Fabrication of g-C₃N₄/ZnO Nanoheterostructures for Effective Degradation of Methylene Blue Dye under Visible Light Irradiation

PARMESHWAR LAL MEENA (✉ parmeshwar1978@gmail.com)

University of Rajasthan <https://orcid.org/0000-0003-4975-7250>

Krishna Poswal

Ajay Kumar Surela

Jitendra Kumar Saini

Research Article

Keywords: g-C₃N₄/ZnO, nanoheterostructures, methylene blue, photodegradation, kinetics

Posted Date: February 25th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1373910/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Fabrication of g-C₃N₄/ZnO Nanoheterostructures for Effective Degradation of Methylene Blue Dye under Visible Light Irradiation

Parmeshwar Lal Meena, Krishna Poswal, Ajay Kumar Surela and Jitendra Kumar Saini

Department of Chemistry, University of Rajasthan, Jaipur-302004 (India)

Email-parmeshwar1978@gmail.com

ABSTRACT

In the present, the g-C₃N₄/ZnO hybrid nanoheterostructures photocatalysts with different weight percents of ZnO have been successfully prepared by a facile grinding, dehydration followed by pyrolysis method. The structural and textural properties of the prepared samples were investigated by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy combine electron dispersive spectroscopy (FESEM-EDS) and UV-vis spectroscopy. The photocatalytic performance of the fabricated g-C₃N₄/ZnO nanostructures was investigated for the degradation of methylene blue (MB) dye and it is determined much higher in compare to the bare g-C₃N₄ nanosheets and ZnO nanorods. The optimized ZnO content in the g-C₃N₄/ZnO photocatalyst was determined to be 25%. In the current study, 99.54% of MB dye is degraded in 60 min of visible light irradiation at pH=10 over g-C₃N₄/ZnO (25%) photocatalyst. The results of the kinetic study reveals that photodegradation reactions have followed the first-order kinetics and the rate constant values of MB photodegradation in presence of prepared g-C₃N₄/ZnO (25%) is determined ~13 and ~7.76 times greater than that of the bare g-C₃N₄ and ZnO respectively. The enhanced photocatalytic efficiency of the fabricated g-C₃N₄/ZnO nanoheterostructures could be due to the creation of heterojunction by the coupling of two semiconductors of well matched band structures in which effective charge transfer has been occurred. The prepared g-C₃N₄/ZnO has demonstrated significant photostability after utilization in four runs of cycles. The decrease in the catalyst performance even after four repeated cycles is approximately 8%. The superoxide free radicals ([•]O₂⁻) are the main reactive species participated in the degradation of MB dye. The current approach of fabrication of heterojunction has presented a competent and simplistic synthetic tactic of creation of visible-light-driven photocatalyst for the effective photocatalytic mineralization of organic dye contaminants in the aqueous medium.

Keywords: - g-C₃N₄/ZnO, nanoheterostructures, methylene blue, photodegradation, kinetics

1. Introduction

Carbon nitride is a fascinating material that has attracted huge interest in the field of material science, because of its unique layered structure and a characteristic electronic band structure,

wide surface area, rigidity, light weight, chemical inertness, water resistivity, and biocompatibility. C_3N_4 has been widely employed in various fields such as in light emitting devices, and metal free electrocatalysis and photocatalysis [1-2]. Among the various allotropes of C_3N_4 , g- C_3N_4 is a promising and charismatic allotrope that has wide range of stability and it possesses π -conjugated electronic structure with a band gap of 2.7 eV [1,3-4]. Owing to the narrow band gap, layered structure, suitable band alignment the g- C_3N_4 is extensively used for water splitting, selective oxidation reactions, and environment pollutant degradation [1,5].

Interestingly, many organic and inorganic substances can be bind to the surface of g- C_3N_4 , since the layered surface of the g- C_3N_4 is adequately competent to tender active sites for binding [6-7]. The photocatalytic ability of pure g- C_3N_4 is restricted due to the poor separation of charge carriers and fast rate of recombination of the photogenerated electron-hole pairs [8-9]. Thus, the constrained photocatalytic efficacy of the g- C_3N_4 can be improved by doping and/or coupling of g- C_3N_4 with other materials such as transition metals, metal oxides and sulphides, carbon materials. etc.[10]. As reported in literature, the photocatalytic performance of the g- C_3N_4 has been greatly advanced by doping and/or coupling of the many semiconductor materials with suitable energy levels such as Bi_2O_3 [11], WO_3 [12], Fe_3O_4 [13], TiO_2 [14-15], CuO [16], ZnO [17-19], MoS_2 [20]. Due to the mixing of these materials the recombination rate of photogenerated electron-hole pairs is considerably suppressed due to separation of charge carrier, thus, the photocatalytic activity is enhanced significantly. Hence, the attempts have been made to dope and /or couple suitable semiconductor material with the g- C_3N_4 to produce hybrid material with the improved photocatalytic performance.

Among the semiconductor materials, ZnO is direct wide bandgap (3.37 eV) semiconductor with high excitation-binding energy of 60 meV. It has been received enormous attention owing to its high photostability and excellent photocatalytic activity [21-22].

Though, the poor photocatalytic performance of ZnO under visible light illumination due to wide bandgap, its application as photocatalyst has been restricted, moreover, high recombination rates of photogenerated charge carriers further limits its activity [21].

Therefore, lots of attempts have been made to amplify absorption of visible light radiation and reduce recombination rate of photogenerated electrons-holes. This can be realized by doping of metal or nonmetal atoms, coupling and/or doping of other semiconductors and surface modification [23-24].

Thus, the coupling of ZnO with graphitic nitride (g- C_3N_4) may construct a visible light active heterostructure with the improved separation efficiency of photogenerated electron– hole

pairs because of appropriate and well overlapping of energy bands [25]. In the past few years, several researchers across the globe have been constructed ZnO/g-C₃N₄ heterostructures using diverse methods and employed effectively for the degradation of numerous water pollutants [21]. constructed djembe-like ZnO and its composite with g-C₃N₄ as a visible-light-driven heterojunction photocatalyst for the degradation of organic dyes, Zhu et al, (2014) [26] prepared carbon-doped zinc oxide (ZnO) hybridized with graphitic carbon nitride (g-C₃N₄) nanocomposite photocatalysts through simple one-step calcination of evaporation-dried mixture of dicyandiamide and zinc nitrate and the photocatalytic activity of the resultant catalyst was examined for the degradation of methylene blue (MB) dye under visible light. Kumaresan et al, (2019)[27] synthesized heterojunction of g-C₃N₄/ZnO binary nanocomposites in 2D/1D by sonication assisted hydrothermal method for effective degradation of RhB dye and 4-chlorophenol under solar light irradiation. Tan et al, (2019)[28] prepared g-C₃N₄/ZnO heterostructure nanocomposites using self-assembly method for the degradation of MB dye under visible light. Manimozhi et al, (2020)[29] synthesized g-C₃N₄/ZnO heterostructure photocatalyst for enhanced degradation of organic dye crystal violet under visible light photon illumination. Zhong et al, (2020)[30] prepared heterostructure g-C₃N₄/ZnO nanorods using hydrothermal, grinding and calcination methods for degradation of MB, eosin RhB dyes, By deposition-precipitation method g-C₃N₄/ZnO nanocomposites photocatalyst has been prepared for degradation of MB[31]. One-step thermal polymerization process was employed for the fabrication of ZnO-Modified g-C₃N₄ and utilized for MB dye degradation [32].

Being motivated from the above studies we have synthesized g-C₃N₄/ZnO nanoheterostructures using novel and simple one step thermolysis method employing zinc acetate and urea as precursors of ZnO and g-C₃N₄. The fabricated g-C₃N₄/ZnO heterostructured nanorods were characterized by using analytical techniques like UV-vis, XRD, FTIR, FESEM and EDS. The photodegradation performance was investigated for the degradation of methylene blue dye under visible light illumination.

2. Materials and methods

2.1. Materials used

Zinc acetate dihydrated [Zn(OAc)₂·2H₂O] and urea (NH₂)₂CO) were procured from Qualikem chemicals and used without purification. Hydrochloric acid (HCl) and nitric acid (HNO₃) were purchased from Renkem chemicals, and sodium hydroxide (NaOH) from CDH. Methylene blue (MB) dye was selected as model pollutant and purchased from TCI

chemicals. Deionized water was used during all the experimental work. All the chemicals were used without further purification.

2.2. Synthesis of ZnO nanorods

ZnO nanoparticles were synthesized by the co-precipitation method. In a typical procedure, 5g of the zinc acetate was dissolved in 100 mL of deionized water under constant stirring for 30 min at room temperature. Then, 3M NaOH solution was added drop-wise to precipitate the solution at room temperature and continue stirring for the next 90 min. Afterward, thus obtained precipitate was filtered, washed several times with DI water, and finally with ethyl alcohol. Lastly, the precipitate was dried in an oven at 85°C for 5 h and subsequently pulverized into a fine powder for further use.

2.3. Synthesis of graphitic carbon nitride (g-C₃N₄) nanosheets

g-C₃N₄ was prepared by direct thermolysis method using urea as precursor. In a typical method, 6.50 g of urea was initially grounded well into fine powder with pastel and mortar for 20 min and then dried over hot plate for 60 min at 85°C. Then after, the dried powder was thermolized in a partially covered silica crucible in a muffle furnace at 550°C for 3 h. A light yellow colored powder of g-C₃N₄ was achieved. Thus, as-prepared yellow colored powder was naturally cooled down to room temperature, grounded well into a fine powder, washed with 0.1M HNO₃, deionized water, and at last with ethyl alcohol. Eventually, the yellow colored was dried in oven for 5 h at 85°C.

2.4. Preparation of g-C₃N₄/ZnO hybrid nanoheterostructures

g-C₃N₄/ZnO heterostructures were prepared by varying quantity of zinc acetate with urea. Initially, zinc acetate with urea were mixed well and grounded in to fine powder using pastel and mortar, and dried over hot plate at 85°C for 60 min. and finally pyrolyzed at 550°C for 3 h in a muffle furnace in a partially covered crucible. Thus, the as-prepared light yellow colored powder was naturally cooled down to room temperature, grounded well into a fine powder, washed with 0.1M HNO₃, deionized water, and at last with ethyl alcohol. Ultimately, the pale yellow colored was dried in oven for 5 h and again calcinated at 550°C for 3 h in a muffle furnace in silica crucible. For the synthesis of g-C₃N₄/ZnO (25%) nanoheterostructures, 10 g of urea with 2.5 g zinc acetate was used, whereas the other g-C₃N₄/ZnO nanoheterostructures were prepared by using 1.0, 1.5 and 5 g of zinc acetate with 10 g of urea under similar reaction conditions. The schematic diagram of the synthesis of g-C₃N₄/ZnO nanoheterostructures is depicted in Fig. 1.

Fig. 1. Schematic representation of the synthesis of g-C₃N₄/ZnO nanoheterostructures

2.5. Characterization of prepared catalysts

The fabricated bare g-C₃N₄ and ZnO, and g-C₃N₄/ZnO nanoheterostructures were characterized by using analytical techniques like UV-vis, XRD, FTIR, FESEM, and EDS. The crystalline structure and phase purity of the as-prepared samples were studied using a powder X-ray diffractometer (XRD) with Cu K α radiation (PANalytical's X'Pert Pro) in the range of 10 to 80° of 2 θ , 0.001 step size and 2°/min of scan speed. The surface morphology and shape of the prepared samples were examined using Field emission scanning electron microscopy (FESEM) (Nova Nano FESEM-450 (FEI)) and elemental composition was studied by energy-dispersive X-ray spectroscopy (EDS) technique. The function groups and bonding in prepared samples were investigated using Fourier transform infrared (FT-IR) spectra measured in the scanning range of 400–4000 cm⁻¹ (Perkin Elmer FT-IR). UV-visible absorption spectra were recorded to evaluate the optical band gaps of the synthesized samples (Shimadzu, UV-2600 spectrophotometer).

2.6. Photocatalytic study

Photocatalytic performances of the prepared samples were investigated by conducting photocatalytic experiments in immersion type photoreactor made up of double layer quartz tube container of 500 mL capacity equipped with 250W sodium vapor lamp. 50 mL of methylene blue dye solution (30 mg/L) with 20 mg of the photocatalyst was magnetically stirred under dark for 30 min to attain adsorption-desorption equilibrium. Afterward, the suspension was illuminated with visible light radiation 60 min. At a particular time interval, 5 mL of dye solution was withdrawn and to remove the catalyst from the solution it was

centrifuged. The residual concentration of the MB dye in the solution was measured spectrophotometrically by measuring the absorbance of solutions at 664nm. The percentage photodegradation of organic dyes was determined by using equation (1). Further, to understand the kinetic behavior of the photodegradation, the experimental data were fitted in a first-order kinetic model as shown by the following equation (2)

$$\% \text{ degradation} = \frac{C_0 - C_t}{C_0} \times 100 = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

$$\ln\left(\frac{C}{C_0}\right) = \ln\left(\frac{A}{A_0}\right) = -kt \quad (2)$$

where C_0 and C_t are the initial and concentration of dye at a certain time interval and A_0 and A_t are the absorbance at initial and at t time, and k is the first-order kinetic rate constant.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the as-prepared g-C₃N₄, ZnO, and g-C₃N₄/ZnO nanoheterostructures are depicted in Fig. 2. It is evident that the XRD pattern of g-C₃N₄ shown two peaks at $2\theta=12.78^\circ$ and 28.02° , which are attributed to (100) and (002) diffraction planes as shown in the inset of Fig. 2 (JCPDS No. 87-1526) [33]. As demonstrated in XRD pattern of the prepared ZnO nanorods (Fig. 2(a), the peaks recorded at $2\theta= 31.80^\circ(100)$, $34.45^\circ(002)$, $36.28^\circ(101)$, $47.53^\circ(102)$, $56.69^\circ(110)$, $62.85^\circ(103)$, $67.75^\circ(200)$, $68.24^\circ(112)$, $69.44^\circ(201)$, $70.71(004)^\circ$ and $77.07^\circ(202)$ (JCPDS 01-070-2551)[34], which are corresponding to the hexagonal wurtzite crystal structure [28]. Moreover, the XRD patterns (Fig. 2 (b-e)) of g-C₃N₄/ZnO nanoheterostructures contain only the diffraction peaks corresponding to the g-C₃N₄ and ZnO, and no other peaks are recorded that substantiates the purity of the produced heterostructures. The intensities of XRD diffraction peaks corresponding to the g-C₃N₄ in g-C₃N₄/ZnO heterostructures increased with decrease of ZnO content. In this way, the presence of sharp and intense XRD-diffraction peaks in the XRD patterns of g-C₃N₄, ZnO, and g-C₃N₄/ZnO is confirmed that the prepared samples have good crystallinity and phase purity. Additionally, the average particle size of the prepared samples is determined using Debye-Scherrer's equation (3).

$$D = \frac{0.9\lambda}{\beta \sin\theta} \quad (3)$$

where D is the average particle size in nm, λ is the wavelength of the radiation ($1.54059\text{\AA}$), β and θ are the half-width of maximum of highest intense peak and angle of diffraction

respectively. The average particle size determined for the g-C₃N₄ nanosheets, and ZnO nanorods, g-C₃N₄/ZnO nanoheterostructures are 8, 18 and 30 nm respectively.

Fig. 2. XRD patterns for g-C₃N₄ nanosheets, ZnO nanorods, and g-C₃N₄/ZnO nanoheterostructures

3.2. FTIR analysis

Fig. 3. FT-IR spectra of g-C₃N₄ nanosheets, ZnO nanorods, and g-C₃N₄/ZnO nanoheterostructures

The FT-IR spectra of the prepared samples are depicted in (Fig. 3). The peak noticed in the FTIR spectrum of bare g-C₃N₄ at 812 cm⁻¹ confirm the presence of s-triazine ring [35-36], and peaks appeared at 1237 cm⁻¹, 1321 cm⁻¹, and 1406 cm⁻¹ related to the C–N stretching vibration, while the other two peaks noticed around 1547 and 1635 cm⁻¹ indexed to C=N stretching vibration respectively [37-38]. The peak reported at 887 cm⁻¹ is attributed to the

deformation mode of the N–H bond. The broad band's recorded in the $3100\text{--}3300\text{ cm}^{-1}$ and $3500\text{--}3700\text{ cm}^{-1}$ regions could be assigned to the N–H and O–H stretching vibrations due to amino and OH groups respectively [39]. The FTIR bands reported at 528 cm^{-1} in the g- $\text{C}_3\text{N}_4/\text{ZnO}$ nanoheterostructures are related to the Zn–O bond vibration [40]. The decreasing intensity of bands in $1100\text{--}1700\text{ cm}^{-1}$ region signifies the interaction between g- C_3N_4 and ZnO. In the FTIR spectrum of ZnO, a sharp peak observed at 526 cm^{-1} is related to the Zn–O bond vibration. Additionally, existences of peaks corresponding to the g- C_3N_4 and ZnO in g- $\text{C}_3\text{N}_4/\text{ZnO}$ nanoheterostructures witnessed the formation of g- $\text{C}_3\text{N}_4/\text{ZnO}$ nanoheterostructures. Thus, the FT-IR spectral analysis confirms the formation of g- C_3N_4 , ZnO, and the g- $\text{C}_3\text{N}_4/\text{ZnO}$ nanoheterostructures.

3.3. FESEM and EDS analysis

Fig. 4. FESEM images for (a-b) g- C_3N_4 nanosheets (c-d) ZnO nanorods, and (e-f) g- $\text{C}_3\text{N}_4/\text{ZnO}$ nanoheterostructures

The FESEM images for the bare g- C_3N_4 and ZnO nanoparticles and g- $\text{C}_3\text{N}_4/\text{ZnO}$ nanoheterostructures are depicted in Fig. 4. As shown in Fig. 4(a-b), bare g- C_3N_4

nanoparticles have the sheet-like shape and smooth surface, whereas the bare ZnO nanoparticles comprise of rod-shaped structures (Fig. 4(c-d)). The FESEM images of g-C₃N₄/ZnO nanoheterostructures contain sheet and rod-like structures which confirm the existence of g-C₃N₄ nanosheets along with ZnO nanorods (Fig. 4 (e-d)). Elemental composition with weight percentages of all the prepared samples was determined by energy-dispersive X-ray spectroscopy (EDS). The EDS spectra of ZnO, g-C₃N₄, and g-C₃N₄/ZnO hybrid nanoheterostructures are shown in Fig. (5a-c), which confirm the presence of Zn and O elements in ZnO, C, and N elements in g-C₃N₄, while C, N, Zn, and O elements in g-C₃N₄/ZnO. The presence and weight percentages of all the elements (Zn, O) in ZnO, (C, N) in g-C₃N₄, and (C, N, Zn, O) in g-C₃N₄/ZnO nanoheterostructures are summarized in Tables depicted inset of Fig. 5.

Fig. 5. EDS spectra of (a) ZnO nanorods, (b) g-C₃N₄ nanosheets and (c) g-C₃N₄/ZnO nanoheterostructures

3.4. Optical properties

The optical properties of the synthesized samples were investigated by consulting UV–vis absorption spectra recorded in the range of 200–800 nm as shown in Fig. 6(a). In compare to bare ZnO substantial red shift in absorption in UV–vis absorption spectra of g-C₃N₄/ZnO nanoheterostructures is observed. Band edge shift in UV–vis absorption spectral lines for bare g-C₃N₄ and ZnO, and g-C₃N₄/ZnO nanoheterostructures is represented in Table 1. The band gap energy values for the synthesized materials were evaluated by plotting Tauc's plots as illustrated in Fig. 6(b). The bandgap energy values for the prepared samples were estimated by applying given typical equation (4) [41].

$$(\alpha h\nu) = A(h\nu - E_g)^n \quad (4)$$

where $h\nu$ is the photon energy, E_g is the bandgap, A is the parameter and α is the absorption coefficient. The bandgap energy values for the g-C₃N₄ nanosheets, ZnO nanorods and g-C₃N₄/ZnO nanoheterostructures were determined from the Tauc plot drawn between $(\alpha h\nu)^{1/n}$ vs. $h\nu$, and extrapolating the straight-line part to $(\alpha h\nu)^{1/n} = 0$. The calculated bandgap energy values for g-C₃N₄ and g-C₃N₄/ZnO, and ZnO samples are listed in Table 1.

Fig. 6. (a) UV absorption spectra, and (b) Tauc plots for ZnO nanorods, g-C₃N₄ nanosheets, and g-C₃N₄/ZnO nanoheterostructures

For the bare g-C₃N₄ and ZnO bandgap energy values are found to be 3.12 eV and 2.72 eV respectively, whereas for the g-C₃N₄/ZnO nanoheterostructures it is varied from 2.80 eV to 3.00 eV as represented in the inset of Fig. 6. The decrease in the band gap energy for g-

C₃N₄/ZnO nanoheterostructures can be attributed to the effective interaction between g-C₃N₄ and ZnO. Moreover, the reduced bandgap energy values for the g-C₃N₄/ZnO nanoheterostructures in compare to ZnO could lead to enhance light absorption in the visible region that has increased the generation of more electron-hole pairs [42]. Additionally, due to the coupling interactions g-C₃N₄ nanosheets and ZnO nanorods could create heterojunction that inspiring transfer of carriers due to which recombination of electrons–holes is delayed [43]. Consequently, the photocatalytic degradation performance of g-C₃N₄/ZnO nanoheterostructures is enhanced under visible-light irradiation. The maximum degradation efficiency is determined for the nanoheterostructures with 25 % of ZnO, since the band gap energy (2.80 eV) for this is determined lowest.

Table 1. Band gap energy values for ZnO nanorods, g-C₃N₄ nanosheets, and g-C₃N₄/ZnO nanoheterostructures

Catalyst	Absorption edge (nm)	bandgap (eV)
ZnO	400	3.12
g-C ₃ N ₄	428	2.72
g-C ₃ N ₄ /ZnO(50%)	402	3.00
g-C ₃ N ₄ /ZnO(25%)	420	2.80
g-C ₃ N ₄ /ZnO(15%)	408	2.85
g-C ₃ N ₄ /ZnO(10%)	405	2.90

3.5. Effect of reaction parameters on photocatalytic activity of catalyst

3.5.1. Effect of dopant (ZnO)

To investigate the role of dopant amount on the photocatalytic performance of g-C₃N₄ for the photodegradation of MB dye solution was studied. The photocatalytic performances of bare g-C₃N₄ and ZnO, and g-C₃N₄/ZnO hybrid nanoheterostructures were examined against the degradation of MB dye solutions with 30 mg/L dye concentrations and 20 mg of catalyst dose amounts at pH=10 under visible light illumination and the results demonstrated in Fig. 7. In the 60 min of visible light irradiation 35.58% and 52.52% of MB is photo-catalytically degraded by pure ZnO and g-C₃N₄ respectively. While, in presence of g-C₃N₄/ZnO nanoheterostructures 86.73%, 99.54%, 95.48%, and 92.65% of the MB dye is degraded by g-C₃N₄/ZnO (50%), g-C₃N₄/ZnO(25%), g-C₃N₄/ZnO(15%), and g-C₃N₄/ZnO(10%) under similar reaction conditions. Thus, the maximum photodegradation performance towards the MB is found to be with the g-C₃N₄/ZnO(25%) nanoheterostructures. The order of photocatalytic performance for the prepared samples is measured as g-C₃N₄/ZnO (25%) > g-C₃N₄/ZnO(15%) > g-C₃N₄/ZnO(10%) > g-C₃N₄/ZnO(50%) > g-C₃N₄ > ZnO. The determined degradation efficiencies of the catalysts are found to be dependable with the order of their

calculated bandgap energies. With increase of ZnO content the catalytic ability increases because of suppression in recombination rate of electron-hole pairs and effective separation of charge carriers due to the transfer of electron from g-C₃N₄ to ZnO. Additionally, at the higher content of g-C₃N₄, the trapping and poor transfer of electrons also reduces photocatalytic performance. Moreover, more amount of ZnO than to optimized value the catalytic ability is decreased due to the poor absorption of visible light radiations because band gap value is found to be increased.

3.5.2. Effect of initial dye concentration

The initial dye concentration is an essential feature in the photocatalytic process. To determine the optimized value of dye concentration, the photocatalytic performance of the prepared g-C₃N₄/ZnO(25%) nanoheterostructures was investigated against the MB dye degradation at 20-35 mg/L of dye concentrations, at pH=10 under the visible light irradiation for 60 min using 20 mg of catalyst amount. The photodegradation efficiency of g-C₃N₄/ZnO (25%) nanoheterostructures against the MB dye is calculated as 90.29%, 93.62%, 99.54%, and 96.13% for the 20, 25, 30 and 35 mg/L of dye concentrations respectively as depicted in Fig. 8. The maximum degradation efficiency is observed for the 30mg/L concentration, which is selected as an optimal dye concentration for next studies. At a lower initial concentration of dye, the less efficiency may be due to less amount of dye adsorbed on the catalyst surface [44]. However, at a higher concentration of dye, the decrease in the degradation efficiency may be due to the decreasing of penetration of light photon or suppressing path length of photons [45].

Fig. 7. Effect of dopant concentration on photodegradation of MB dye

Fig. 8. Effect of initial dye concentration on photodegradation of MB over the g-C₃N₄/ZnO nanoheterostructures

3.5.3. Effect of pH of the solution

The influence of solution pH on the photocatalytic performance for the MB dye over g-C₃N₄/ZnO nanoheterostructures is investigated by changing pH value from 4 to 12 in a 50 mL of dye solution with 30mg/L dye concentration and 20 mg catalyst amount under 60 min of visible light irradiation (Fig. 9(a)). At the lower pH value, in acidic medium, at pH= 4 the 85.06% of the MB is degraded which is increased to 90.43% on increasing pH value to 6. In contrast, when pH is changed into alkaline medium from the normal pH condition, the photodegradation efficiency is increased considerably and maximum degradation performance is determined at pH 10(99.54%).

Fig. 9: Effect of pH on photodegradation of MB over the g-C₃N₄/ZnO nanoheterostructures

However, in strong alkaline medium at pH 12, the photodegradation efficiency is decreased. It is apparent from Fig. 9(b), the point zero charge (PZC) is found to be 6.7. Below to this, in the acidic medium, at lower pH the catalyst surface is positively charged due to the adsorption of excess of H⁺ ions, which electrostatically repel the cationic dye MB molecules, due to which lower degradation efficiency is determined. Contrary, in alkaline medium above the pH (6.7) catalyst surface acquires negative charge due to the adsorption of OH⁻, which

attract electrostatically to the cationic dye molecules that lead to increase the adsorption of MO dye. Due to this the degradation of MB dye would be further enhanced [46]. Moreover, in alkaline pH OH^- ions can produce hydroxyl ($\bullet\text{OH}$) radicals that also triggers the degradation rate of dye. However, at higher pH in stronger alkaline medium, the degradation activity decreased due to the competition between dye molecules and OH^- for the adsorption on the catalyst surface.

3.5.4. Effect of catalyst dose amount

The influence of catalyst dose amount on the photodegradation performance of MB dye under visible light exposure is studied by varying the catalyst dose amount from 10 to 25 mg in 50 ml of dye solution at pH=10 and room temperature conditions. The results are shown in Fig. 10. As shown in Fig. 10, the photodegradation efficiency is increased from 84.34 % to 99.54%, on increasing the dose amount of catalyst from 10 to 20 mg. However, efficiency is decreased to 94.53% on a further increase of dose amount of catalyst to 25 mg. At lower amount of catalyst the available free active sites are less, on increasing dose amount of catalyst free active sites on the surface increase, because of this photodegradation activity is enhanced. However, furthermore increase in catalyst amount the degradation activity declined due to the scattering of light photons and poor penetration.

Fig. 10. Effect of dose amount of $\text{g-C}_3\text{N}_4/\text{ZnO}$ nanoheterostructures on photodegradation of MB dye

3.6. Photocatalytic activity

The photocatalytic performance of the as-synthesized bare ZnO and $\text{g-C}_3\text{N}_4$, and $\text{g-C}_3\text{N}_4/\text{ZnO}$ nanoheterostructures was assessed by the photodegradation of MB dye under visible light exposure. Before testing the photocatalytic abilities of the prepared samples, the adsorption capacities for MB dye were evaluated. The dye solution with catalyst was stirred in dark for 30min to achieve the adsorption-desorption equilibrium before being exposed to visible light.

Control experiment for photodegradation of MB dye in the absence of photocatalyst was also performed under similar conditions as enlightened in the photocatalytic experiment. In a typical method, all the photocatalytic experiments in the presence of catalysts were conducted under the optimized conditions of pH, initial dye concentration, and catalyst dose amount at room temperature. The residual concentration of MB dye at different time intervals was evaluated from intensities of UV-vis. absorption spectral peaks at 664 nm. The results of the photodegradation experiments are shown in Fig. 11. Particularly, the time-dependent UV-vis. absorption spectra are displayed in Fig. 12(a-f) representing degradation of MB dye over bare g-C₃N₄ nanosheets and ZnO nanorods, and various g-C₃N₄/ZnO nanoheterostructures.

As shown in Fig. 11, the self-degradation of MB dye is slight under the exposure of visible light, which represents that the MB dye is significantly stable in absence of catalyst under visible light illumination. Though, apparent degradation of MB is observed under visible light exposure over the pure ZnO and g-C₃N₄ catalysts. Contrary, a remarkable decrease in the concentration of MB dye is determined when the photocatalysis experiment was performed in the presence of g-C₃N₄/ZnO nanoheterostructures.

Besides, the catalytic performance of the g-C₃N₄ was changed with the variation of ZnO nanorods content into the g-C₃N₄ nanosheets, and the maximum photodegradation efficiency is determined for g-C₃N₄/ZnO(25%) nanoheterostructures photocatalyst. It reveals that the ZnO nanorods have considerably changed the photocatalytic performance of the g-C₃N₄ nanosheets. However, the presence of excess amount of ZnO than that of the optimized amount with the g-C₃N₄, the photodegradation performance has shown decrement. The increase in the photocatalytic performance of g-C₃N₄ with the ZnO might be due to the enhancement in visible-light absorption due to the modification of bandgap energy and interruption in recombination rate of the electrons-holes in comparison to bare g-C₃N₄ with the ZnO catalysts. Additionally, the presence of more surface-active sites onto g-C₃N₄ increases the adsorption rate of dye molecules, and the layered structure of g-C₃N₄ increases the transfer of photogenerated electron-hole from g-C₃N₄ to ZnO due to the formation of heterojunction. Conversely, the presence of more or less amount of ZnO than that of the optimized amount, the photodegradation performance of the prepared heterostructures are determined relatively less, because of poor absorption of visible light radiations under similar reaction conditions due to the large bandgap energy values as shown in Table. 1.

Fig. 11. Photodegradation of MB dye over bare-ZnO nanorods, g-C₃N₄ nanosheets, and g-C₃N₄/ZnO nanoheterostructures.

Fig. 12. Time-dependent UV-vis. absorption spectra of MB dye over (a) bare ZnO nanorods, (b) bare g-C₃N₄ nanosheets, (c) g-C₃N₄/ZnO(50%), (d) g-C₃N₄/ZnO(25%), (e) g-C₃N₄/ZnO(15%), and (f) g-C₃N₄/ZnO(10%) nanoheterostructures under visible light irradiation

3.7. Kinetics of photodegradation

The kinetic performance of the MB dye degradation catalyzed by the fabricated catalysts was studied by fitted the experimental data to the first-order kinetic model equation (2). Fig. 13 represents the kinetic plots of $\ln(C/C_0)$ vs. irradiation time (min).

It is obvious from the kinetics results that experimental data are well fitted to the first-order kinetic model and follow the pseudo-first-order kinetics. The calculated rate constant (k) and correlation coefficient (R^2) values in the presence of bare g-C₃N₄ and ZnO, and g-C₃N₄/ZnO nanoheterostructures are listed in Table 2. It is obvious from the rate constant data as shown in Table 2, for the g-C₃N₄/ZnO (25%) nanoheterostructures, the highest value of the rate constant is determined, which is approximately ~13 and ~7.76 times greater than to the bare ZnO nanorods and g-C₃N₄ nanosheets for the MB dye degradation under the similar reaction conditions. The existence of larger surface area and more surface active sites, and presence of more reacting species in presence of visible light photons have enhanced the photocatalytic performance of nanoheterostructures. At different pH values of dye solution, the rate constant values are also determined and summarized in Table 3.

Fig. 13. Pseudo-first-order kinetics plot for photodegradation of MB dye over bare ZnO nanorods, g-C₃N₄ nanosheets, and g-C₃N₄/ZnO nanoheterostructures under visible light irradiation

Fig. 14 illustrates the kinetic plot of MB dye at different pH values of dye solution. The highest value of rate constant is calculated at pH=10. Moreover, the photocatalytic degradation capacity of the as-prepared g-C₃N₄/ZnO nanoheterostructures is compared with the some previously reported studies and mentioned in Table 4.

Table 2. Pseudo first-order kinetic parameters for photodegradation of MB dye over ZnO nanorods, g-C₃N₄ nanosheets and g-C₃N₄/ZnO nanoheterostructures under visible light irradiation

Catalyst	R2	Rate constant (min ⁻¹) x10 ⁻³	% degradation
ZnO	0.992	6.53	35.58
g-C ₃ N ₄	0.992	11.30	52.58
g-C ₃ N ₄ /ZnO(2)	0.985	32.52	86.74
g-C ₃ N ₄ /ZnO(4)	0.99	87.73	99.54
g-C ₃ N ₄ /ZnO(6)	0.991	49.93	95.48
g-C ₃ N ₄ /ZnO(8)	0.998	40.66	92.68
Blank	0.918	0.849	5.06

Fig. 14. Pseudo-first-order kinetics plot for photodegradation of MB dye over g-C₃N₄/ZnO (25%) nanoheterostructures under visible light irradiation at various pH values of the solution.

Table 3. Pseudo first-order kinetic parameters for photodegradation of MB dye over g-C₃N₄/ZnO (25%) nanoheterostructures under visible light irradiation at various pH values of solution

pH	R2	Rate constant (min ⁻¹) x10 ⁻³	% degradation
4	0.971	32.13	85.06
6	0.986	38.15	90.43
8	0.988	46.26	94.07
10	0.99	87.73	99.54
12	0.982	61.93	97.62

Table 4. Comparative study of photodegradation efficiencies of some previously reported catalyst over different dyes

Catalyst	Irradiation source	Dye	Degradation time (min)	% degradation	Rate constant(k)	Ref.
g-C ₃ N ₄ @ZnO	Visible	MB	120	91	0.0128 min ⁻¹	[31]
ZnO modified g-C ₃ N ₄	Solar light	MB	120	90	0.0306 min ⁻¹	[32]
g-C ₃ N ₄ /ZnO	Visible light	MB	60	86	0.032 min ⁻¹	[47]
ZnO/g-C ₃ N ₄	Visible light	MB	75	87	0.0489 min ⁻¹	[48]
g-C ₃ N ₄ /ZnO	Visible	MG	45	95	0.061 min ⁻¹	[48]
g-C ₃ N ₄ /ZnO	Visible light	MB	120	60	0.52261 h ⁻¹	[49]
g-C ₃ N ₄ @ZnO	Visible	MB	120	96.40	0.02629 min ⁻¹	[50]
g-C ₃ N ₄ /ZnO	Visible	MB	60	99.54	0.08773 min ⁻¹	Current study

3.8. Reusability

The photostability and reusability of the g-C₃N₄/ZnO nanoheterostructures catalyst is studied by performing the recyclability and reusability photocatalytic experiments for MB dye for four cyclic runs under visible light exposure as shown in Fig. 15. The used photocatalyst is recollected by centrifugation at the end of each experimental run of use, washed with deionized water and ethyl alcohol, and dried in the oven for 3.5 h at 80°C before utilize in the next run of use under the similar reactions conditions as shown in experimental section. The photocatalytic performance of the g-C₃N₄/ZnO heterostructures catalyst is determined to be nearly the same for each run of use. After four runs of reuse, in the photodegradation efficacy of the catalyst, a slight decrease is calculated. However, the efficiency of the catalyst is still reported approx 92% for MB dye under visible-light irradiation. This reveals that the as-prepared g-C₃N₄/ZnO catalyst has demonstrated good stability and reusability under visible light illumination. The slight decrement in the photocatalytic activity of the catalyst could be

accredited to the loss in the amount of photocatalyst during the process of recollection and deposition of intermediate species on the active sites formed during the degradation of dyes.

Fig. 15. Recyclability of g-C₃N₄/ZnO nanoheterostructures catalyst under visible light illumination in four-run of cycles

3.9. Detection of reactive oxidative species

Usually, the main reactive species expected to be engaged in the photocatalytic process are hydroxyl radicals ($\cdot\text{OH}$), holes (h^+), and superoxide radicals ($\text{O}_2^{\cdot-}$). To validate the role of reactive species participated in the photodegradation of MB dye, the reactive species scavenger experiments were performed using tertiary butyl alcohol (t-BuOH), sodium salt of ethylenediaminetetraacetic acid (2Na-EDTA), and benzoquinone (BQ), as $\cdot\text{OH}$, h^+ , and $\text{O}_2^{\cdot-}$ scavengers, respectively, and the photodegradation of MB dye determined using a UV-vis. spectrophotometer after 60 min of visible light irradiation.

Fig. 16. Trapping experiment results for MB dye

It is apparent from Fig. 16, the photocatalytic activity of the g-C₃N₄/ZnO heterostructures catalyst under visible light illumination is significantly decreased to 53.84 % on the addition

of superoxide radical scavenger (BQ), Contrary, the slight decrement in the activity is determined on the mixing of hydroxyl radical (t-BuOH) and hole (EDTA) scavengers, suggesting that superoxide radicals are the main reactive species involved in the photocatalytic degradation of MB dye.

3.10. Photodegradation mechanism

Upon the basis of the results of reactive species scavenger experiments and valance band (VB) edge potential (E_{VB}) and conduction band (CB) edge potential (E_{CB}) values, the plausible photodegradation mechanism for the degradation of MB dye over the g-C₃N₄/ZnO heterostructures photocatalyst can be projected. The E_{VB} and E_{CB} values for g-C₃N₄ and ZnO can be determined using the relation as given in Eqs (5)-(6).

$$E_{VB} = \chi - E_e + 0.5E_g \quad (5)[51]$$

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

where χ is the absolute electronegativity of g-C₃N₄ and ZnO, values of χ were 4.74 eV and 5.6 eV for g-C₃N₄ and ZnO respectively [21], E_e is the energy of free electrons on the hydrogen scale (≈ 4.5 eV) and E_g is the bandgap energy values. The bandgap energy values determined for the g-C₃N₄ and ZnO are 2.72 eV and 3.12 eV respectively. Therefore, the E_{VB} and E_{CB} values are calculated as 1.6 eV and -1.12 eV for g-C₃N₄ and 2.66 eV and -0.46 eV for ZnO.

Thus, the discrete locations of VB and CB edge potentials of ZnO and g-C₃N₄ reveal that a type II heterojunction has been created due to the interaction effects [52]. After the above-detailed analysis and literature studies, a visible light induced plausible photocatalytic mechanism for photodegradation of MB dye over the g-C₃N₄/ZnO nanoheterostructures photocatalyst is suggested and schematically depicted in Fig. 17. Under visible light exposure only the g-C₃N₄ is excited and the photogenerated electron-holes are produced in the VB of g-C₃N₄. The photogenerated electrons move from VB of g-C₃N₄ to the corresponding CB. Due to the creation of heterojunction between g-C₃N₄ and ZnO, and more negative value of the CB edge potential of g-C₃N₄ (-1.12 eV vs. NHE) [53-54] than that of ZnO (-0.46 eV) [54-55], the photogenerated electrons from the CB of g-C₃N₄ could transfer to the CB of ZnO. The accumulated electrons on the CB of ZnO move to the surface of heterojunction and reduce dissolved O₂ molecules into superoxide radicals (O₂^{•-}) because the CB edge potential of the ZnO (-0.46 vs. NHE) is more negative than the standard redox potential $E^\circ(\text{O}_2/\bullet\text{O}_2^-)$ (-0.33 eV vs. NHE) [56-57]. In this way the produced superoxide radicals degrade the MB dye molecules into non-hazardous products.

On the other hand, the photogenerated holes stay in the VB of g-C₃N₄, but could not oxidize OH⁻ or H₂O to •OH radicals, since the VB edge potential of g-C₃N₄ (1.6 eV vs. NHE) is more negative than that of the standard redox potential of E°(•OH/OH⁻) (1.99 eV vs. NHE) [57]. However, the holes are capable to decompose dye molecules directly. In this manner, the transfer of charge carriers is improved and the rate of recombination of the photo-generated electrons-holes pairs is effectively suppressed by the doping of ZnO. Consequently, the photocatalytic performance of the prepared g-C₃N₄/ZnO is enhanced against the dye molecules in comparison to the bare components (g-C₃N₄ and ZnO) of the heterojunction. The relevant reactions are listed below as in Eqs. (7)-(12).

Fig. 17. Photocatalytic degradation mechanism of g-C₃N₄/ZnO nanoheterostructures photocatalyst for degradation of MB dye under visible light irradiation

4. Conclusions

The g-C₃N₄/ZnO hybrid nanoheterostructures photocatalysts with different weight percents of ZnO precursor have been successfully prepared by a facile grinding, dehydration followed by calcination method. The photocatalytic performance of the fabricated g-C₃N₄/ZnO nanostructures is determined much higher in compare to the bare g-C₃N₄ and ZnO. The optimized ZnO content in the g-C₃N₄/ZnO (25%) photocatalyst is 16%. 99.54% of MB dye is degraded in 60 min of visible light irradiation at pH=10 over g-C₃N₄/ZnO (25%) photocatalyst. The results of the kinetic behavior of photodegradation reaction for MB dye have been followed the first-order kinetics and the rate constant value of MB photodegradation in presence of prepared g-C₃N₄/ZnO (25%) are determined ~13 and ~7.76 times higher than that of g-C₃N₄ nanosheets and ZnO nanorods respectively. The enhanced photocatalytic efficiency of the g-C₃N₄/ZnO nanoheterostructures fabricated is due to the creation of heterojunction by the coupling of two semiconductors of well matched band structures in which effective charge transfer is proceed. The prepared g-C₃N₄/ZnO has demonstrated considerable photostability after the use of four cycles. The decrease in the catalyst performance even after four repeated cycles is approximately 8%. Besides, the results obtained from scavenger experiments have been demonstrated that the electrons and the superoxide free radicals (O_2^-) are the main reactive species participated in the degradation of MB dye. The current approach of fabrication of heterojunction has presented a competent and simplistic synthetic tactic of creation of visible-light-driven photocatalyst for the effective photocatalytic mineralization of organic dye contaminants in the aqueous medium. Furthermore, the results of the study validate that as a future perspective, the as-synthesized g-C₃N₄/ZnO nanoheterostructures can be effectively applied as a cost-effective, sustainable, and competent photocatalyst for environmental applications.

Acknowledgments

The authors gratefully acknowledge to the Department of Chemistry, University of Rajasthan, Jaipur (India), MRC, MINT, Jaipur, and Manipal University, Jaipur for technical support. K.S. thanks to the UGC-India and J.K.S. thanks to the CSIR-India for their fellowships.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

References

1. L. Shang, T. Bian, B. Zhang, B. Zhang, L.-Z. Wu, C. Tung, Y. Yin, T. Zhang, Graphene-Supported Ultrafine Metal Nanoparticles Encapsulated by Mesoporous

- Silica: Robust Catalysts for Oxidation and Reduction Reactions. *Angew. Chem. Int. Ed.* 53, 250-254(2014).
2. X. Zhang, X. Xie, H. Wang, J. Zhang, B. Pan, Y. Xie, Enhanced Photoresponsive Ultrathin Graphitic-phase C_3N_4 Nanosheets for Bioimaging. *J. Am. Chem. Soc.*, 135, 18-21(2018).
 3. J. Hong, X. Xia, Y. Wang, R. Xu, Mesoporous Carbon Nitride with In Situ Sulfur Doping for Enhanced Photocatalytic Hydrogen Evolution from Water Under Visible Light. *J. Mater. Chem.*, 22, 15006-15012(2012).
 4. W. Liu, B. Wang, biomimetic synthesis of C-doped g- C_3N_4 spinous hollow microspheres from sunflower pollen with enhanced visible-light photocatalytic performance. *Fullerenes, Nanotubes and Carbon Nanostructures*, 29(12), 966-973(2021). DOI: 10.1080/1536383X.2021.1921741
 5. X.Wang, X. Chen, A. Thomas, X. Fu, Antonietti, M. Metal-Containing Carbon Nitride Compounds: A New Functional Organic-Metal Hybrid Material. *Adv. Mater.* 21, 1609-1612(2009).
 6. F. Dong, L. Wu, Y. Sun, M. Fu, Z. Wu, S.C. Lee, Efficient Synthesis of Polymeric g- C_3N_4 Layered Materials as Novel Efficient Visible Light Driven Photocatalysts. *J. Mater. Chem.* 21, 15171-15174(2011).
 7. Y. Wang, H. Li, J. Yao, X. Wang, M. Antonietti, Synthesis of Boron Doped Polymeric Carbon Nitride Solids and their Use as Metal-Free Catalysts for Aliphatic C–H Bond Oxidation. *Chem. Sci.*, 2, 446-450(2011).
 8. K. Takanabe, K. Kamata, X. Wang, M. Antonietti, J. Kubota, K. Domen, Photocatalytic Hydrogen Evolution on Dye-Sensitized Mesoporous Carbon Nitride Photocatalyst with Magnesium Phthalocyanine. *Phys. Chem. Chem. Phys.*, 12, 13020-13025(2010).
 9. J. X. Sun, Y.P. Yuan, L.G. Qiu, X. Jiang, A.J. Xie, Y. H. Shen, J. F. Zhu, Fabrication of Composite Photocatalyst g- C_3N_4 -ZnO and Enhancement of Photocatalytic Activity Under Visible Light. *Dalton Trans.*, 41, 6756-6763(2012).
 10. W. K. Jo, N. C. S. Selvam, Enhanced Visible Light-Driven Photocatalytic Performance of ZnO-g- C_3N_4 Coupled with Graphene Oxide as a Novel Ternary Nanocomposite. *J. Hazard. Mater.*, 299, 462-470(2015).
 11. M. Alhaddad, R. M. Navarro, M. A. Hussein, R. M. Mohamed, Bi_2O_3 /g- C_3N_4 nanocomposites as proficient photocatalysts for hydrogen generation from aqueous

- glycerol solutions beneath visible light, *Ceramics International*, (2020). doi: <https://doi.org/10.1016/j.ceramint.2020.06.271>
12. W. Yu J. Chen, T. Shang, L. Chen, L. Gu, T. Peng, Direct Z-scheme g- C₃N₄/WO₃ photocatalyst with atomically defined junction for H₂ production. *Appl. Catal. B.*, 219 693–704(2017).
 13. A. Habibi-Yangjeh, M. Mousavi, K. Nakata, Boosting visible-light photocatalytic performance of g- C₃N₄/Fe₃O₄ anchored with CoMoO₄ nanoparticles: novel magnetically recoverable photocatalysts. *J. Photochem. Photobiol. A Chem.*, 368, 120–136(2019).
 14. J. Yu, S. Wang, J. Low, W. Xiao, Enhanced photocatalytic performance of direct Z-scheme g-C₃N₄-TiO₂ photocatalysts for the decomposition of formaldehyde in air. *Phys. Chem. Chem. Phys.*, 15, 16883–16890(2013).
 15. H. Yan, H. Yang, TiO₂-g-C₃N₄ Composite Materials for Photocatalytic H₂ Evolution under Visible Light Irradiation. *J Alloy Compd.*, 509, L26-L29(2011).
 16. T. Aditya, J. Jana, A. Pal, T. Pal, One-Pot Fabrication of Perforated Graphitic Carbon Nitride Nanosheets Decorated with Copper Oxide by Controlled Ammonia and Sulfur Trioxide Release for Enhanced Catalytic Activity, *ACS Omega*, 3, 9318–9332(2018). DOI: 10.1021/acsomega.8b00968
 17. R. Ding, S. Cao, H. Chen, F. Jiang, X. Wang, Preparation of tellurium doped graphitic carbon nitride and its visible-light photocatalytic performance on nitrogen fixation. *Colloids and Surfaces A*, 563, 263-270(2019). doi:10.1016/j.colsurfa.2018.12.020.
 18. J. Fu, S. Wang, Z. Wang, K. Liu, H. Li, H. Liu, J. Hu, X. Xu, H. Li, M. Liu, Graphitic carbon nitride based single-atom photocatalysts. *Frontiers of Physics*, 15(3), 33201(2020). <https://doi.org/10.1007/s11467-019-0950-z>
 19. H. Guo, C.-G. Niu, C.-Y. Feng, C. Liang, L. Zhang, X.-J. Wen, Y. Yang, H.-Y. Liu, L. Li, L.-S. Lin, Steering exciton dissociation and charge migration in green synthetic oxygen-substituted ultrathin porous graphitic carbon nitride for boosted photocatalytic reactive oxygen species generation. *Chemical Engineering Journal*, 385, 123919(2020). doi:10.1016/j.cej.2019.123919.
 20. P. Fageria, K.Y. Sudharshan, R. Nazir, M. Basu, S. Pande, Decoration of MoS₂ on g-C₃N₄ surface for efficient hydrogen evolution reaction, *Electrochimica Acta*, (2017). doi: 10.1016/j.electacta.2017.11.184.
 21. S. Prabhu, M. Pudukudy, S. Harish, M. Navaneethan, S. Sohila, K. Murugesan, R. Ramesh, Facile construction of djembe-like ZnO and its composite with g-C₃N₄ as a

- visible-light-driven heterojunction photocatalyst for the degradation of organic dyes. *Materials Science in Semiconductor Processing*, 106, 104754(2020). <https://doi.org/10.1016/j.mssp.2019.104754>
22. J. Wang, Z. Wang, B. Huang, Y. Ma, Y. Liu, X. Qin, X. Zhang, Y. Dai, Oxygen vacancy induced band-gap narrowing and enhanced visible light photocatalytic activity of ZnO, *ACS Appl. Mater. Interfaces*, 4, 4024–4030(2012). <https://doi.org/10.1021/am300835p>.
 23. X. Pang, C. Cui, M. Su, Y. Wang, Q. Wei, W. Tan, Construction of self-powered cytosensing device based on ZnO nanodisks@g- C₃N₄ quantum dots and application in the detection of CCRF-CEM cells. *Nano Energy*, 46, 101–109(2018). <https://doi.org/10.1016/j.nanoen.2018.01.018>.
 24. J. Liu, X.-T. Yan, X.-S. Qin, S.-J. Wu, H. Zhao, W.-B. Yu, L.-H. Chen, Y. Li, B.-L. Su, Light-assisted preparation of heterostructured g- C₃N₄/ZnO nanorods arrays for enhanced photocatalytic hydrogen performance, *Catal. Today*, (2019). <https://doi.org/10.1016/j.cattod.2019.02.028>.
 25. D.M. Chen, K.W. Wang, T.Z. Ren, H. Ding, Y.F. Zhu, Synthesis and characterization of the ZnO/mpg- C₃N₄ heterojunction photocatalyst with enhanced visible light photoactivity. *Dalton Trans*, 43, 13105–13114(2014).
 26. Y.-P. Zhu, M. Li, Y.-L. Liu, T.-Z. Ren, Z.-Y. Yuan, Carbon-Doped ZnO Hybridized Homogeneously with Graphitic Carbon Nitride Nanocomposites for Photocatalysis. *The Journal of Physical Chemistry C*, 118, 10963–10971(2014). [dx.doi.org/10.1021/jp502677h](https://doi.org/10.1021/jp502677h)
 27. N. Kumaresan, M.M.A. Sinthiya, M. Sarathbavan, K. Ramamurthi, K. Sethuraman, R.R. Babu, Synergetic effect of g- C₃N₄/ZnO binary nanocomposites heterojunction on improving charge carrier separation through 2D/1D nanostructures for effective photocatalytic activity under the sunlight irradiation, *Separation and Purification Technology*, (2019). doi: <https://doi.org/10.1016/j.seppur.2019.116356>
 28. Tan, X.; Wang, X.; Hang, H.; Zhang, D.; Zhang, N.; Xiao, Z.; Tao, H. Self-assembly method assisted synthesis of g- C₃N₄/ZnO heterostructure nanocomposites with enhanced photocatalytic performance. *Optical Materials*, 2019, 96, 109266. <https://doi.org/10.1016/j.optmat.2019.109266>
 29. R. Manimozhi, M. Mathankumar, A.P. Gnana Prakash, Synthesis of g- C₃N₄/ZnO heterostructure photocatalyst for enhanced visible degradation of organic dye. *Optik*, (2020). <https://doi.org/10.1016/j.ijleo.2020.165548>

30. Q. Zhong, H. Lan, M. Zhang, H. Zhu, M. Bu, Preparation of heterostructure g-C₃N₄/ZnO nanorods for high photocatalytic activity on different pollutants (MB, RhB, Cr(VI) and eosin). *Ceramics International*, (2020). <https://doi.org/10.1016/j.ceramint.2020.01.265>
31. R. C. Ngullie, S. O. Alaswad, K. Bhuvaneswari, P. Shanmugam, T. Pazhanivel, P. Arunachalam, Synthesis and characterization of efficient g-C₃N₄/ZnO nanocomposites photocatalyst for photocatalytic degradation of methylene blue. *Coatings*, 10, 500(2020). doi:10.3390/coatings10050500
32. D. R. Paul, S. Gautam, P. Panchal, S.P. Nehra, P. Choudhary, A. Sharma, ZnO-Modified g- C₃N₄: A potential photocatalyst for environmental Aapplication. *ASC, Omega*, (2020). <https://dx.doi.org/10.1021/acsomega.9b02688>
33. A. Priya, R. A. Senthil, A. Selvi, P. Arunachalam, C.S. Kumar, J. Madhavan, R. Boddula, R. Pothu, A.M. Al-Mayouf, A study of the photocatalytic and photoelectrochemical activity of as-synthesized WO₃/g- C₃N₄ composite photocatalysts for AO7 degradation. *Mater. Sci. Energy Technol.*, 3, 43–50(2020).
34. S. Balu, S. Velmurugan, S. Palanisamy, S.-W. Chen, V. Velusamy, T.C.K. Yang, El-S. I. El-Shafey, Synthesis of α -Fe₂O₃ decorated g- C₃N₄/ZnO ternary Z-scheme photocatalyst for degradation of tartrazine dye in aqueous media. *Journal of the Taiwan Institute of Chemical Engineers*, 99, 258–267(2019). <https://doi.org/10.1016/j.jtice.2019.03.011>
35. L. Li, S.-Q. Sun, Y.-X. Wang, C.-Y. Wang, Facile synthesis of ZnO/g-C₃N₄ composites with honeycomb-like structure by H₂ bubble templates and their enhanced visible light photocatalytic performance. *Journal of Photochemistry and Photobiology A: Chemistry*, (2017). <https://doi.org/10.1016/j.jphotochem.2017.12.016>
36. R. Malik, P. S. Rana, V. K. Tomer, V. Chaudhary, S.P. Nehra, S. Duhan, Visible light-driven mesoporous Au-TiO₂/SiO₂ photocatalysts for advanced oxidation process. *Ceramics International*, 42, 10892–10901(2016).
37. C. K. Fan, Q. Feng, G.Q. Xu, J. Lv, Y. Zhang, J.Q. Liu, Y.Q. Qin, Y.C. Wu, Enhanced photocatalytic performances of ultrafine g-C₃N₄ nanosheets obtained by gaseous stripping with wet nitrogen. *Appl. Surf. Sci.*, 427, 730–738(2018).
38. Q. Xu, B. Cheng, J. Yu, G. Liu, Making co-condensed amorphous carbon/g-C₃N₄ composites with improved visible-light photocatalytic H₂-production performance using Pt as co-catalyst. *Carbon*, 118, 241–249(2017).

39. H. Montigud, B. Tanguy, G. Demazeau, I. Alves, S. Courjault, C₃N₄: Dream or reality? Solvothermal synthesis as macroscopic samples of the C₃N₄ graphitic form. *Journal of Materials Science*, 35(10), 2547–2552(2000).
40. F. Ghahramanifard, A. Rouhollahi, O. Fazlolahzadeh, Electrodeposition of Cu-doped p-type ZnO nanorods; effect of Cu doping on structural, optical and photoelectrocatalytic property of ZnO nanostructure, *Superlattices Microstruct.*, 114, 1–14(2018). <https://doi.org/10.1016/j.spmi.2017.07.019>.
41. J. Thomas, Synthesis of Sm³⁺-doped graphitic carbon nitride nanosheets for the photocatalytic degradation of organic pollutants under sunlight. *Catal. Today*, 310, 11–18(2018).
42. N. Li, Y. Tian, J. Zhao, J. Zhang, W. Zuo, L. Kong, H. Cui, Z-scheme 2D/3D g- C₃N₄@ZnO with enhanced photocatalytic activity for cephalixin oxidation under solar light. *Chem. Eng.*, 352, 412–422(2018).
43. M. Wu, Y. Gong, T. Nie, J. Zhang, R. Wang, H. Wang, B. He, Template-free synthesis of nanocage-like g- C₃N₄ with high surface area and nitrogen defects for enhanced photocatalytic H₂ activity. *J. Mater. Chem. A*, (2019). doi: DOI: 10.1039/c8ta12076e
44. H. Osman, Z. Su, X. Ma, Efficient photocatalytic degradation of Rhodamine B dye using ZnO/graphitic C₃N₄ nanocomposites synthesized by microwave. *Environ. Chem. Lett.*, 15, 435-441(2017).
45. R. C. Pawar, Y. Son, Y.J. Kim, S. H. Ahn, C. S. Lee, Integration of ZnO with g- C₃N₄ structures in core-shell approach via sintering process for rapid detoxification of water under visible irradiation. *Current Applied Physics*, 16,101-108(2018).
46. I.-H. Tseng, Y.-M. Sung, P.-Y. Chang, C.-Y. Chen, Anatase TiO₂-decorated graphitic carbon nitride for photocatalytic conversion of carbon dioxide. *Polymers*, 11, 146(2019).
47. N. Chidhambaram, K. Ravichandran, Fabrication of g- C₃N₄/ZnO nanocomposites for enhanced visible light-driven photocatalytic activity. *Mater. Res. Express*. (2017). <https://doi.org/10.1088/2053-1591/aa7abd>
48. K. Ravichandran, K. Kalpana, R. Uma, E. Sindhuja, S.K. Seelan, Cost-effective fabrication of g- C₃N₄/ZnO composite film coated stainless steel meshes for visible light-responsive photocatalysts. *Mater. Res. Bull.*, 99, 268-280(2018).
49. T. Xu, X. Wang, H. Hang, D. Zhang, N. Zhang, Z. Xiao, H. Tao, Self-assembly method assisted synthesis of g- C₃N₄/ZnO heterostructure nanocomposites with enhanced photocatalytic performance. *Optical Materials*, 96,109266(2019).

50. E. Jang, D.W. Kim, S.H. Hong, Y.M. Park, T. J. Park, Visible light-driven g-C₃N₄@ZnO heterojunction photocatalyst synthesized via atomic layer deposition with a specially designed rotary reactor. *Applied Surface Science*, 487, 206–210(2019). <https://doi.org/10.1016/j.apsusc.2019.05.035>
51. X. Lin, J. Xing, W. Wang, Z. Shan, F. Xu, F. Huang, Photocatalytic Activities of Heterojunction Semiconductor Bi₂O₃/BaTiO₃: A Strategy for the Design of Efficient Combined Photocatalysts. *J. Phys. Chem. C*, 111, 18288-18293(2007).
52. Y.C. Shi, S.S. Chen, J.J. Feng, X.X. Lin, W. Wang, A. J. Wang, Dicationic ionic liquid mediated fabrication of Au@Pt nanoparticles supported on reduced graphene oxide with highly catalytic activity for oxygen reduction and hydrogen evolution. *Appl. Surf. Sci.*, 441, 438–447(2018). <https://doi.org/10.1016/j.apsusc.2018.01.240>.
53. J. C. Wang, H.C. Yao, Z.Y. Fan, L. Zhang, J. S. Wang, S.Q. Zang, Z. J. Li, Indirect Z-scheme BiOI/g-C₃N₄ photocatalysts with enhanced photoreduction CO₂ activity under visible light irradiation, *ACS Appl. Mater. Interfaces*, 8, 3765–3775(2016).
54. M. A. Qamar, S. Shahid, M. Javed, S. Iqbal, M. Sher, M.B. Akbar, Highly efficient g-C₃N₄/Cr-ZnO nanocomposites with superior photocatalytic and antibacterial activity. *Journal of Photochemistry & Photobiology A: Chemistry*, 401, 112776(2020). <https://doi.org/10.1016/j.jphotochem.2020.112776>
55. S. C. Yan, S. B. Lv, Z. S. Li, Z.G. Zou, Organic-inorganic composite photocatalyst of g-C₃N₄ and TaON with improved visible light photocatalytic activities, *Dalton Trans.*, 39, 1488–1491(2010).
56. X. L. Fu, W.M. Tang, L. Ji, S.F. Chen, V₂O₅/Al₂O₃ composite photocatalyst: Preparation, characterization, and the role of Al₂O₃. *Chem. Eng. J.*, 180, 170–177(2012).
57. W. Liu, M. Wang, C. Xu, S. Chen, X. Fu, Significantly enhanced visible-light photocatalytic activity of g-C₃N₄ via ZnO modification and the mechanism study. *Journal of Molecular Catalysis A: Chemical*, 368–369, 9-15(2013).