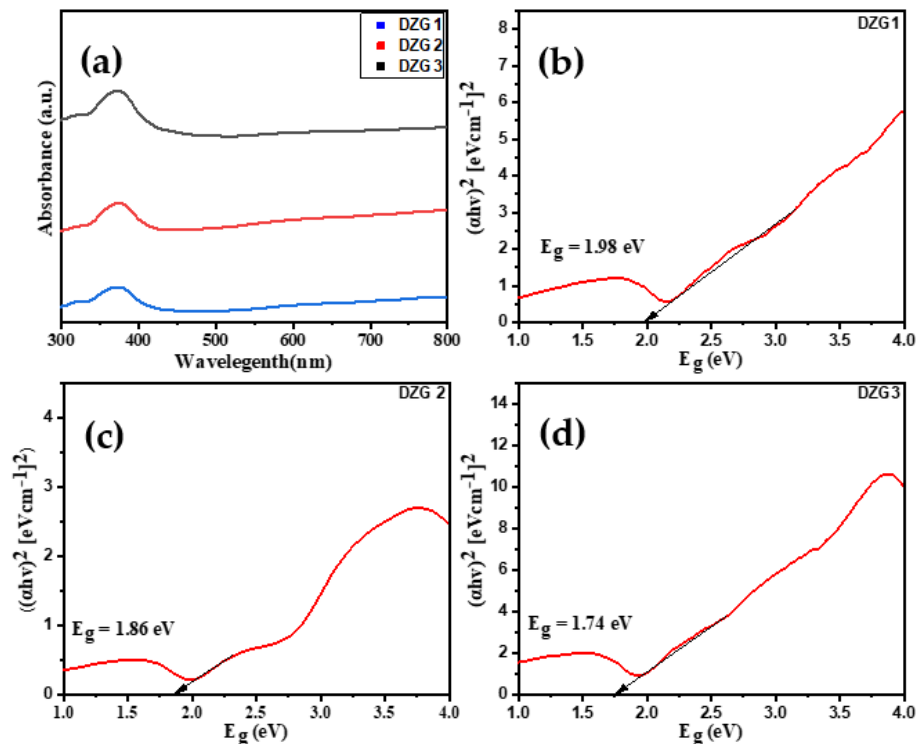


Figure 4. (a) UV-Vis spectrum; (b)–(d) Tauc's plot of Dy^{3+} doped $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites (DZG1, DZG2, and DZG3).

4.5. Dielectric properties

The real part of dielectric permittivity (ϵ') represents the material's ability to retain electric polarization, while the imaginary part (ϵ'') reflects its capacity to dissipate power through electric loss [38]. The following formula is used to calculate ϵ' :

$$\epsilon' = \frac{c t}{A \epsilon_0} \quad (14)$$

Here, "c", "t" and "A" indicate capacitance, thickness and surface area of pellet, ϵ_0 is the permittivity of free space having value $8.85 \times 10^{-12} \text{ m}^{-3} \text{ kg}^{-1} \text{ s}^4 \text{ A}^2$. The loss factor of a dielectric material (ϵ'') is calculated from Equation (15):

$$\epsilon'' = \tan \delta \times \epsilon' \quad (15)$$

Here, ϵ'' denotes the loss factor, while δ indicates the loss angle [39,40]. The dielectric constant (ϵ') varies with applied frequency, as shown in Figure 5(a). In Dy^{3+} doped $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites (DZG1, DZG2, and DZG3), dielectric constant values increased with increasing $\text{g-C}_3\text{N}_4$ content. Figure 5(b) shows the relation between the dielectric loss factor (ϵ'') with $\log f$. With increasing frequency, the decrease in dielectric constant and loss indicates improved charge carrier mobility and reduced polarization lag, favoring efficient electron hopping between $\text{Fe}^{2+}/\text{Fe}^{3+}$ sites. The DZG3 composite exhibits comparatively higher dielectric permittivity and lower impedance, reflecting enhanced charge transport and reduced recombination probability. These dielectric characteristics directly support the improved photocatalytic efficiency of DZG3 by facilitating effective separation and migration of photogenerated charge carriers.

The following formula can be used to determine the dielectric material's tangent loss (δ) [41].

$$\tan (\delta) = \frac{1}{2 \pi f R C} \quad (16)$$

The variation of tangent loss (δ) with frequency is illustrated in Figure 5(c). Notably, the tangent loss peaks at lower frequencies, indicating that higher material levels contribute to greater energy dissipation as heat.

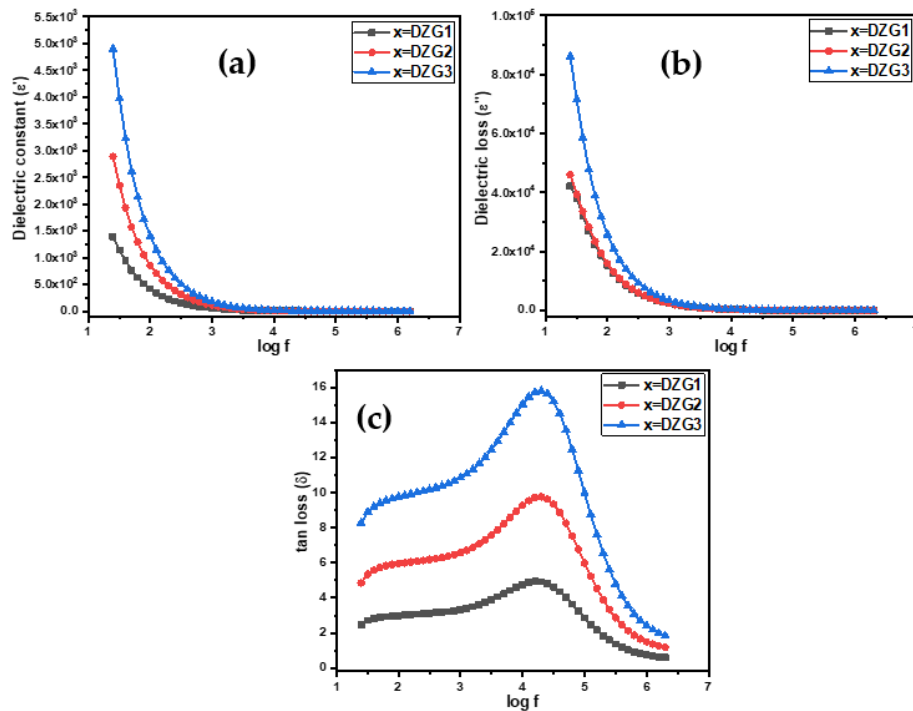


Figure 5. Log f verses (a) ϵ' ; (b) ϵ'' ; (c) $\tan \delta$ (d) Dy^{3+} doped $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites (DZG1, DZG2, and DZG3).

The conductivity of the material is determined using the formula:

$$\sigma = \sigma_{ac} + \sigma_{dc} \quad (17)$$

The second term on the right side of Equation (17), referred to as DC conductivity, remains invariant with frequency. In contrast, the first term, known as AC conductivity, varies with frequency and can be calculated using the Equation (18):

$$\sigma_{ac} = \pi f \epsilon'' \epsilon_0 \quad (18)$$

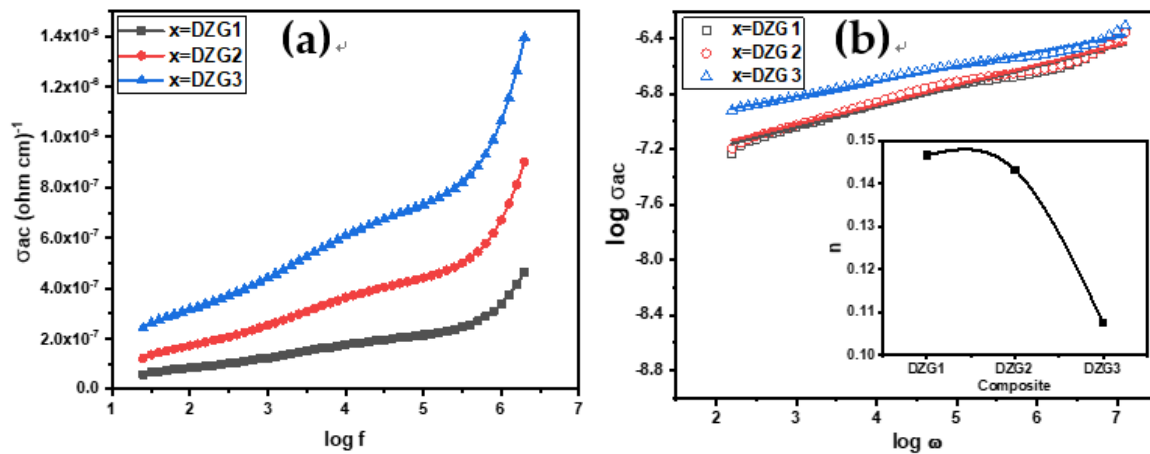
Here, ϵ'' stands for the imaginary part of the dielectric constant and ϵ_0 for the permittivity of free space. For prepared composites, the variation of AC conductivity with the log f is shown in Figure 6(a). Plotting the graph of $\log(\sigma_{ac})$ versus $\log(\omega)$, as illustrated in Figure 6(b), enables the determination of the exponent "n" through the relation (Equation (19)):

$$\sigma(\omega) = B \times \omega^n \quad (19)$$

With an intercept equal to $\log B$ at $\log \omega = 0$ and a slope equal to the exponent "n", the plot of $\log(\sigma_{ac})$ against $\log(\omega)$, shows a nearly constant relationship. The value of 'n' ranges between 0 and 1. When "n" equals 0, electrical conduction remains independent of frequency. Conversely, as "n" approaches value greater than 0 but less than or equal to 1, electrical conduction becomes frequency dependent. The prepared samples exhibit frequency-dependent behaviour, as indicated by the exponent values which range from 0.10 to 0.15.

For Dy^{3+} doped $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites (DZG1, DZG2, and DZG3) composites, Figure 6(c,d) show the complex and electrical modulus (M' and M'') varies with the $\log \omega$. The complex and electrical modulus, calculated using the equations below, are essential for determining the total electrical modulus (M_{total}):

$$M_{total} = M' + j M'' \quad (20)$$



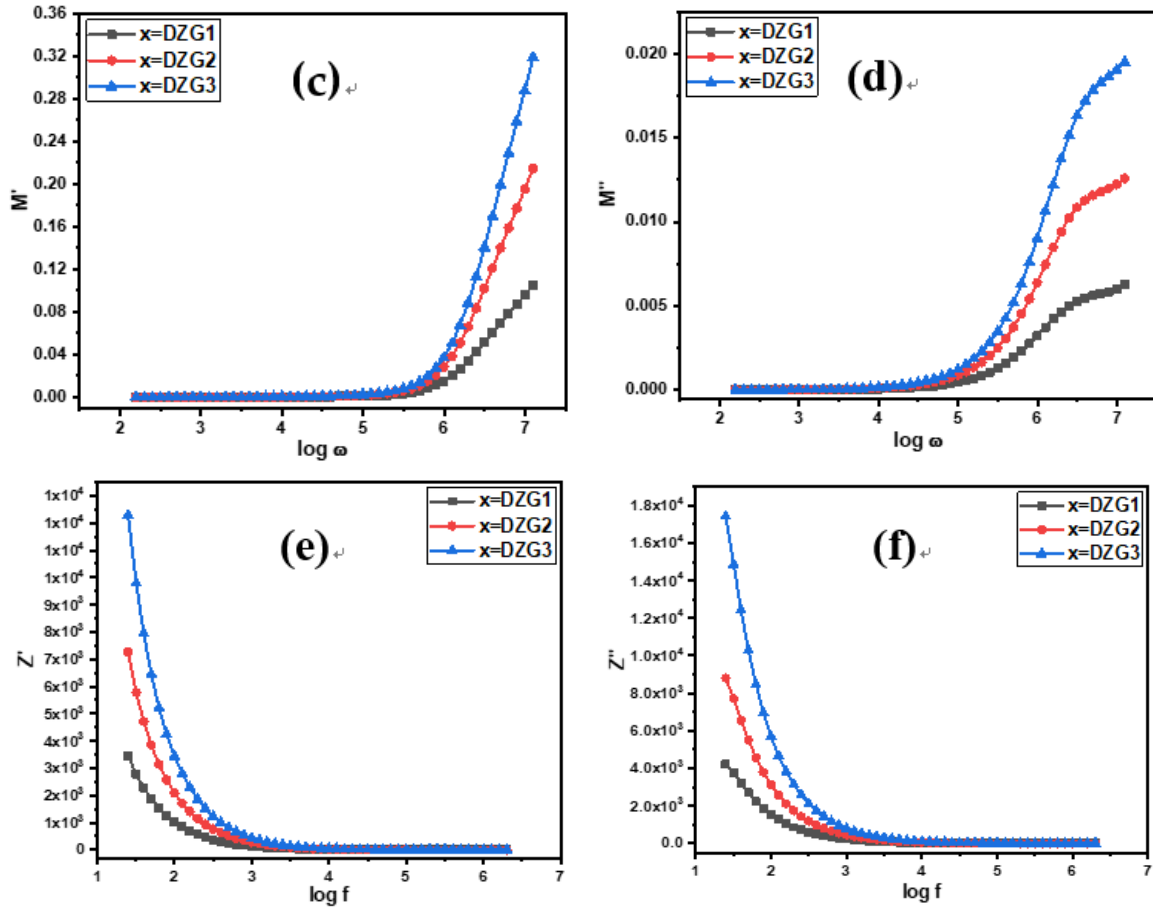


Figure 6. Frequency verses (a) σ_{ac} ; (b) $\log \sigma_{ac}$ vs. $\log \omega$ (dotted line and solid line represent experimental and linear fit, respectively), inset: Frequency exponent “n” vs. composites; (c) M' ; (d) M'' ; (e) Z' ; (f) Z'' of Dy^{3+} doped $ZnFe_2O_4/g-C_3N_4$ nanocomposites (DZG1, DZG2, and DZG3).

Equation (21) can be used to calculate the first factor in the above equation:

$$M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad (21)$$

Equation (22) can be used to find the second factor in Equation (20):

$$M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (22)$$

Both complex and electrical modulus at lower frequencies retain a constant value, which can be attributed to the ionic polarization, as illustrated in Figure 6(e,f) [42]. The variation of the frequency-dependent real part of impedance (Z') is depicted in Figure 6(e). The impedance can be computed using the following relation, taking into account both its real and imaginary parts [43]:

$$Z = Z' + jZ'' \quad (23)$$

where Z' stands for the complex impedance's resistive component and Z'' for its reactive component. Grain boundaries play a major role in the higher values of impedance (Z') at lower frequencies; however, as frequency increases, this influence decreases. Notably, the substitution of Dy^{3+} ions lead to a reduction in Z' , showing an improvement in the material's conductivity at minimum frequencies. Figure 6(f) shows the relationship between frequency and the imaginary part (Z'') of impedance. At lower frequencies, the value of Z'' increases with the substitution of Dy ions. Furthermore, a greater

Z'' value and a general rise in material impedance (Z'') resulted from additional increases in Dy content.

4.6. Effect of different parameters on RhB degradation

The efficiency of the photocatalyst in degrading RhB under sunlight is directly affected by pH amount of the solution. The research is carried out to evaluate the effect of pH on the degradation of RhB. For this purpose, at various pH ranges of 2–9, the ability of the photocatalyst degradation of RhB was checked. Diluted HCl or NaOH is used to change the pH of the solution. Due to the formation of aromatic hydroxylase species, the degradation efficiency of RhB decreased at pH values (i.e., 9). The condition of optimum pH is essential for preventing the wastage of excess amount of catalyst and maximizing the absorption of visible light for improved photodegradation [44]. Dy^{3+} doped $ZnFe_2O_4/g-C_3N_4$ nanocomposites (DZG1, DZG2, and DZG3) for DZG3 exhibits a maximum degradation efficiency of 96.5% at pH 8 within 75 min as shown in Figure 7(a). The enhanced performance was attributed to the increased availability of active sites, efficient charge separation facilitated by Dy^{3+} doping and the strong adsorption of RhB at the catalyst surface. The production of hydroxyl radicals ($\bullet OH$), which are essential for the degradation process, is encouraged by the slightly alkaline pH 8 environment while the radicals seen at higher pH levels (such as pH 9) are reduced. This optimal pH condition ensures efficient visible light absorption and prevents excessive catalyst consumption, highlighting the significance of tailoring reaction parameters for practical water purification applications.

The efficiency of RhB dye degradation increased for all catalysts, but especially for DZG3, when the catalyst dosage was raised from 10 to 80 mg for 50ml of dye solution at pH 8 and exposed to radiation for 75 min, as Figure 7(b) illustrates. The more catalyst load there were, the more active sites there were on the photocatalytic surface, which led to an increase in hydroxyl radicals. The photo degradation efficiency of prepared material at different concentrations were enhanced from 70% to 96.5% as the composite dosage was enhanced from 10 to 40 mg. Additionally, it was noted that a continued rise in photocatalyst dosage led to a decrease in degradation efficiency in all samples. The reason for this is that as the catalyst dose increases, the number of active sites much enhanced causing penetration of light slow due to shielding effect.

To optimize the oxidant dose, the concentration of H_2O_2 varied from 2 to 14 mM. The impact of oxidant dosage on dye degradation is studied using prepared composites. Figure 7(c) demonstrates that increasing the oxidant dose causes degradation to increase up to a point, after which it begins to decrease. The optimization process of H_2O_2 was carried out by following experimental conditions such as pH = 5, catalyst dosage = 40 mg Dy^{3+} doped $ZnFe_2O_4/g-C_3N_4$ nanocomposites (DZG1, DZG2, and DZG3) with 10 ppm RhB dye for 75 min irradiation time. The effects of varying H_2O_2 concentrations from 2 to 14 mM on RhB photodegradation were observed, as shown in Figure 7(c). When H_2O_2 dosage was increased from 2 to 6 mM, RhB removal efficiency increased correspondingly from 71% to 95.5% for Dy^{3+} doped $ZnFe_2O_4/g-C_3N_4-X$ ($X = 0.2, 0.3, 0.4$). Increasing the concentration of H_2O_2 in RhB. The formation of ($\bullet OH$) radicals was enhanced by the dye solution critical for the degradation process [45].

The effect of irradiation time on degradation (%) at optimum conditions was analyzed and represented in Figure 7(d). By taking samples out of the dye solution at various times, the percentage of degradation was determined. A noticeable increase in RhB degradation was observed in the early phases of irradiation. Over time, the rate of breakdown decreases. RhB requires a specific amount of time to be fully degraded by the catalyst's active site. This is because the pH of the solution affects the generation of ($\bullet OH$) radicals, which causes the degradation rate in removal processes to progressively slow down [46]. When the process is just getting started, these radicals are essential for the breakdown of RhB molecules. However, the rate of degradation slows down as the irradiation increases. The slow saturation of the catalyst's active sites and the loss of easily accessible RhB molecules in the solution are the causes of this decrease.

A photocatalyst's stability and reusability must be examined from an economic and environmental perspective. After completing the degradation reaction, the composites were recovered using a magnet, washed three times with distilled water and oven-dried at 80 °C. Once dried, the composites were reused for subsequent cycles. Every composite undergoes a reusability study at the same optimal conditions, such as pH 8, oxidant dose 8 milli M and composite dosage 40 mg/50 mL for tested samples (DZG1, DZG2, and DZG3). Figure 7(e) shows that the photocatalyst can be reused up to five times while maintaining 84% photocatalytic activity and causing little loss in product yield.

4.7. Kinetics of photodegradation reaction

The experimental data of Dy³⁺ doped ZnFe₂O₄/g-C₃N₄ nanocomposites (DZG1, DZG2, and DZG3) composites was analyzed using the pseudo first-order kinetic model for the quantitative investigation of RhB degradation shown in Figure 7(f). The Equation (24) is specifically created for photocatalytic studies when the pollutant concentration is taken in the millimolar range.

$$\ln \frac{C_0}{C_t} = -kt \quad (24)$$

Figure 8 shows a linear relationship between $\ln (C_0/C_t)$ and reaction time. Where C_t is the final concentration of RhB at time t and C_0 is the initial concentration degradation of RhB by ternary and binary composites following first order. The first-order R^2 values for DZG1, DZG2, and DZG3 composites are 0.9336, 0.9453, and 0.9426, respectively. The reaction rate constants and R^2 values for Rhodamine B (RhB) degradation are shown in Table 4. A detailed comparison of photocatalysis of the current work with previously reported work is given in Table 5.

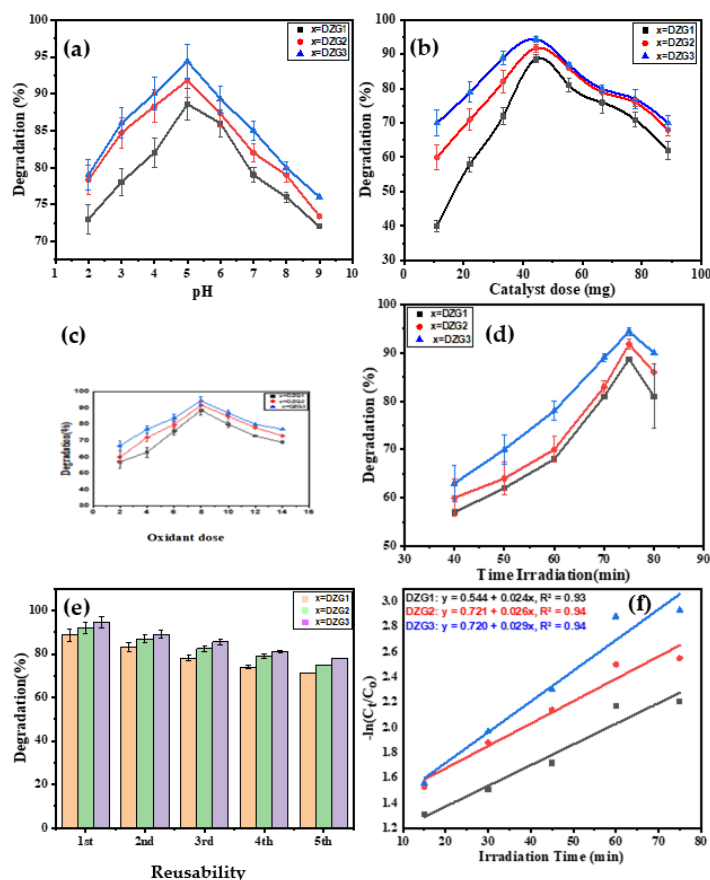


Figure 7. Effects of (a) pH; (b) catalyst dose; (c) oxidant dose; (d) irradiation time; (e) reusability; (f) first-kinetic model of Dy³⁺ doped ZnFe₂O₄/g-C₃N₄ nanocomposites (DZG1, DZG2, and DZG3) on d egradation efficiency.

Table 4. Kinetic model fitting of first order for RhB degradation using composites.

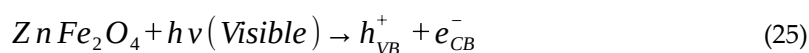
Photocatalyst	K (min ⁻¹) 1st order	R ² value for pseudo-1st order
DZG1	0.00036	0.9336
DZG2	0.00032	0.9453
DZG3	0.00029	0.9426

Table 5. Comparison of photocatalytic performance of the current work with reported literature.

Material/Composite	Dye used	Degradation time (min)	Efficiency (%)	Reference
ZnFe ₂ O ₄ /ZnO	Congo red	75	93	[47]
ZnFe ₂ O ₄ /CdS-GO	RhB	40	82	[48]
ZnFe ₂ O ₄ /CoFe ₂ O ₄	MB	180	100	[23]
ZnFe ₂ O ₄ /Ag	tetracycline	80	90	[18]
ZnFe ₂ O ₄ /CdS	RhB	60	93	[49]
ZnFe ₂ O ₄ /CNTs	RhB	120	72	[21]
ZnFe ₂ O ₄ /WO ₃	Crystal Violet	45	90	[50]
ZnFe ₂ O ₄ /g-C ₃ N ₄	Uranium	90	94.62	[51]
Dy ³⁺ -ZnFe ₂ O ₄ /g-C ₃ N ₄	RhB	75	96.5	Present work

4.8. Photodegradation mechanism

A photocatalytic mechanism is illustrated in Figure 8. As illustrated in Figure 8, Dy³⁺ ions introduce intermediate 4f energy levels within the ZnFe₂O₄/g-C₃N₄ heterojunction, acting as electron-trapping and transfer centers. These localized energy states facilitate interfacial charge migration from ZnFe₂O₄ to g-C₃N₄, suppress reverse electron transfer, and significantly reduce electron-hole recombination. Consequently, the prolonged charge-carrier lifetime enhances the generation of reactive oxygen species (•OH and •O₂⁻), leading to improved RhB photodegradation efficiency. When there is visible light, the movement of electrons (e⁻) from ZnFe₂O₄ to g-C₃N₄ and the transfer of holes (h⁺) from g-C₃N₄ to ZnFe₂O₄ occur through Dy³⁺ as an electron mediator. In this process, the valence band holes of ZnFe₂O₄ and conduction band electrons of g-C₃N₄ undergo charge transference through a conventional heterojunction mechanism. The photoinduced holes in the valence band (VB) of ZnFe₂O₄ are absorbed through, using H₂O to produce •OH radicals. Additionally, the photoinduced electrons in the conduction band (CB) of g-C₃N₄ are captured by dissolved oxygen. Consequently, the •O₂⁻ anion reacts with H₂O₂ to generate the hydroxyl radical, which efficiently degrades the RhB dye. RhB breaks down into certain inorganic ions, CO₂, and H₂O. Therefore, it suggests using the Dy³⁺-doped ZnFe₂O₄/g-C₃N₄ composite as a photocatalyst due to its high photocatalytic activity, longer charge-carrier lifetime, and higher charge-separation efficiency. Specifically, Dy³⁺ can promote electron transfer from ZnFe₂O₄ to g-C₃N₄ and suppress the reverse transfer to ZnFe₂O₄. Consequently, the photoactivity of Dy³⁺ doped ZnFe₂O₄ with g-C₃N₄ was significantly improved. Some steps involved in this process are given:



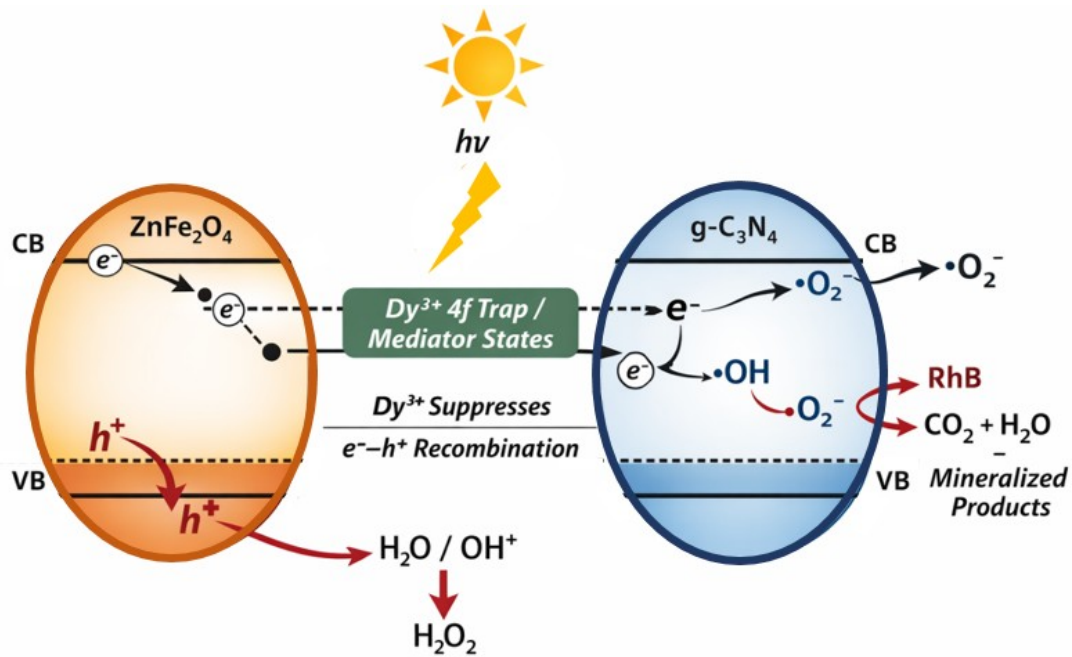
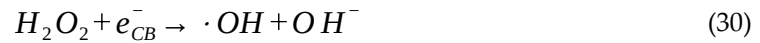
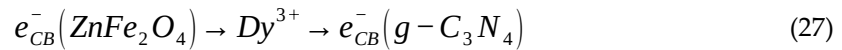
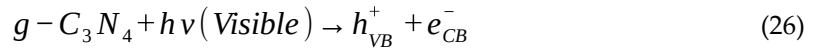


Figure 8. Schematic diagram of photocatalytic activity.

5. Conclusion

This study presents the novel application of Dy^{3+} -doped $ZnFe_2O_4$ supported on $g-C_3N_4$ as an efficient electron-mediated photocatalyst for dye degradation under solar light irradiation. Dy^{3+} -doped $ZnFe_2O_4/g-C_3N_4$ nanocomposites (DZG1, DZG2, and DZG3) were successfully synthesized via a simple co-precipitation method and systematically characterized using XRD, SEM/EDX, FTIR, UV-Vis spectroscopy, and dielectric analyses. Structural investigations confirmed the formation of a cubic spinel $ZnFe_2O_4$ phase, while morphological studies revealed improved particle dispersion upon $g-C_3N_4$ incorporation. Dielectric studies exhibited pronounced frequency-dependent behavior, with variations in dielectric constant, dielectric loss, and tangent loss, indicating enhanced charge transport and polarization effects that support efficient photocatalytic activity. Among the synthesized composites, the DZG3 sample demonstrated superior photocatalytic performance, achieving 96.5% RhB degradation within 75 min under optimized conditions, including

pH 8, a catalyst dosage of 40 mg/100 mL, and an H_2O_2 concentration of 8 mM. Compared to DZG1 and DZG2, the enhanced activity of DZG3 is attributed to improved visible-light absorption, efficient charge separation, and the electron mediator role of Dy^{3+} ions at the $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ interface. Furthermore, the Dy^{3+} -doped $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites exhibited good durability, magnetic recoverability, and reusability, highlighting their potential for practical environmental remediation applications. The facile synthesis route and stable photocatalytic performance underscore the feasibility of this material system for scalable wastewater treatment. Overall, this work demonstrates an effective strategy to enhance the photo-efficiency and recyclability of $\text{g-C}_3\text{N}_4$ -based photocatalysts through rare-earth-mediated heterojunction engineering, with the DZG3 ($x = 0.4$) composite showing the most promising performance.

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Author Contributions: SA contributed to the experiments, software, formal analysis, writing-original draft, and editing; HA contributed to the supervision, conceptualization, project management, and writing-review; KA and MZ contributed by providing resources and writing-review. All authors have read and approved the final manuscript. All authors contributed to editorial changes in the manuscript. All authors have participated sufficiently in the work and agreed to be accountable for all aspects of the work.

Conflicts of 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.

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