Facile thermal synthesis of g–C3N4/ZnO nanocomposite with antibacterial properties for photodegradation of Methylene blue

Mohammad Javad Hakimi-Tehrani, S A Hassanzadeh-Tabrizi *, Narjes Koupaei, Ali Saffar-Teluri and Mahdi Rafiei

Abstract
Semiconductors as photocatalysts are ideal materials for wastewater remediation. A nanocomposite of g–C3N4 and ZnO was produced using a two-step in situ synthesis technique to achieve a better photocatalyst. The samples were assessed via UV–vis diffuse reflection spectroscopy, transmission electron microscopy, photoluminescence spectroscopy, Fourier transform infrared analysis, and x-ray diffraction. The photodegradation of methylene blue as an organic dye model was assessed to assess the photocatalytic characteristics of the fabricated samples. The antibacterial characteristics of synthesized samples were also investigated. The findings revealed that the photodegradation efficiency of the binary g–C3N4/ZnO systems was better than that of pure g–C3N4. Under irradiation, the photodegradation yield of g–C3N4/ZnO with a 15 wt.% of ZnO was up to 3.5 times better than that of pristine g–C3N4. The feature of enhanced separation of photoinduced holes and electrons resulting from heterojunction creation among g–C3N4 and ZnO surfaces might be attributed to this photocatalytic activity enhancement. The synthesized binary nanocomposites showed suitable antibacterial properties against Staphylococcus aureus and Escherichia coli bacteria.

1. Introduction
Consumption of lots of fossil fuels and production factory waste by populations have resulted in fast reduction of resources and alarming levels of environmental pollution in the modern world [1–3]. Water pollution is currently being recognized as a major problem for humans, as it is regularly affected by a variety of harmful chemicals from industries such as textiles, cosmetics, food, and paint [4–6]. There are various ways available for dealing with contaminated water in this respect, but visible-light-activated photocatalysis procedures are regarded to be a successful strategy that may have captivated the world due to its limitless solar energy [7–9]. Photocatalytic characteristics of semiconductors are highly dependent on their intrinsic physicochemical natures, comprising their band-gap position, surface properties, particle size, etc [10–13].

The most stable form of C3N4, polymeric g–C3N4 or g–C3N4 (g stands for graphitic), with a band gap of around 2.7 eV [14], has potential applications for the energy industry [15, 16], hydrogen generation [17–20], gas sensors [21, 22], and solar cells [23–25]. The g–C3N4 has recently been studied as a visible-light-activated semiconductor for splitting H2O into O2 and H2 molecules under visible light [26–32]. It also works as a catalyst for the removal and photodegradation of organic-based pollutants in H2O [33, 34] or in the air [35]. The g–C3N4 semiconductor has desirable and useful properties for different applications because of its great chemical and thermal stability. Nevertheless, fast recombination of photoproduced electron–hole (e–h) pairs is a problem in this material. This phenomenon reduces the yield of catalytic efficiency of bare g–C3N4 [36, 37].

Synthesis of nanosheet with mesoporous structures [38], alteration via reversible protonation [39], adding different elements [40, 41], combining with conductive nanomaterials like graphene [42] and noble metal [43], and adding other semiconductor materials [44, 45] have all been tried to ameliorate the catalytic efficiency of g–C3N4 under visible light. For instance, Zhang et al [46] produced g–C3N4/LaFeO3/Ag nanocomposite with a
Z-scheme heterojunction. They showed that the prepared nanosystem exhibits high photocatalytic activity for the photodegradation of methylene blue and tetracycline hydrochloride. Tian et al [47] synthesized two-dimensional g-C3N4/MoS2/graphene tertiary composite via an in situ adsorption method and showed the prepared samples have high photodegradation activities under visible light for the removal of Rhodamine B.

One of the most efficient ways for separating photogenerated e-h pairs and increasing photocatalytic efficiency is semiconductor coupling [48, 49]. Combining g-C3N4 with ZnO to create a multi-component system is a unique and practical method for improving light harvesting and e-h separation. The creation of a heterojunction between g-C3N4 and ZnO might explain the inhibition of e-h recombination and improved harvesting of photons in the visible region [50]. The goal of the present investigation is to synthesis g-C3N4/ZnO nanocomposite via an in situ thermal decomposition to have a clean interface between these two semiconductors. Then, the photocatalytic efficiency of the produced composites was examined via MB removal. The antibacterial characteristics of samples were also assessed.

2. Experimental

2.1. Materials
Zinc acetate dihydrate (Zn(OAC)2H2O, Sinchem, 99%) and urea (CO(NH2)2, Sinchem, >98%) were utilized as the raw materials of ZnO and g-C3N4, respectively.

2.2. Fabrication of pristine g-C3N4 and g-C3N4/ZnO nanosheets
10 grams of (CO(NH2)2) in an Al2O3 crucible were heated until they were thermally decomposed at 555 °C for two hours at a heating rate of 4 °C min−1 to yield pure g-C3N4 powder. The bulk g-C3N4 was then ground into a powder and heat-treated in an electrical oven at 355 °C for 3 h at the same rate. The second process is necessary for exfoliating g-C3N4 powder into g-C3N4 nanosheets. The g-C3N4/ZnO samples were produced in the same way, but before the second heat treatment, the g-C3N4 powder was blended with different amounts of (Zn(OAC)2).2H2O.

2.3. Characterization
An x-ray Philips PW3040 diffractometer with copper radiation (λ=0.154 nm) was utilized to record the photocatalysts’ x-ray diffraction (XRD) information. SEM (TESCAN, model MIRA III) was utilized to evaluate the morphology of specimens. TEM micrographs were taken with a CM120 microscope and a 100 kV accelerating voltage. FTIR spectroscopy was utilized to investigate the surface molecular structure (AVATAR Thermo). UV–vis spectra had been utilized with a Shimadzu UV-2450. An Avaspec 2048 TEC fluorescence spectrometer was utilized to take the photoluminescence (PL) spectra. To analyze the emission spectra, the samples were stimulated at a wavelength of 326 nm.

2.4. Photocatalytic evaluation
Under irradiation, the photodegradation of MB (10 mg/l) was generally carried out in a Pyrex beaker with 50 mg of the samples distributed in 50 ml of methylene blue solutions. The resultant specimen was blended without light for thirty minutes to have an adsorption and desorption equilibrium before being lighted. At regular intervals, three milliliters of solution were taken from the beaker, centrifuged, and examined using UV–visible spectrophotometry (Optizen 3220UV) at 664 nm (maximum UV wavelength that MB absorb).

2.5. Antibacterial properties
The antibacterial characteristics of the synthesized specimens against Escherichia coli as gram-negative and Staphylococcus aureus as gram-positive bacteria were investigated by the agar well diffusion method. The bacterial strains were purchased from Persian Type Culture Collection. The turbidity of the bacterium suspension was equal to the turbidity of the 0.5 McFarland solution. For preparation culture medium, in sterilized Petri plates, the sterilized Muller–Hinton agar solution was placed, and the plates were maintained until the medium hardened. After that, using a sterilized plastic borer, wells were drilled into the Petri plates. The germs were inoculated into the agar plates using a sterilized swab. Suspensions of 0.02 g of samples were added to the wells. Sterilized water and tetracycline were used as negative and positive controls, respectively. After that, the cultivated specimens were kept at 37 °C for 24 h. A ruler was utilized to calculate the inhibition zones that had developed.
3. Results and discussion

The XRD arrays of pristine g–C₃N₄ and binary nanocomposite are presented in figure 1. The peak at 13.1° is due to the (100), pertinent to the in-plane packing motif. The peak at 27.5° pertains to the (002) stacking structures (ICSD 87–1526). These peaks confirm the creation of g–C₃N₄ [26]. The g–C₃N₄ has a plane filling arrangement interlayer deposition structure with a period of 0.0675 nm [51, 52]. Furthermore, it is found that there are diffraction peaks at 31.74°, 34.44°, 36.26°, 47.5°, 56.52°, 62.86° and 67.92°, related to (100), (002), (101), (102), (110), (103) and (112) planes of ZnO, respectively (JCPDS No.36–1451). The XRD results the synthesized ZnO has hexagonal wurtzite assembly.

Scanning electron microscope images, EDS and MAP analysis were utilized to study the structure of the samples. Figures 2 and 3 present the structure of the pure g–C₃N₄ and binary g–C₃N₄/ZnO composite. The images clearly reveal that the structure of g–C₃N₄ is flat, comprising of layer morphology which is common for this material. It seems that ZnO nanoparticles cling to the g–C₃N₄ surfaces. The EDS analyses show C and N for pure sample and C, N, Zn and O for binary specimens, which confirm the formation of g–C₃N₄ and ZnO in the samples. MAP analyses exhibit a uniform distribution of elements which is important for the photocatalytic activity of a multicomponent semiconductor system.

TEM was employed to examine the sizes and morphologies of binary nanocomposites. The darker parts in the image may be ascribed to ZnO, while the grey region could be given to g–C₃N₄, as seen in figure 4. The surface and edge of the g–C₃N₄ are decorated with ZnO nanoparticles. The interaction between the ZnO particles and the g–C₃N₄ was strong enough that the ultrasonication procedure for dispersion of the samples on the copper gride for TEM investigation was unable to peel these nanoparticles away, implying the formation of a proper connection between two semiconductors which is critical for facile electron and hole movement among ZnO and g–C₃N₄.

The chemical groups of pure g–C₃N₄ and binary nanocomposite were assessed via FTIR, as presented in figure 5. The stretching vibration associated to the O–H part of the water molecules in the specimens and the N–H vibrations of the g–C₃N₄ edge-deficient loop is responsible for the absorption peak between 3200 and 3500 cm⁻¹ [26]. Typical C–N or C=N have absorption peaks in the region of 1201 to 1699 cm⁻¹ [52]. The triazine ring vibration in g–C₃N₄ is binary C₃N₄/ZnO nanocomposite shows a small redshift when compared to pristine g–C₃N₄ (811 cm⁻¹), showing that g–C₃N₄ interacts with ZnO [53]. Naturally, the interaction of g–C₃N₄ with ZnO enhances both the development of heterojunctions and electron transport during photochemical reactions.

The effectiveness of e-h separation in the samples was determined using photoluminescence analysis. Radiative recombination of photoelectrons and generated holes is known to cause photoluminescence emissions on semiconductors [54]. It can be seen in figure 6, pristine g–C₃N₄ presents a broad PL peak at about

![Figure 1. XRD patterns of pure g–C₃N₄ and g–C₃N₄/ZnO samples.](image-url)
461 nanometer. This peak may be attributed to the band gap emission of g–C₃N₄. The binary nanocomposite had much less emission intensity than pure g–C₃N₄. It indicates e-h recombination in g–C₃N₄ was successfully suppressed following the development of heterojunction structures between g–C₃N₄ and ZnO.

An UV–vis spectrometer was employed to evaluate the optical performance of all specimens (figure 7). Between 380 nm and 800 nm, the absorption peaks of the specimens were red-shifted, denoting considerably increased absorption, and the absorbance intensity increased with adding ZnO to g–C₃N₄. The Kubelka–Munk
formula (equation (1)) was utilized to measure the band gap energy of g–C₃N₄ and ZnO.

\[
(F(R)hv)^n = k(hv - E_g)
\]

where \( F(R) = \frac{(1 - R)^2}{2R} \) and \( R \) is reflectance. \( E_g, k, h, \) and \( \nu \) are band gap energy, a constant, Planck’s constant, and light frequency, respectively. The \( n = 0.5 \) for the indirect band gap and \( n = 2 \) for the direct band gap. For pristine g–C₃N₄ and binary g–C₃N₄/ZnO composites, the value of \( n \) is 0.5 [55]. For g–C₃N₄ and binary composite, the extrapolated intercept in figure 8 yields \( E_g \) values of 2.73 and 2.68 eV, respectively. The decreased band gap energy of the binary nanocomposite might contribute to higher visible light harvesting, promoting the production of more \( e^-\cdot h^+ \) pairs, and therefore increased photoactivity [56].

Figure 9 depicts the photodegradation results of the pristine g–C₃N₄ and composites with different amounts of ZnO. Without the catalyst, no deterioration was identified under irradiation, indicating that the MB was highly stable in this situation. It takes time about 30 min to get the equilibrium. Compared to g–C₃N₄, the photocatalytic efficiency of the binary nanocomposite was greater under light irradiation. As can be seen, the amount of ZnO had a profound influence on the photodegradation yield of the specimens. Low loading
amounts of ZnO result in an effective decreasing interface between two semiconductors, thus decreasing the efficiency of photoinduced e-h separation and their easy transfer. On the other hand, a high amount of ZnO increases the portion of the semiconductor that works just under ultraviolet light, causing a lower efficiency of harvesting visible light. Therefore, a proper weight percent of g–C3N4 to ZnO is critical to have the best photodegradation efficiency. In the present study, the g–C3N4–15 wt% ZnO (ZnO:g–C3N4 weight ratio of 0.18:1) had the highest photodegradation efficiency. The photodegradation efficiency after 90 min irradiation was 25 and 73% for pure g–C3N4 and g–C3N4–15wt.%ZnO, respectively. This result might be due to the proper heterojunction structures in the binary composite samples, which leads to minimal charge barrier recombination and adequate active sites. The photocatalytic process under irradiation was fitted to pseudo-first-order kinetics, as presented in figure 10, with the reaction rate constant (k) estimated using the famous rate law equation (equation (2)) [57].

\[
-ln \left( \frac{C}{C_0} \right) = kt
\]  

Figure 6. PL spectra of pure g–C3N4 and g–C3N4/ZnO nanocomposite.

Figure 7. UV–vis diffused absorbance spectra of (a) g–C3N4 and (b) g–C3N4/ZnO nanocomposite.
results show adding proper amounts of ZnO could effectively increase the reaction rate constant and thus ameliorate photodegradation yield.

For effective use of photocatalysts, the catalyst’s reusability is a critical factor. In other words, it is important for a photocatalyst to maintain its characteristics after several uses [58, 59]. Repeated photodegradation experiments of the g–C₃N₄/ZnO nanocomposite were carried out to validate the catalytic life time of the synthesized samples. For this aim, the used composites were centrifuged, separated, and dried at 55 °C for 24 h and then the samples were utilized for further photocatalyst experiments. Figure 11 displays the reusability of g–C₃N₄/ZnO nanocomposites after different cycles. The results reveal that after the several runs, there is no sharp decline in photodegradation activity. Therefore, the produced g–C₃N₄/ZnO nanocomposites demonstrated excellent stability during the photodegradation activity.

In the photodegradation process, organic compounds are attached to the photocatalyst and destroyed directly via charge carriers like holes or indirectly through the hydroxyl and superoxide species [60, 61]. After a sequence of reactions, organic molecules are generally destroyed into water and carbon dioxide molecules. However, the development of intermediate molecules was also reported [46, 62]. The photoinduced electron and hole movement in this binary system could be explained by Z-scheme or type-II mechanisms [63, 64]. Trapping tests were set up to investigate the prominent mechanism in this nanocomposite, as shown in figure 12. For this aim, triethanolamine (TEA) as the hole scavenger, benzoquinone (BQ) as the superoxide scavenger, and isopropanol (IP) as the hydroxyl radical scavenger were used. As can be seen, BQ and TEA
hindered photoactivity remarkably. The results show superoxide in the CB and hole in the VB have the most decisive influence on photodegradation yield. Moreover, IP does not have much effect on photodegradation suggesting hydroxyl radicals are not mainly involved in the reactions. The oxygen to superoxide redox potential is $-0.33$ eV \[65\]. The valance band positions of g–C\textsubscript{3}N\textsubscript{4} and ZnO are $-1.3$ and $-0.5$ eV, respectively, which are favorable for the formation of superoxide species. The redox potential of $·\text{OH}$ to $\text{OH}^-$ is $+1.99$ eV \[66\]. The g–C\textsubscript{3}N\textsubscript{4} and ZnO have valance band positions at $+1.4$ and $+2.7$ eV, respectively. According to valance band position, the photogenerated holes on the g–C\textsubscript{3}N\textsubscript{4} could not react with H\textsubscript{2}O to create $·\text{OH}$ species, whereas ZnO could do. If the Z-scheme is a main mechanism of photocatalyst, holes must remain in the ZnO valance band and oxidize water to $·\text{OH}$ species. Then, $·\text{OH}$ radicals participate in photoreactions. However, the findings of trapping tests confirm the profound role of holes and a minor function of $·\text{OH}$ in the photoreactions. It shows that the type-II junction is a more probable mechanism compared to Z-scheme for this binary composite in the present work.

The photocatalytic mechanism of binary composites is postulated based on the findings of the photocatalysis investigation, as illustrated in figure 13. Electrons in g–C\textsubscript{3}N\textsubscript{4} move from the valance band (VB) into the conduction band (CB) when exposed to light, resulting in a corresponding number of holes in the valance band. In comparison to ZnO, the CB of g–C\textsubscript{3}N\textsubscript{4} is more negative. Therefore a portion of photoproduced electrons could be transported from the CB of g–C\textsubscript{3}N\textsubscript{4} to the CB of ZnO at the heterojunction contact \[51, 67\]. The valance bond of g–C\textsubscript{3}N\textsubscript{4} has a less positive value than that of ZnO. The photoinduced holes produced in the
valence band of ZnO could move from the valence band of ZnO to g–C3N4. The photoinduced e and h eventually become separated, prolonging the lifespan of the photogenerated carriers. The photoproduced electrons combine with O2 molecules to generate superoxide species. In addition, photoproduced holes in the solution could not interact with H2O and OH– to generate ·OH as discussed before. Organic dyes and reagents can be degraded by superoxide and hole species, as confirmed by trapping experiments which may produce CO2 and H2O. Therefore, the photocatalytic efficiency of the binary composite may be enhanced via the movement of e-h between two semiconductors which results in the separation of photogenerated e and h.

Antibacterial characteristics of g–C3N4 and binary nanocomposites were studied against two Gram-positive and Gram-negative strains by determining their inhibition zone, as shown in figure 14. As can be seen, the binary g–C3N4/ZnO nanocomposites with 15wt.% ZnO have higher antibacterial properties against both *Staphylococcus aureus* and *Escherichia coli* bacteria compared to pure g–C3N4 specimens. Zone inhibitions against *Escherichia coli* bacteria for g–C3N4/ZnO, g–C3N4 and positive control were 26, 18 and 19 mm, respectively. These values against *Staphylococcus aureus* for g–C3N4/ZnO, g–C3N4 and positive control were 24, 22 and 24 mm, respectively. Different possible mechanisms were reported for the antibacterial actions of nanomaterials. First, inorganic materials release ions in the environment of bacteria. For instance, it was...
reported that Zn$^{2+}$ ions released from zinc oxide could attach and enter inside the cells, thus killing the bacteria [68, 69]. Another mechanism is the creation of reactive oxygen groups (ROS), which may be activated in the semiconductor materials like ZnO and CuO [70–72]. These reactive species would destroy the bacteria membrane and damage the integrity of the bacterium. In the present work, Zn$^{2+}$ ions could increase oxidative stress in the cells and combine with the bacteria. This phenomenon could have an adverse effect on the fluidity of the cell membrane and change the normal function of bacteria [73].

Figure 14. Pictures of the inhibition zone of the samples against *Escherichia coli* and *Staphylococcus aureus* bacteria.
4. Conclusions

The g–C₃N₄/ZnO nanocomposite was prepared and characterized. XRD and FTIR studies revealed significant coordination of ZnO with g–C₃N₄ and minor degradation of the crystalline arrangement of pristine g–C₃N₄ when ZnO was added. PL and DRS analyses showed that the binary nanocomposite had a lower emission intensity and better visible light harvesting compared to g–C₃N₄, resulting in more active sites, photoinduced e-h pairs, and lower e-h recombination. These benefits could result in a higher photocatalytic potential. According to photocatalytic test results, g–C₃N₄/ZnO nanocomposite showed a 3.3-fold increase in the apparent rate constant toward MB dye degradation compared to pure g–C₃N₄. This research presents a simple synthesis technique for making g–C₃N₄/ZnO nanocomposite, which has commercial potential.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

S A Hassanzadeh-Tabrizi  https://orcid.org/0000-0001-8425-4822

References

[1] Gaya U I and Abdullah A H 2008 Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems J. Photochem. Photobiol. C Photochem. Rev. 9 1–12
[2] Guo F, Cai Y, Guan W, Huang H and Liu Y 2017 Graphite carbon nitride/ZnIn₂S₄ heterojunction photocatalyst with enhanced photocatalytic performance for degradation of tetracycline under visible light irradiation J. Phys. Chem. Solids 110 370–8
[3] Emsaki M, Hassanzadeh-Tabrizi S A and Saffar-Teluri A 2018 Microemulsion synthesis of ZnO–ZnWO₄ nanoparticles for superior photocatalytic degradation of organic dyes in water J. Mater. Sci. Mater. Electron. 29 2384–90
[4] Xu Q, Feng J, Li L, Xiao Q and Wang J 2015 Hollow ZnFe₂O₄/TiO₂ composites: high-performance and recyclable visible-light photocatalyst J. Alloys Compd. 641 110–8
[5] Bora L V and Mewada R K 2017 Visible/solar light active photocatalysts for organic effluent treatment: fundamentals, mechanisms and parametric review Renew. Sustain. Energy Rev. 76 1393–421
[6] Aydoghmish S M, Hassanzadeh-Tabrizi S A and Saffar-Teluri A 2019 Facile synthesis and investigation of NiO–ZnO–Ag nanocomposites as efficient photocatalysts for degradation of methylene blue dye Ceram. Int. 45 14934–42
[7] Yu C, Cao F, Li G, Wei R, Jimmy C Y, Jin R, Fan Q and Wang C 2013 Novel noble metal (Rh, Pd, Pt)/BiOX (Cl, Br, I) composite photocatalysts with enhanced photocatalytic performance in dye degradation Sep. Purif. Technol. 120 110–22
[8] Yang J, Duan W, Jiang H, Luo S and Luo Y 2015 Mesoporous TiO₂@Ag₂PO₄ photocatalyst with high adsorbility and enhanced photocatalytic activity under visible light Mater. Res. Bull. 70 129–36
[9] Nazari M, Golestoni-Fard F, Bayati R and Eftekhar-Yekta B 2015 Enhanced photocatalytic activity in anodized WO₃-loaded TiO₂ nanotubes Superlattices Microstruct. 80 91–101
[10] Dong F, Zhao Z, Xiong T, Ni Z, Zhang W, Sun Y and Ho W-K 2013 In situ construction of g–C₃N₄/g–C₃N₄ metal-free heterojunction for enhanced visible-light photocatalysis ACS Appl. Mater. Interfaces 5 11392–401
[11] Xiang Q, Yu J and Jaroniec M 2012 Graphene-based semiconductor photocatalysts Chem. Soc. Rev. 41 782–96
[12] Tong H, Ouyang S, Bi Y, Umerzawa N, Oshikiri M and Ye J 2012 Nano–photocatalytic materials: possibilities and challenges Adv. Mater. 24 294–51
[13] Di Paola A, García-López E, Marci G and Palmsinos I 2012 A survey of photocatalytic materials for environmental remediation J. Hazard. Mater. 211 3–29
[14] Wang X, Blechert S and Antonietti M 2012 Polymeric graphitic carbon nitride for heterogeneous photocatalysis ACS Catal. 2 1596–606
[15] Kroke E and Schwarz M 2004 Novel group 14 nitrides Chem. Soc. Rev. 34 178–95
[16] Vinn A 2008 Two-dimensional hexagonally-ordered mesoporous carbon nitrides with tunable pore diameter, surface area and nitrogen content Adv. Funct. Mater. 18 816–27
[17] Ito H, Nakazi T, Sakukubo A, Yamada N, Kanda K, Niih M and Saitoh H 2008 Hydrogen–storage characteristics of hydrogenated amorphous carbon nitrides Thin Solid Films 516 6573–9
[18] Yang S J, Cho J H, Oh G H, Nahm K S and Park C R 2009 Easy synthesis of highly nitrogen–enriched graphitic carbon with a high hydrogen storage capacity at room temperature Carbon N. Y. 47 1585–91
[19] Bai X D, Zhong D, Zhang G Y, Ma X C, Liu S, Wang E G, Chen Y and Shaw D T 2001 Hydrogen storage in carbon nitride nanobells Appl. Phys. Lett. 79 1552–4
[20] Li Q, Yang J, Feng D, Wu Z, Wu Q, Park S S, Ha C-S and Zhao D 2010 Facile synthesis of porous carbon nitride spheres with hierarchical three-dimensional mesostructures for CO₂ capture Nano Res. 3 5632–42
[21] Lee S P 2011 Synthesis of carbon nitride films for micro humidity sensors Sensors 8 1508–18
[22] Lee S P, Lee J G and Chowdhury S 2008 CMOS humidity sensor system using carbon nitride film as sensing materials Sensors 8 2662–72
[23] Zhou Z B, Cui R Q, Peng Q J, Hadi G M, Ding Z M and Liu J W 2002 Schottky solar cells with amorphous carbon nitride thin films prepared by ion beam sputtering technique Sol. energy Mater. Sol. cells 70 487–93
[24] Zhang Y and Antonietti M 2010 Photocurrent generation by polymeric carbon nitride solids: an initial step towards a novel photovoltaic system Chem. Asian J. 5 1307–11
[25] Di Noto V and Negro E 2010 Development of nano-electrocatalysts based on carbon nitride supports for the ORR processes in PEM fuel cells Electrochem. Acta 55 7564–74
[26] Wang X, Maeda K, Thomas A, Takanabe K, Xin G, Carlson J M, Domen K and Antonietti M 2009 A metal-free polymeric photocatalyst for hydrogen production from water under visible light Nat. Mater. 8 76–80

[27] Zhang Y, Mori T and Ye J 2012 Polymeric carbon nitrides: semiconducting properties and emerging applications in photocatalysis and photoelectrochemical energy conversion Sci. Adv. Mater. 4 282–91

[28] Maeda K, Wang X, Nishihara Y, Lu D, Antonietti M and Domen K 2009 Photocatalytic activities of graphitic carbon nitride powder for water reduction and oxidation under visible light J. Phys. Chem. C 113 4940–7

[29] Wang X, Maeda K, Chen X, Takanabe K, Domen K, Hou Y, Fu X and Antonietti M 2009 Polymer semiconductors for artificial photosynthesis: hydrogen evolution by mesoporous graphitic carbon nitride with visible light J. Am. Chem. Soc. 131 1680–1

[30] Di X, Wang X, Thomas A and Antonietti M 2010 Making metal–carbon nitride heterojunctions for improved photocatalytic hydrogen evolution with visible light ChemCatChem 2 834–8

[31] Zhang J, Chen X, Takanabe K, Maeda K, Domen K, Ebbing JD, Fu X, Antonietti M and Wang X 2010 Synthesis of a carbon nitride structure for visible-light catalysis by copolymerization Angew. Chemie Int. Ed. 49 441–4

[32] Kailasam K, Epping JD, Thomas A, Losse S and Junge H 2011 Mesoporous carbon nitride–silica composites by a combined sol–gel/thermal condensation approach and their application as photocatalysts Environ. Sci. 4 4668–74

[33] Yan S-C, Li Z-S and Zou Z-G 2009 Photodegradation performance of g–C3N4 fabricated by directly heating melamine Langmuir 25 10397–401

[34] Liu J, Zhang T, Wang Z, Dawon G and Chen W 2011 Simple pyrolysis of urea into graphitic carbon nitride with recyclable adsorption and photocatalytic activity J. Mater. Chem. 21 14398–401

[35] Zhu J, Wei Y, Chen W, Zhao Z and Thomas A 2010 Graphitic carbon nitride as a metal-free catalyst for NO decomposition Chem. Commun. 46 6965–7

[36] Wen J, Xia J, Chen X and Li X 2017 A review on g–C3N4-based photocatalysts Appl. Surf. Sci. 391 72–123

[37] Patnaik S, Sahoo D P and Parida K 2018 Recent advances in anion doped g–C3N4 photocatalysts: A review Carbon N. Y. 172 682–711

[38] Shi X, Liu J, Ji H, Mo Z, Li Y, Huang L, Du D, Xu H and Li H 2016 Template-free synthesis of 2D porous ultrathin nonmetal-doped g–C3N4 nanosheets with highly efficient photocatalytic H2 evolution from water under visible light Appl. Catal. B Environ. 187 144–53

[39] Zhang Y, Thomas A, Antonietti M and Wang X 2009 Activation of carbon nitride solids by protonation: morphology changes, enhanced ionic conductivity, and photocatalytic experiments J. Am. Chem. Soc. 131 50–1

[40] Liu Q and Zhang J 2013 Graphene supported Co–g–C3N4 as a novel metal–macrocylic electrocatalyst for the oxygen reduction reaction in fuel cells Langmuir 29 3821–8

[41] Liu J 2016 Effect of phosphorus doping on electronic structure and photocatalytic performance of g–C3N4: insights from hybrid density functional calculations J. Alloys Compd. 672 271–6

[42] Liao G, Chen S, Quan X, Yu H and Zhao H 2012 Graphene oxide modified gC3 N4 hybrid with enhanced photocatalytic capability under visible light irradiation J. Mater. Chem. 22 2721–6

[43] Jang I, Kang T, Cho W, Kang Y-S, Oh S-G and Im S 2015 Preparation of silver nanowires coated with TiO2 using chemical binder and their applications as photoanodes in dye sensitized solar cell J. Phys. Chem. Solids 86 122–30

[44] Jo W-K, Adinaveen T, Vijaya J and Selvam NCS 2016 Synthesis of Mo3S5 nanosheet supported Z–scheme TiO2/gC3N4 photocatalysts for the enhanced photocatalytic degradation of organic water pollutants Rsc Adv. 6 10487–97

[45] Li X, Li M, Yang J, Li X, Hu T, Wang J, Sui Y, Wu X and Kong L 2014 Synergistic effect of efficient adsorption g–C3N4/ZnO composite for photocatalytic property J. Phys. Chem. Solids 75 441–6

[46] Zhang W, Ma Y, Zhu X, Liu S, An T, Bao J, Hu X and Tian H 2021 Fabrication of Ag decorated g–C3N4/LaFeO3: Z–scheme heterojunction as highly efficient visible–light photocatalyst for degradation of methylene blue and tetracycline hydrochloride J. Alloys Compd. 864 158914

[47] Tian H, Liu M and Zheng W 2018 Constructing 2D functionalized carbon nanosheets layered MoS2/graphene ternary nanojunction with enhanced photocatalytic activity Appl. Catal. B Environ. 225 468–76

[48] Zhang J, Zhang M, Sun R and Wang X 2012 A facile band alignment of polymeric carbon nitride semiconductors to construct type heterojunctions J. Chem. Educ. 51 10145–9

[49] Hassanzadeh–Tabrizi S A 2021 Synthesis of NiFe2O4 nanoparticles immobilized on mesoporous g–C3N4 sheets and application for degradation of antibiotics J. Photochem. Photobiol. A Chem. 418 113398

[50] Yuan X, Duan S, Wu G, Sun L, Cao G, Li D, Xu H, Li Q and Xiao D 2018 Enhanced catalytic ozonation performance of highly stabilized mesoporous ZnO doped g–C3N4 composite for efficient water decontamination Appl. Catal. A Gen. 551 129–38

[51] Sun J-X, Yuan Y-P, Qiu L-G, Jiang X, Xie A-J, Shen Y-H and Zhu J-F 2012 Fabrication of composite of Ag decorated g–C3N4/Fe3O4: Z–scheme heterojunction as highly efficient visible–light photocatalyst for degradation of methylene blue and tetracycline hydrochloride J. Alloys Compd. 864 158914

[52] Li X, Zhang J, Shen L, Ma Y, Lei W, Cui Q and Zou G 2009 Preparation and characterization of graphitic carbon nitride nanorods by photoelectrochemical synthesis of graphene photocatalyst through pyrolysis of melamine Appl. Phys. A 94 387–92

[53] Wang J, Xia Y, Zhao H, Wang G, Xiang L, Xu J and Komarneni S 2017 Oxygen defects-mediated Z–scheme charge separation in g–C3N4/ZnO photocatalysts for enhanced visible–light degradation of 4–chlorophenol and hydrogen evolution Appl. Catal. B Environ. 206 406–16

[54] Zhang X, Qin J, Xue Y, Yu P, Zhang B, Wang L and Liu R 2014 Effect of aspect ratio and surface defects on the photocatalytic activity of ZnO nanorods Sci. Rep. 4 1–8

[55] Yoon M, Seo M, Jeong C, Jang J H and Jeon K S 2005 Synthesis of liposome–templated titania nanodisks: optical properties and photocatalytic activities Chem. Mater. 17 6069–79

[56] Fatima S, Ali S I, Isqbal M Z and Riazwan S 2017 The high photocatalytic activity and reduced band gap energy of La and Mn co-doped BiFeO3/graphene nanoplatelet (GNP) nanocomposites RSC Adv. 7 35928–37

[57] Mahvi A H, Ghanbarian M, Nasser S and Khairi A 2009 Mineralization and discoloration of textile wastewater by TiO2 nanoparticles J. Desalination 239 309–16

[58] Hassanzadeh–Tabrizi S A, Nguyen C C and Do T O 2019 Synthesis of Fe3O4/Pt/Ga NC composite immobilized on g–C3N4 for localized plasmon photocatalytic hydrogen evolution Appl. Surf. Sci. 489 741–54

[59] Hassanzadeh–Tabrizi S A and Do T O 2018 Sol–gel synthesis and photocatalytic activity of ZnO–Ag–Sm nanoparticles for water treatment J. Mater. Sci. Mater. Electron. 29 10986–91

[60] Tian H, Shen K, Hu X, Qiao L and Zheng W 2017 N–Co doped graphene quantum dots–graphene–TiO2 nanotubes composite with enhanced photocatalytic activity J. Alloys Compd. 691 369–77

[61] Wenderich K and Mul G 2016 Methods, mechanism, and applications of photoeposition in photocatalysis: a review Chem. Rev. 116 14567–619
[62] Shen K, Xue X, Wang X, Hu X, Tian H and Zheng W 2017 One-step synthesis of band-tunable N, S co-doped commercial TiO$_2$/graphene quantum dots composites with enhanced photocatalytic activity RSC Adv. 7 23319–27

[63] Wong K T, Kim S C, Yun K, Choong C E, Nah I W, Jeon B-H, Yoon Y and Jang M 2020 Understanding the potential band position and e–/h + separation lifetime for Z-scheme and type-II heterojunction mechanisms for effective micropollutant mineralization: Comparative experimental and DFT studies Appl. Catal. B Environ. 273 119034

[64] Kim D and Yong K 2021 Boron doping induced charge transfer switching of a C$_3$N$_4$/ZnO photocatalyst from Z-scheme to type II to enhance photocatalytic hydrogen production Appl. Catal. B Environ. 282 119538

[65] Li K, Xue Y, Zhang L and Han Y 2020 β-FeOOH/Fe–TiO$_2$ heterojunctions on Ti for bacteria inactivation under light irradiation and biosealing Biomater. Sci. 8 6004–16

[66] Bai Y, Wang P-Q, Liu J-Y and Liu X-J 2014 Enhanced photocatalytic performance of direct Z-scheme BiOCl–gC$_3$N$_4$ photocatalysts Rsc Adv. 4 19456–61

[67] Zhang G, Zhang J, Zhang M and Wang X 2012 Polycondensation of thiourea into carbon nitride semiconductors as visible light photocatalysts J. Mater. Chem. 22 8083–91

[68] Mao C, Xiang Y, Liu X, Cui Z, Yang X, Yeung K W K, Pan H, Wang X, Chu P K and Wu S 2017 Photo-inspired antibacterial activity and wound healing acceleration by hydrogel embedded with Ag/Ag@AgC$_3$/ZnO nanostructures ACS Nano 11 9010–21

[69] Xiang Y, Zhou Q, Li Z, Cui Z, Liu X, Liang Y, Zhu S, Zheng Y, Yeung K W K and Wu S 2020 A Z-scheme heterojunction of ZnO/C/Dots/C$_3$N$_4$ for strengthened photoresponsive bacteria-killing and acceleration of wound healing J. Mater. Sci. Technol. 57 1–11

[70] Applerot G, Lipovsky A, Dror R, Perkas N, Nitzan Y, Lubart R and Gedanken A 2009 Enhanced antibacterial activity of nanocrystalline ZnO due to increased ROS-mediated cell injury Adv. Funct. Mater. 19 842–52

[71] Li Y, Zhang W, Niu J and Chen Y 2012 Mechanism of photogenerated reactive oxygen species and correlation with the antibacterial properties of engineered metal-oxide nanoparticles ACS Nano 6 5164–73

[72] Salehi-Abari M, Koupaei N and Hassanzadeh–Tabrizi S A 2020 Synthesis and Characterisation of semi-interpenetrating network of Polycaprolactone/polyethylene glycol diacrylate/zeolite-CuO as wound dressing Mater. Technol. 35 290–9

[73] Liu J, Wang Y, Ma J, Peng Y and Wang A 2019 A review on bidirectional analogies between the photocatalysis and antibacterial properties of ZnO J. Alloys Compd. 783 898–918