

Research Article

In Situ g-C₃N₄@ZnO Nanocomposite: One-Pot Hydrothermal Synthesis and Photocatalytic Performance under Visible Light Irradiation

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Received 4 December 2020; Accepted 3 May 2021; Published 11 May 2021

Academic Editor: Matjaz Valant

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In situ g-C₃N₄@ZnO nanocomposites (with 0, 1, 3, 5, and 7 wt.% of g-C₃N₄ in nanocomposite) were synthesized via a one-pot hydrothermal method using precursors of urea, zinc nitrate hexahydrate, and hexamethylenetetramine. The g-C₃N₄@ZnO nanocomposites were characterized by X-ray diffraction, scanning electron microscope, diffuse reflectance spectroscopy, and photoluminescence spectroscopy. The photocatalyst activity of g-C₃N₄@ZnO nanocomposites was evaluated via methylene blue degradation experiment under visible light irradiation. The g-C₃N₄@ZnO nanocomposites showed an enhancement in photocatalytic activity in comparison to pure ZnO which increased with the g-C₃N₄ content (1, 3, 5, and 7 wt.%) in nanocomposites. The photocatalytic activity reached the highest efficiency of 96.8% when the content of g-C₃N₄ was 7.0 wt.%. Nanocomposite having 7.0 wt.% of g-C₃N₄ also showed good recyclability with degradation efficiency higher than 90% even in the 4th use. The improvement of photocatalytic activity could be attributed to the adsorption ability and effective separation of electron-hole pairs between g-C₃N₄ and ZnO. This work implies a simple method to in situ prepare the nanocomposite material of g-C₃N₄ and semiconductors oxide for photocatalyst applications with high efficiency and good recyclability.

1. Introduction

The economic development in recent decades has led to very serious environmental problems due to the uncontrolled release of harmful pollutants in water and air. Developing cost-effective and simple technologies for removing harmful pollutant is one of the most attentive matters to research recently [1–3]. Photocatalysis is considered a promising technique to treat contaminated water because the photocatalysis process is eco-friendly and economical and is capable of degrading several organic dyes or pollutants [1, 4–13].

Zinc oxide (ZnO) is a metal oxide semiconductor with a direct wide bandgap (3.2 eV), high mechanical, thermal, and chemical stability, nontoxic nature, and low cost [14–16]. ZnO is considered one of the most promising materials for photocatalytic application. However, due to the large bandgap, ZnO exhibits relatively low photocatalytic activity under visible light in comparison with under UV light. Moreover, the fast recombination of charge carriers in ZnO restricts its practical applicability [15, 17–20]. To efficiently overcome these limitations, many efforts have been made to improve the photocatalytic activity of ZnO-based

photocatalysts through doping or compositing with metals, nonmetals, carbon-based materials (graphene, graphene oxide, and reduced graphene oxide) [21, 22] or coupling with visible bandgap semiconductor to create Z-scheme [15, 23, 24]. However, the development of an efficient ZnO-based photocatalyst with improved photocatalytic efficiency is still in progress.

Graphitic carbon nitride (g-C₃N₄) is a stable, metal-free, *p*-conjugative, and *n*-type polymeric semiconductor with a narrow bandgap (2.7 eV) [23] which could act as a desirable partner to ZnO to make a good visible-light-responsive photocatalytic composite [25–28]. Therefore, coupling ZnO with g-C₃N₄ could yield an excellent heterostructure to improve charge separation, especially since the two materials have well-matched, overlapping band structures. Previous research has shown that these heterostructures exhibit an improvement in photocatalytic activity. The improvement is explained via the transfer of a visible-light-induced electron from the conduction band (CB) of the g-C₃N₄ to the CB of ZnO [2, 29–31].

In this paper, an attempt has been made to prepare and characterize in situ nanocomposite g-C₃N₄@ZnO using the one-pot hydrothermal method at low temperature. Effects of g-C₃N₄ content on the microstructural, optical properties and photocatalytic activities of g-C₃N₄@ZnO were investigated via X-ray diffraction, PL spectra, diffuse reflectance spectra, and scanning electron microscopy analysis. The photocatalytic activity was evaluated through the degradation experiment of methylene blue (MB) dye under visible-light irradiation. The recyclability of nanocomposite was also studied. Besides, the photocatalytic mechanism of g-C₃N₄@ZnO was also discussed.

2. Materials and Methods

2.1. Samples Preparation. All chemicals were of analytical grade and were used without any further purification. Graphitic carbon nitride (g-C₃N₄) was synthesized by pyrolyzing urea in a muffle furnace at 520°C for 2h. After cooling down gradually to room temperature (RT), the annealed sample was ground by an agate mortar to obtain the g-C₃N₄ powder in light yellow colour for further use.

Nanocomposites of zinc oxide and graphitic carbon nitride were synthesized by the one-step hydrothermal method via the following process: dissolving 1.485 g Zn(NO₃)₂·6H₂O into 50 ml bidistilled water, dissolving 0.700 g HMTA into 50 mL bidistilled water, mixing two solutions with the [HMTA]/[Zn²⁺] volume ratio of 1 : 1 under stirring for 10 mins at RT, and adding g-C₃N₄ into these solutions. The resulting mixture was transferred to an autoclave for the hydrothermal route at 90°C for 6 h. The products were collected and rinsed twice with absolute ethanol and distilled water and then dried in the oven at 80°C for 24 h. Finally, a fine white to grey powder was obtained. We named the samples prepared with different g-C₃N₄ content as 1, 3, 5, and 7 wt.% as Z-1C, Z-3C, Z-5C, and Z-7C, respectively.

2.2. Characterization. The crystal structure and phase purity were obtained by using the X-ray diffraction (XRD) system of X'Pert Pro (PANalytical) MPD with CuK- α 1 radiation

(= 1.54056 Å) at a scanning rate of 0.03°/2s in the 2θ range from 20° to 80°. The crystal analysis was performed by HighScore Plus software using the ICDD database. The morphology of the g-C₃N₄@ZnO nanocomposite was analysed by scanning electron microscopy (SEM). The distribution of g-C₃N₄ in the ZnO platform was evaluated via the elemental mapping images using Tabletop Microscope HITACHI TM4000Plus. The diffusion reflectance spectra of samples were obtained by JASCO V-750 using 60 mm Integrating Sphere ISV-922. The PL spectra of the samples were measured by NanoLog fluorescence spectrometer (HORIBA JOBIN YVON) with imaging spectrometer iHR 320 and xenon lamp light source with an excitation wavelength of 325 nm.

2.3. Photocatalytic Experiment. The photocatalytic efficiencies of the g-C₃N₄@ZnO nanocomposites and pristine ZnO were evaluated via methylene blue (MB) degradation experiment at room temperature. Typically, 50 mg of the photocatalyst was dispersed in 100 mL MB aqueous solution (10 mg/L). The above mixture was stirred in dark for 60 min to achieve an adsorption-desorption equilibrium. The mixture was then illuminated under visible irradiation using a 250 W Osram lamp equipped with a 420 nm cut-off filter at room temperature. A mixture of 5 mL solution was sampled at each 15-minute interval and then was centrifuged to remove the photocatalyst solids at 7000 rpm for 10 mins. The UV-Vis absorption spectra of the resulting supernatant were measured by a Cary 100 spectrophotometer (VARIAN) to determine the MB concentration.

The degree of MB degradation (*D*) was estimated through the remaining MB concentration in aliquot which is proportional to the intensity of 664 nm characteristic peak in UV-Vis spectra. The MB degradation is calculated via the following equation:

$$D = \frac{C_o - C_t}{C_o} \times 100\% = \frac{I_o - I_t}{I_o} \times 100\%, \quad (1)$$

where *C*_o (mg/L) is the initial MB concentration; *C*_{*t*} (mg/L) is the MB concentration in aliquots at time *t* during the photocatalytic reaction; *I*_o is the intensity of 664 nm peak in UV-Vis spectrum of initial MB solution. It is the intensity of 664 nm peak in UV-Vis spectrum of aliquots at time *t* during the photocatalytic reaction.

3. Results and Discussion

3.1. XRD Analysis. The XRD patterns of the g-C₃N₄@ ZnO nanocomposite with g-C₃N₄ contents and ZnO are presented in Figure 1 (the XRD pattern of pure g-C₃N₄; see supplementary figure S1 in which the characteristic peaks of g-C₃N₄ are well observed [31]). The characteristic diffraction peaks of ZnO can be attributed to the hexagonal wurtzite structure (JCPDS 36-1451 card) [32]. The diffraction peaks of a g-C₃N₄@ZnO nanocomposite are similar to those of pure ZnO. No diffraction peaks corresponding to g-C₃N₄ are observed in g-C₃N₄@ZnO nanocomposite. Furthermore, no

other new crystal phases in the preparation process are found.

To understand the effect of g-C₃N₄ on the structure and crystallite size of ZnO, the Williamson-Hall formula is used to analyse the XRD data which is expressed as follows [33–35]:

$$\beta * \cos \theta = \frac{0.9 * \lambda}{D} + 2\varepsilon * \sin \theta, \quad (2)$$

where β is the full width at half maximum of the peak at the diffraction angle 2θ , θ is the diffraction angle, $\lambda = 1.54060 \text{ \AA}$ is a wavelength of the used X-ray, ε is the micro strain, and d is the average crystallite size.

A plot of $\beta * \cos \theta$ versus $\sin \theta$ is a linear presentation of the data XRD, and the crystallite size and micro strain are, respectively, obtained from the intercept and slope of the line. The results obtained are listed in Table 1. The results demonstrate that the crystallite size of ZnO is also strongly affected by the appearance of g-C₃N₄, in which the average crystallite size of ZnO reduces from 49.5 nm to 40.8 nm in correspondence with the increase of g-C₃N₄ content in nanocomposite materials. The appearance of g-C₃N₄ also causes the micro strain to reduce in samples where the strain reduces from 0.00407 to 0.00323 when g-C₃N₄ content increases from 1 to 7%. The results show the strong effect of g-C₃N₄ on the crystal properties of in situ nanocomposites.

3.2. SEM Analysis. The SEM observations presented in Figure 2 detail the surface morphologies of the prepared samples. As shown in Figure 2(a), pure g-C₃N₄ is fluffy and porous. Pure ZnO is composed of a large number of aggregated nanorods (Figure 2(b)). Notably, the ZnO nanorods in g-C₃N₄@ZnO nanocomposite are well dispersed over the composite surface (Figures 2(c)–2(f)).

Figure 3 shows the element mapping images including C, N, O, and Zn in g-C₃N₄@ZnO sample with 7 wt.% g-C₃N₄. The mapping images show that the elements C, N, O, and Zn appear in Z-7C and the elements are uniformly distributed in the nanocomposite which also implies that there is coappearance of g-C₃N₄ and ZnO in the nanocomposite.

3.3. UV-Vis Diffuse Reflectance Spectroscopy Analysis. UV-vis diffuse reflectance spectroscopy (DRS) was conducted to investigate the effect of g-C₃N₄ on the optical properties of g-C₃N₄@ZnO samples. The incorporation of g-C₃N₄ into ZnO leads to a decrease in the UV-vis reflectance (or the increase of the absorption) over the entire wavelength range. As presented in Figure 4, the sharp fundamental reflectance edge rises at about 390 nm for the pure ZnO nanorods, with almost no absorption in the visible-light region which is consistent with the fact that ZnO NRs almost can only make use of ultraviolet light [35]. Compared to the pure ZnO and g-C₃N₄, the g-C₃N₄@ZnO extends the absorbance to not only the ultraviolet region but also the visible region, suggesting that the recombination rate of the photoinduced electrohole pairs was successfully reduced in the heterostructured g-C₃N₄@ ZnO nanocomposite.

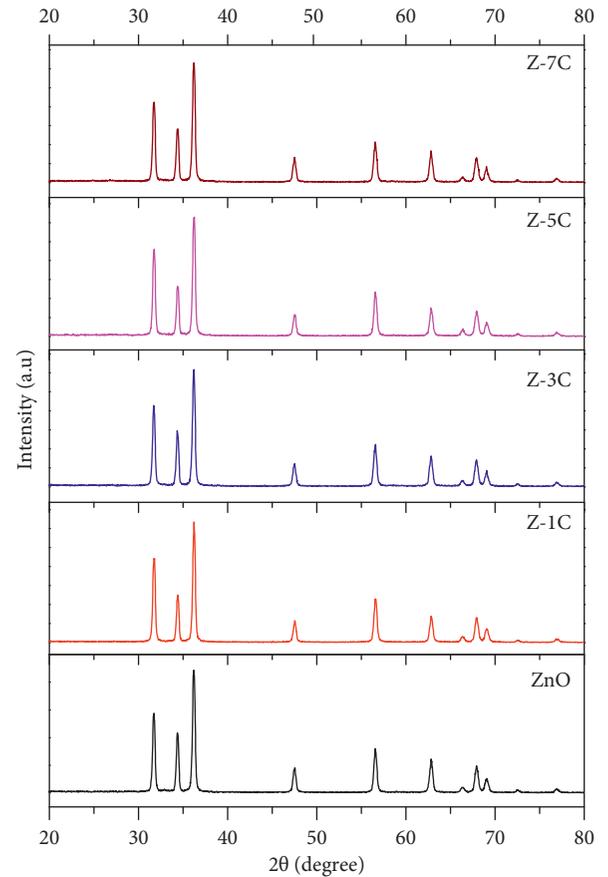


FIGURE 1: XRD pattern of g-C₃N₄@ZnO nanocomposite samples on the range from 20 to 80°.

TABLE 1: The average crystallite size of ZnO and nanocomposite samples calculated via Williamson-Hall formula.

Samples	D Williamson-Hall (nm)	Micro strain (ε)	R^2
ZnO	49.5	0.00362	0.9952
Z-1C	47.8	0.00407	0.9921
Z-3C	46.2	0.00392	0.9959
Z-5C	44.7	0.00371	0.9935
Z-7C	40.8	0.00323	0.9931

From the DRS data, there are routes to get the information of bandgap value (called optical bandgap) indirectly using modified Kubelka-Munk function [36–38].

In the Kubelka-Munk method, the relation between the function of diffuse reflectance $F(R)$ and the incident photon energy $h\nu$ is expressed in the following equation:

$$F(R)h\nu = D(h\nu - E_g)^n, \quad (3)$$

where $F(R)$ is determined from diffuse reflectance R via the formula $F(R) = (1-R)^2/2R$; $h\nu$ is the incident photon energy; D is an arbitrary coefficient; $n = 1/2$ and 2 for direct and indirect allowed recombinations, respectively, and E_g is the optical bandgap of the sample [38].

From this relation, we can extrapolate the value of E_g from the plots of $[F(R) * h\nu]^2$ versus $h\nu$ as shown in Figure 4(b) for ZnO or we can evaluate based on the plot of

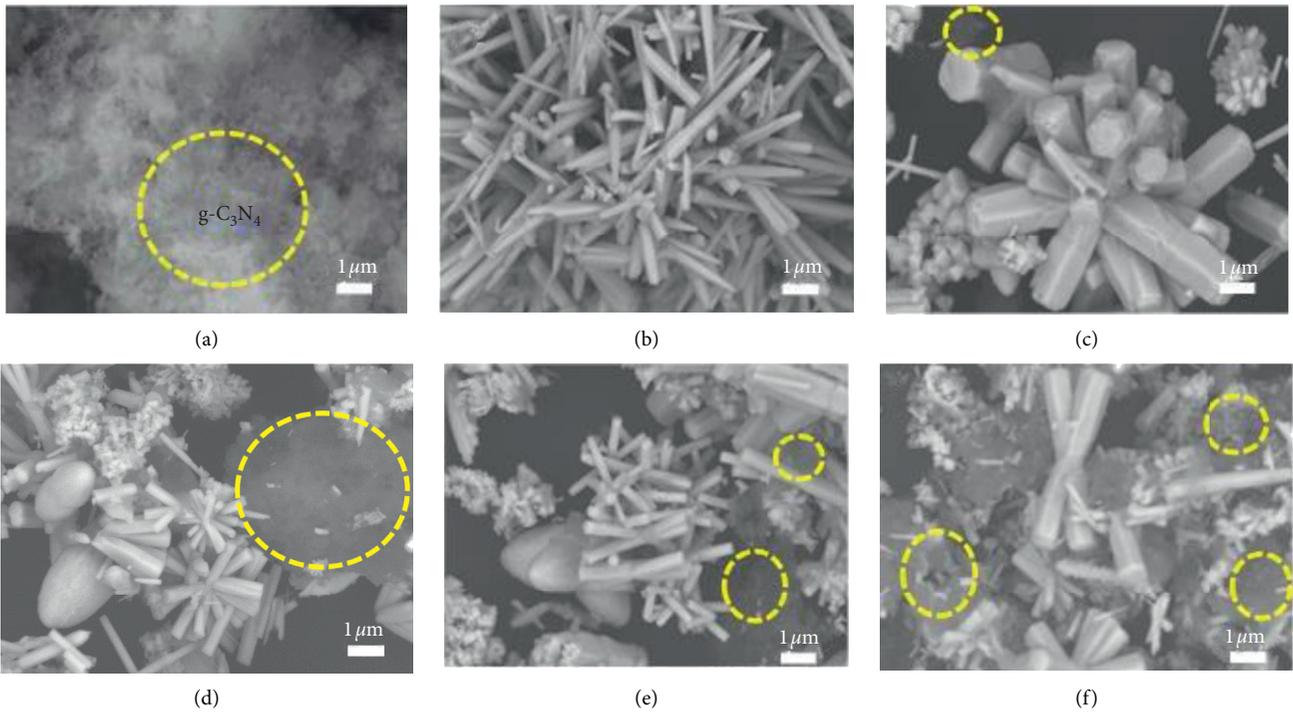


FIGURE 2: SEM images of (a) $g\text{-C}_3\text{N}_4$, (b) ZnO, (c) Z-1C, (d) Z-3C, (e) Z-5C, and (f) Z-7C.

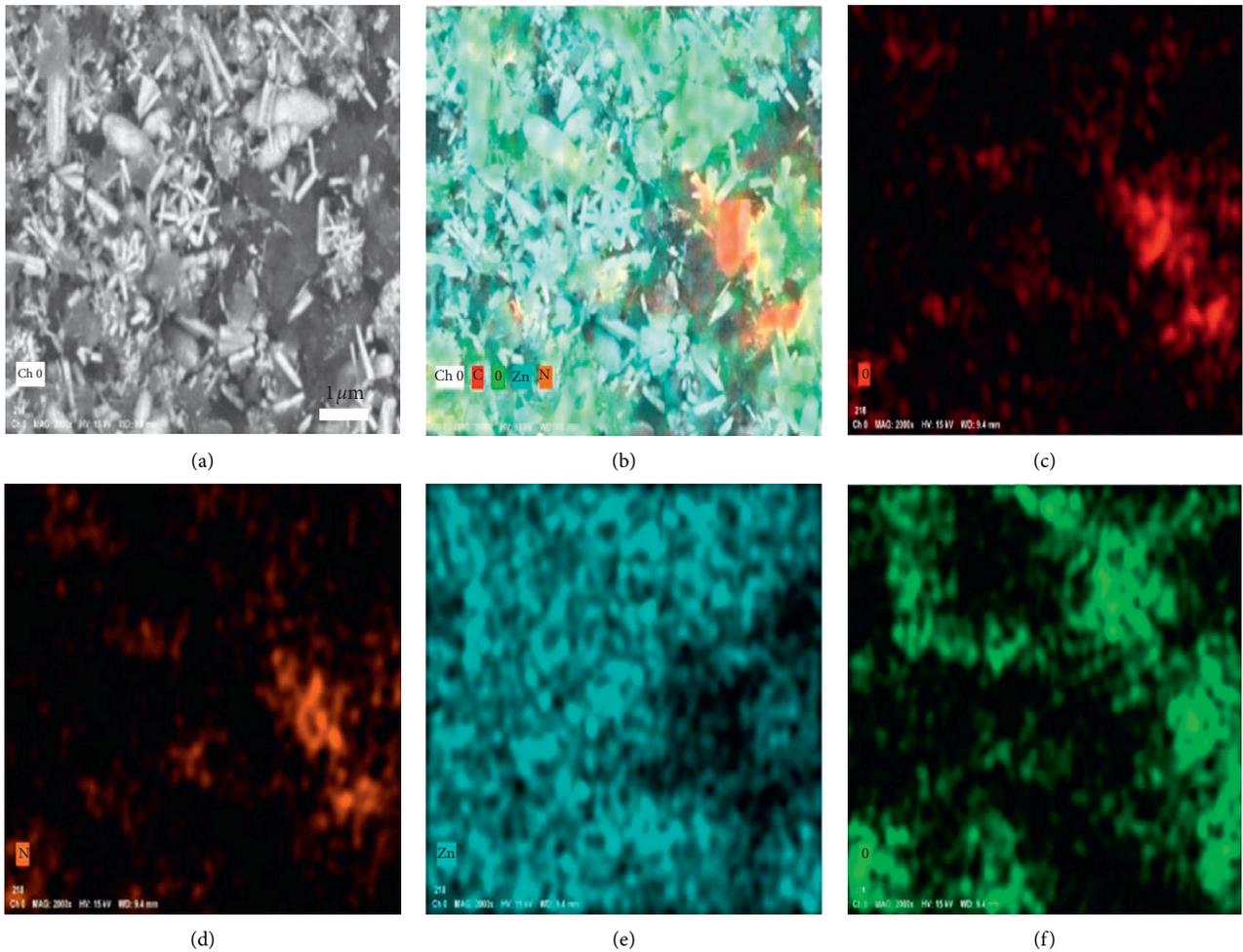


FIGURE 3: The EDX elemental mapping images of C, N, O, and Zn of Z-7C sample.

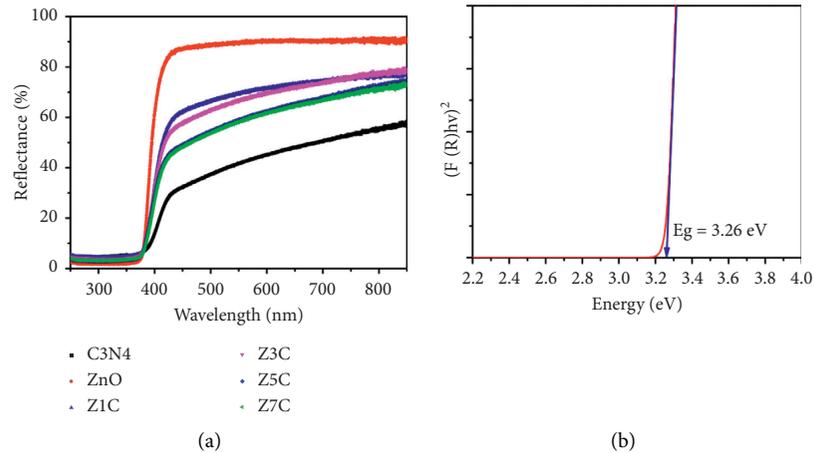


FIGURE 4: Reflectance spectra of g-C₃N₄@ZnO nanocomposites (a) and $(F(R)hv)^2$ versus (hv) plot of pure ZnO (b).

$[F(R) * hv]^{1/2}$ versus hv as shown in Figure S2 for g-C₃N₄ and g-C₃N₄@ZnO. The optical bandgap of the pure g-C₃N₄ has an optical bandgap of 2.85 eV, which agrees well with the previous reports [29, 39, 40]. The pure ZnO nanorod has an optical bandgap of 3.26 eV. Interestingly, the optical bandgap of composites ranges from 3.05 to 3.09 eV and decreases with the increase of g-C₃N₄ content. In detail, the extracted optical bandgaps of nanocomposites Z-1C, Z-3C, Z-5C, and Z-7C are 3.09 eV, 3.08 eV, 3.07 eV, and 3.05 eV, respectively. The decrease in optical bandgap energy results in higher absorption and a higher possibility of photo-generation carriers under visible irradiation. In g-C₃N₄@ZnO composites, the inbuilt electric field on the interface of heterojunction can efficiently promote photocarriers to move to the oriented direction and to change Fermi level. Thus, light absorption and the separation possibility of the photocarriers is enhanced and its photocatalytic performance is further enhanced.

3.4. Photocatalytic Activities. Figure 5(a) presents the absorption spectra of the MB solution mixed with Z-7C samples at different reaction times. It can be seen that Z-7C sample is the absorption peak that reduces continuously with the irradiation time, indicating that the MB aqueous solution is decomposed with the presence of the Z-7C sample under a quasi-sunlight source. To quantify the photocatalytic performance of the synthesized samples in the degradation reaction of the MB, the residual concentration of MB is calculated from the residual intensity of the absorption peak at 664 nm.

Figure 5(b) shows the ratio between the residual MB concentration and the initial MB concentration at different reaction times under visible light using different photocatalytic-blank, pure ZnO, g-C₃N₄, and Z-1C, Z-3C, Z-5C, and Z-7C samples, respectively. All composite samples show good photocatalytic activity under the quasi-sunlight. The photocatalytic performances of blank, pure ZnO, g-C₃N₄, and Z-1C, Z-3C, Z-5C, and Z-7C samples are 4.4%, 24.4%, 82.2%, 65.8%, 92.3%, 93.0%, and 96.8%, respectively. This

result implies that the hybridization helps increase the MB degradation under the light irradiation and sample Z-7C shows the highest photocatalytic efficiency. The enhanced photocatalytic activity possibly profited from the efficient photoinduced charge from ZnO to g-C₃N₄.

The MB degradation process was further investigated by the reaction kinetics [39, 41]. The process was fitted via the following equation:

$$\ln\left(\frac{C_0}{C}\right) = kt, \quad (4)$$

where k (min^{-1}) corresponds to the constant rate, C_0 and C represent the MB concentration, and t denotes the reaction time. Figure 5(c) shows the related kinetics data over the catalysts under visible-light irradiation. It can be seen that the regression curve of the natural logarithm of normalized MB concentration versus reaction time is approximately linear, indicating that the kinetics of MB degradation over the photocatalysts follow first-order reaction kinetics.

The fitted constant rate (k) values are presented in Figure 5(d). The degradation rate of the Z-7C nanocomposite was 0.0320 min^{-1} , which is about 24.6 times higher than that of pure ZnO (0.0013 min^{-1}). This indicates that the incorporation of g-C₃N₄ on ZnO nanorods has largely influenced the constant rate.

Photocatalytic degradation of MB under visible-light irradiation of Z-7C sample on photocatalytic amount is illustrated in Figure 6(a). It shows an increase in degradation efficiency with the photocatalytic amount. The photocatalytic performance is the highest at 50 mg photocatalyst (Figure 6(b)). However, with the g-C₃N₄@ZnO weight increase exceeding 50 mg, the photocatalytic activities begin to decrease. It is deduced that excess adsorption of MB leads to a decrease in the capacity of light trapping and blocks the generation of photogenerated electrons and holes. The adsorption should achieve suitable intensity, which could guarantee enough photocatalytic activity. Therefore the photocatalyst had realized an optimal balance between MB adsorbing capacity and photon acquisition capability when the weight of g-C₃N₄ was 50 mg.

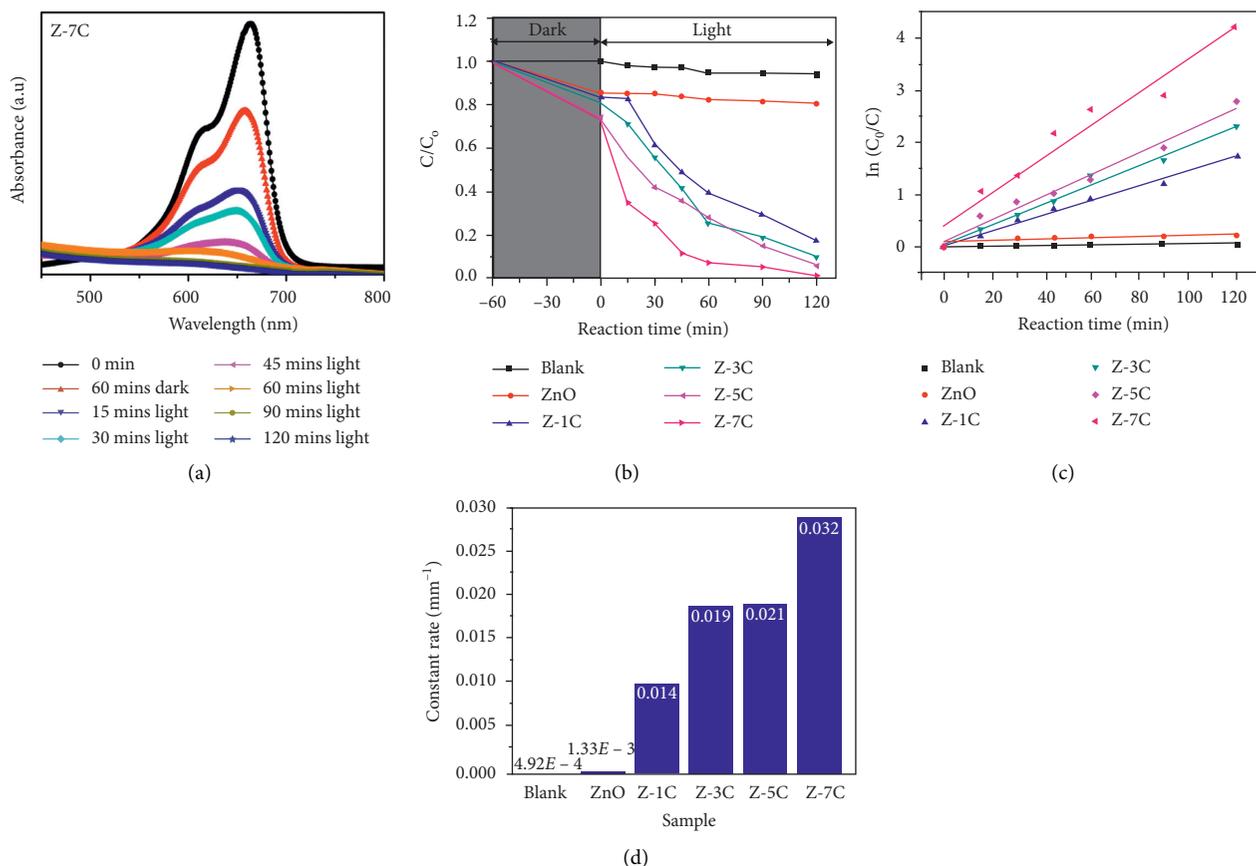


FIGURE 5: (a) Absorption spectra of Z-7C samples. (b) Photocatalytic degradation of MB under visible-light irradiation. (c) Determination of the constant rate (k) of the photocatalytic degradation of MB by kinetic linear simulation plots. (d) The constant rate (k) of the photocatalytic degradation of MB by samples.

Besides, the recyclability of the fabricated $g\text{-C}_3\text{N}_4@\text{ZnO}$ photocatalysts was also studied with 50 mg photocatalyst assessed, and results are shown in Figure 6(c). The recycling experiments were carried out by centrifuging and drying the photocatalyst after the degradation cycle and reusing it during the next cycle. The photocatalytic activity measured under visible-light irradiation, for four cycles, is presented in Figure 6(c). The results demonstrate that the $g\text{-C}_3\text{N}_4@\text{ZnO}$ nanocomposites had stable cyclic performance as a photocatalyst.

The photocatalytic activity of $g\text{-C}_3\text{N}_4@\text{ZnO}$ (7 wt.%) was compared with the previously reported (Table 2). $g\text{-C}_3\text{N}_4@\text{ZnO}$ is more advantageous than the other catalysts in terms of photocatalytic ability, ease of synthesis, structural stability, and morphologies. Notably, the results presented in Table 2 could not be comparable due to the variation in other experimental conditions such as catalyst amount, power of the light source, distance from the light source, and preparation methodology. The present work possesses the advantage of in situ synthesis of $g\text{-C}_3\text{N}_4@\text{ZnO}$ nanocomposite with enhanced photocatalytic activity.

The steady-state PL spectra were also utilized to examine the separation and recombination processes of the photo-induced electron-hole pairs. A high fluorescence intensity generally corresponds to the significant recombination of

electron-hole pairs. Figure 7(a) exhibits the room temperature PL spectra of $g\text{-C}_3\text{N}_4$, ZnO, and 7 wt.% $g\text{-C}_3\text{N}_4@\text{ZnO}$ composite samples. As depicted in Figure 7(a), all samples presented a broad luminescence peak, which centres at approximately 450 nm with a certain shift in the peak position with $g\text{-C}_3\text{N}_4$ contents. This emission peak is originated from direct band-to-band transitions. This emission peak is originated from direct band-to-band transitions [45–47]. The pure ZnO exhibited a broad intense deep-level (DL) emission which appeared in the range of 400–750 nm [48, 49]. When the $g\text{-C}_3\text{N}_4$ ratio increases, the luminescence peak intensity of $g\text{-C}_3\text{N}_4@\text{ZnO}$ composites increases first and then decreases, indicating a more efficient charge carrier pathway formed with a relatively high $g\text{-C}_3\text{N}_4$ content. It is also observed that the PL intensity of Z-7C (7 wt.% $g\text{-C}_3\text{N}_4$) samples decreased the most in comparison with the bare $g\text{-C}_3\text{N}_4$. This result indicates that the $g\text{-C}_3\text{N}_4@\text{ZnO}$ composite had lower recombination rates of electrons and holes under visible-light irradiation compared to other composites and pristine ZnO and $g\text{-C}_3\text{N}_4$.

To probe the active species in the photocatalytic reaction, triethanolamine (TEOA), isopropanol (IPA), and p-benzoquinone (BQ) were introduced into the system as the scavengers of holes (h^+), hydroxyl radicals ($\cdot\text{OH}$), and superoxide radicals ($\cdot\text{O}_2^-$), respectively. The measurements

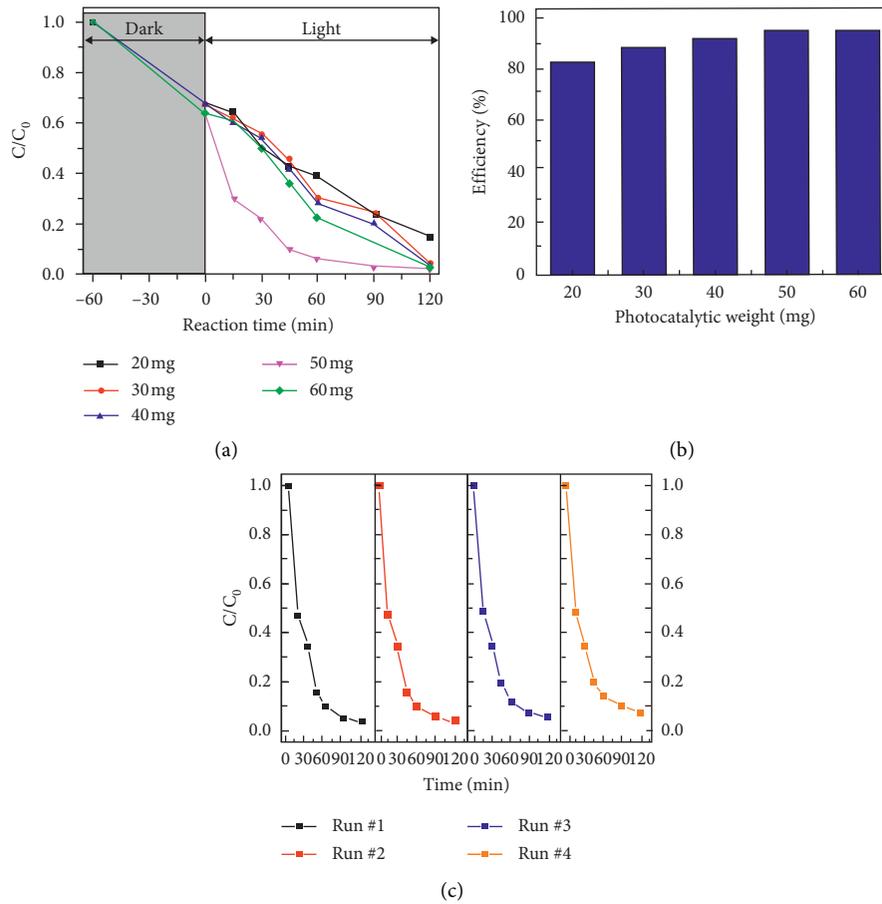


FIGURE 6: (a) Photocatalytic degradation of MB under visible-light irradiation of Z-7C sample with the different photocatalytic amount. (b) The photocatalytic performance of MB under visible-light irradiation of Z-7C sample on photocatalytic weights. (c) Cyclic performance of the Z-7C photocatalysts towards MB under visible-light irradiation.

TABLE 2: A comparison of photocatalytic activity of g-C₃N₄@ZnO (7%) on the degradation of MB under visible light with recently reported catalysts.

Catalyst	Dye conc. (ppm)	Catalyst amount (mg)	Solution volume (ml)	Time (min)	Light power (watt)	Degradation (%)	Constant rate k (min ⁻¹)	References
ZnO/g-C ₃ N ₄	10	—	100	50	500	95	0.038	[41]
ZnO-CN	10	20	100	150	UV light 365 nm	99	0.012	[42]
g-C ₃ N ₄ /ZnO	1	20	30	90	Mild UV	99	—	[43]
g-C ₃ N ₄ /AgBr/ZnO	5	40	100	80	300	96.3	0.041	[44]
g-C ₃ N ₄ @ZnO	10	50	100	120	250	96.8	0.032	Present study

were similar to the aforementioned photocatalytic activity tests, except for the addition of scavengers to the MB solution before visible-light irradiation. The concentrations of TEOA, IPA, and BQ were 10, 10, and 1 mmol L⁻¹, respectively.

The MB degradation rates with different scavengers were summarized in Figure 8.(b) The results indicate that a large number of $\cdot\text{O}_2^-$ were generated when g-C₃N₄@ZnO was irradiated under visible light and played an important role in the degradation of the MB. Therefore, degradation of the dyes was slightly suppressed when isopropyl alcohol was added because

of a small amount of OH generated through $\cdot\text{O}_2^-$ reacting with H⁺. Degradation of the MB was significantly inhibited because of the addition of benzoquinone to capture $\cdot\text{O}_2^-$.

The recombination of electrons and holes was restrained when TEOA was added to the system as a scavenger to capture holes. At the same time, more electrons migrated to the surface of the photocatalyst and reacted with O₂ to form $\cdot\text{O}_2^-$, which could enhance the degradation of the MB under visible-light irradiation by g-C₃N₄@ZnO. Therefore, the main active species are $\cdot\text{OH}$, $\cdot\text{O}_2^-$, and h⁺ in the MB

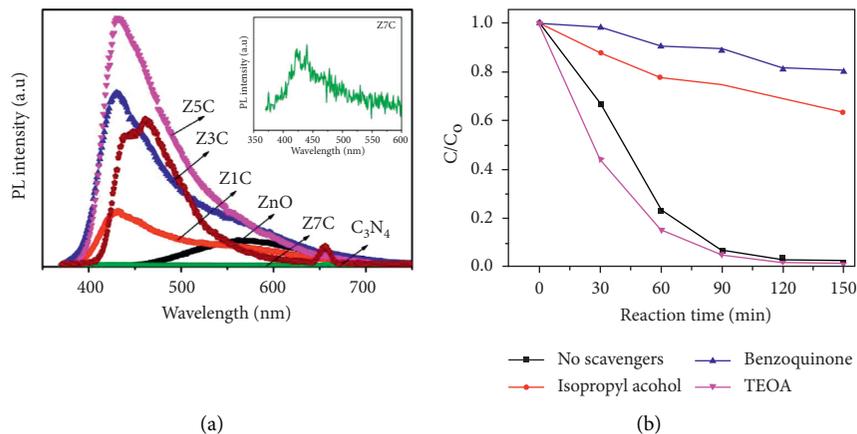


FIGURE 7: (a) PL spectra of ZnO, g-C₃N₄, and g-C₃N₄@ZnO composite. (b) Results of active species trapping experiments.

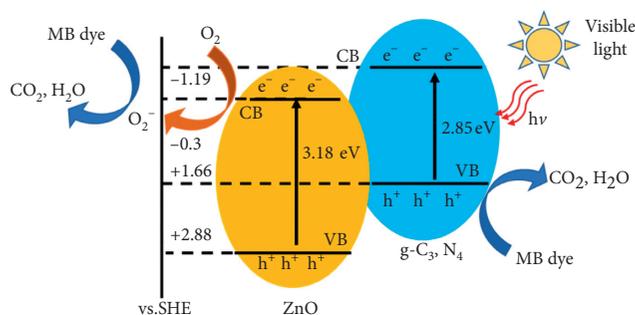


FIGURE 8: Simplified schematic diagram of the energy band structure and electron-hole pair separation in g-C₃N₄@ZnO nanocomposite.

degradation process. The result is following the reported results [47, 50, 51].

The enhanced photocatalytic activity of g-C₃N₄@ZnO nanocomposite under visible-light irradiation can be explained as follows (Figure 8): The band positions of the g-C₃N₄@ZnO can be calculated by the following empirical formulas [25, 41, 52]:

$$E_{VB} = X + 0.5Eg - Ee, \quad (5)$$

$$E_{CB} = E_{VB} - Eg, \quad (6)$$

where E_{VB} is the valence band potential; E_{CB} is the conduction band potential; X is the absolute electronegativity of the semiconductor; Ee is the energy of free electrons on the hydrogen scale ($Ee = 4.5$ eV). The X values for g-C₃N₄ and ZnO are 4.73 and 5.79 eV, respectively. Eg is the bandgap of the semiconductor and it can be extracted from reflectance spectra data.

According to Equations (5) and (6), the value E_{CB} of g-C₃N₄ and ZnO is about -1.19 and -0.3 eV, respectively. E_{VB} of g-C₃N₄ and ZnO are estimated to be 1.66 and 2.88 eV, respectively. The result is following the reported results [25, 29, 35, 36].

Under visible-light irradiation, only g-C₃N₄ absorbed visible light and was excited. Because the conduction band

(CB) edge of g-C₃N₄ was more negative than that of ZnO, the photoinduced electrons on CB of g-C₃N₄ can transfer easily to the CB of ZnO [42], while the holes in the VB of g-C₃N₄ could oxidize MB directly. Moreover, electrons in the CB of ZnO were trapped by O₂ dissolved in the solution to generate superoxide radicals, which could further oxidize the MB.

4. Conclusions

In summary, the in situ heterojunction structure of g-C₃N₄@ZnO nanocomposites with different g-C₃N₄ contents (0, 1, 3, 5, and 7 wt.%) was prepared via a one-step hydrothermal method. The direct introduction of g-C₃N₄ into nanocomposite causes the decrease of crystalline size, optical bandgap, and the change of morphology of nanocomposite. g-C₃N₄ remarkably enhances the photocatalytic performance of g-C₃N₄@ZnO nanocomposites under visible-light irradiation in comparison with pure ZnO. Nanocomposite having 7 wt.% of g-C₃N₄ shows the highest photocatalytic activity and good recyclability. The superior photocatalytic performance of the Z-7C nanocomposite was 0.0320 min⁻¹, which is about 24.6 times higher than that of pure ZnO (0.0013 min⁻¹). This enhancement might be assigned to the wider and stronger absorption of visible light of g-C₃N₄@ZnO nanocomposite-narrower optical bandgap and higher absorbance, which are preferable for enhancing photocatalytic performance. Moreover, the g-C₃N₄ lamellar structure is useful for photoinduced carriers to be rapidly transferred, which is beneficial for the direct transfer of photoinduced carriers in heterojunction. These results imply a simple method to prepare an effective photocatalyst working under visible-light irradiation.

Data Availability

The data are available upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This research was funded by the Hanoi University of Science and Technology (HUST) under Project no. T2018-TĐ-203.

Supplementary Materials

XRD pattern of g-C₃N₄ is shown in Figure S1. The characteristic diffraction peaks of the pure g-C₃N₄ appearing at 27.4° and 13.1° can be indexed to the (002) and (100) planes, which are attributed to the characteristic interlayer structure and interplanar stacking peaks of aromatic systems, respectively. We can evaluate based on the plot of $[F(R) * hv]^{1/2}$ versus hv as shown in Figure S2 for g-C₃N₄ and g-C₃N₄@ZnO. The optical bandgap of the pure g-C₃N₄ has an optical bandgap of 2.85 eV, which agrees well with the previous reports [29, 39, 40]. Interestingly, the optical bandgap of composites ranges from 3.05 to 3.09 eV and decreases with the increase of g-C₃N₄ content. In detail, the extracted optical bandgaps of nanocomposites Z-1C, Z-3C, Z-5C, and Z-7C are 3.09 eV, 3.08 eV, 3.07 eV, and 3.05 eV, respectively. (Supplementary Materials)

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