Synthesis of novel and stable g-C₃N₄-Bi₂WO₆ hybrid nanocomposites and their enhanced photocatalytic activity under visible light irradiation

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Graphitic carbon nitride (g-C₃N₄) nanosheets with a thickness of only a few nanometres were obtained by a facile deammoniation treatment of bulk g-C₃N₄ and were further hybridized with Bi₂WO₆ nanoparticles on the surface via a solvothermal method. The composite photocatalysts were characterized by powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy, UV–vis diffuse reflection spectroscopy and X-ray photoelectron spectroscopy (XPS). The HR-TEM results show that the nano-sized Bi₂WO₆ particles were finely distributed on g-C₃N₄ sheet surface, which forms heterojunction structure. The UV–vis diffuse reflectance spectra (DRS) show that the absorption edge of composite photocatalysts shifts towards lower energy region in comparison with those of pure g-C₃N₄ and Bi₂WO₆. The degradation of methyl orange (MO) tests reveals that the optimum activity of 8:2 g-C₃N₄-Bi₂WO₆ photocatalyst is almost 2.7 and 8.5 times higher than those of individual g-C₃N₄ and Bi₂WO₆. Moreover, the recycle experiments depict high stability of the composite photocatalysts. Through the study of the influencing factors, a possible photocatalytic mechanism is proposed.
The enhancement in both photocatalytic performance and stability was caused by the synergistic effect, including the effective separation of the photogenerated electron-hole pairs at the interface of g-C$_3$N$_4$ and Bi$_2$WO$_6$, the smaller the particle size and the relatively larger specific surface area of the composite photocatalyst.

1. Introduction

Semiconductor photocatalysts have drawn much attention in the past decades because they represent a promising technology to use natural sunlight energy to promote chemical reactions, such as water-splitting, pollutant degradation and organic transformation [1,2]. Up to now, a mass of oxide and sulfide semiconductor photocatalysts have been developed for photocatalytic reactions, for example, the extensively investigated titanium dioxide and zinc sulfide [2,3]. However, the traditional photocatalysts are active only in the UV region and have high electron-hole recombination rates, which led to its inability to make full use of solar energy and reduce the photocatalytic performance [4]. Thus, it is still a challenging task looking for the sustainable, high-efficiency and visible-light-responsive photocatalytic materials.

Recently, non-metallic polymer photocatalyst g-C$_3$N$_4$, which shows superior photocatalytic activity for hydrogen production through water-splitting under visible light irradiation, was reported by Wang et al. [5]. Unlike traditional wide band-gap photocatalysts, this novel g-C$_3$N$_4$ photocatalyst possesses a narrow band gap (2.71 eV) and favourable thermal and chemical stability, which make it a unique electronic structure and highly condensed [5]. In addition, carbon and nitrogen elements, the composition of g-C$_3$N$_4$, are abundant in natural source. All these merits of g-C$_3$N$_4$ make it a valuable photocatalyst for solar energy-driven applications. However, the photocatalytic activity of g-C$_3$N$_4$ is still restricted due to the high electron-hole recombination rate and low specific surface area (generally below 10 m$^2$ g$^{-1}$ for the bulk g-C$_3$N$_4$) [6]. To further improve the photocatalytic activity of g-C$_3$N$_4$, many strategies have been proposed, including element doping, designing a textural porosity, as well as coupling g-C$_3$N$_4$ with heterogeneous semiconductor composites [7–9].

To reduce the recombination rates of photogenerated electron-hole pairs, construction of heterojunctions by coupling of two semiconductors was proved to be an effective strategy. Up to now, several g-C$_3$N$_4$-based heterojunction composites have been reported, for instance, g-C$_3$N$_4$-TiO$_2$, g-C$_3$N$_4$-ZnO, g-C$_3$N$_4$-CdS, g-C$_3$N$_4$-BiOBr and g-C$_3$N$_4$-TaON [10–14]. All these composites exhibit enhanced photocatalytic performance with respect to the sole component, which was ascribed to the effective separation of charged carriers. Considering the band structures of two coupled semiconductors, three types of heterojunction structures are usually formed. Type II heterojunction was regarded as the most effective band structure to separate charged carriers, in which the electrons transfer from one semiconductor to the other, while the holes migrate reversely [15]. According to the conduction band (CB) and valence band (VB) potential value of g-C$_3$N$_4$ (−1.13 and 1.58 eV, respectively), it was considered that the Bi$_2$WO$_6$ (0.46 and 3.26 eV, respectively) is one of the most suitable components to form type II heterojunction with g-C$_3$N$_4$ based on energy levels [16–18]. Furthermore, the crystal structure of Bi$_2$WO$_6$ comprises accumulated layers of alternating bismuth oxide (Bi$_2$O$_2$)$_{2+}$ and tungsten oxide (WO$_4$)$_{2-}$ sheets, which is favourable for charge transfer in plane.

This paper presents a facile strategy to produce hybrid g-C$_3$N$_4$ nanosheets with Bi$_2$WO$_6$ nanoparticles by two steps. First, bulk g-C$_3$N$_4$ was synthesized by thermal polycondensation of melamine. To make the specific surface area of g-C$_3$N$_4$ larger, the bulk g-C$_3$N$_4$ was treated by a simple deammoniation process at 500°C for 3h, and then the g-C$_3$N$_4$ nanosheets with several nanometres thickness were obtained. Second, using g-C$_3$N$_4$ nanosheets as bases, Bi$_2$WO$_6$ nanoparticles were deposited onto g-C$_3$N$_4$ surface by a solvothermal process and a series of composite photocatalysts with different weight ratio were prepared. It was found that the two components coexisted and closely constructed a heterojunction structure. Furthermore, owing to the larger specific surface area and well-matched band structures, the activity of the obtained composed catalysts was significantly high than those of the pure Bi$_2$WO$_6$ and g-C$_3$N$_4$ respectively. In addition, these composed catalysts were very stable and could be used multiple times, retaining a relatively high photocatalytic activity. Finally, through the analysis of the capture experiment, the possible photocatalytic mechanism was put forward.
2. Experimental set-up

2.1. Synthesis

All chemicals used were commercially available and used without further purification. Bulk g-C₃N₄ was prepared by the thermal treatment of 4 g melamine at 550°C for 4 h in a muffle furnace under an ambient pressure. Further deammoniation treatment was performed at 500°C for 3 h [19,20]. After reaction, the alumina crucible was cooled to room temperature. The resultant yellow product was collected for further use.

The g-C₃N₄-Bi₂WO₆ composite photocatalysts were obtained by hybridization of g-C₃N₄ nanosheet with Bi₂WO₆ nanoparticles through a solvothermal method. In a typical procedure, a certain amount of g-C₃N₄ sheets were added into 30 ml triethylene glycol (TEG) and sonicated for 30 min, and then a certain percentage of Bi(NO₃)₃·5H₂O dissolved in 20 ml TEG by stirring and added dropwise to the above suspension. The mixture was stirred for 1.5 h at room temperature to form a homogeneous solution. Meanwhile, a certain amount of Na₂WO₄·2H₂O solid was added to 20 ml ethylene glycol (EG) to obtain a uniform solution. After stirring and dissolving, the solution was added rapidly to the above mixture suspension and then stirred for another 3 h at room temperature. After that, the solution was transferred into a Teflon-lined steel autoclave and kept at 200°C for 12 h. Subsequently, the precipitate was collected by centrifugal separation, washed with distilled water and ethanol several times, and then dried at 60°C for 12 h. Finally, the obtained g-C₃N₄-Bi₂WO₆ photocatalysts were ground for further use. In the same procedure, different mass ratios of g-C₃N₄-Bi₂WO₆ at 2:8, 5:5 and 8:2 were prepared and denoted as 2:8 g-C₃N₄-Bi₂WO₆, 5:5 g-C₃N₄-Bi₂WO₆ and 8:2 g-C₃N₄-Bi₂WO₆, respectively. The pure Bi₂WO₆ sample was synthesized according to the same method without g-C₃N₄.

2.2. Characterization

XRD patterns were recorded on a PANalytical X’pert PRO powder diffractometer equipped with a Cu Kα radiation source (λ = 0.15405 nm). FT-IR spectra were measured on a Thermo Electron Nicolet-Nexus 470 FT-IR spectrometer (KBr disc). X-ray photoelectron spectroscopy (XPS) of the photocatalysts was performed on an ESCALAB 250Xi (Thermo Electron Corporation, USA). SEM was employed to observe the morphology of samples (Hitachi S-4800 microscope). TEM and HR-TEM were applied to characterize the microstructure of the samples (JEOL, JEM-2100). UV–vis diffuse reflectance spectra (DRS) were measured using a UV–vis spectrometer (Shimadzu, UV-3600, Japan). The photoluminescence (PL) spectra of the photocatalysts were obtained by a VARIAN fluorescence spectrophotometer.

2.3. Photocatalytic tests

The photocatalytic activity of the catalysts was tested by degrading the methyl orange (MO) solution under a visible light using a 500 W xenon lamp with a 420 nm cut-off filter as the light source. The specific test procedure was as follows: 50 mg of the sample was dispersed in 50 ml of methyl orange solution (5 mg l⁻¹) and stirred for 120 min under dark conditions to achieve adsorption equilibrium. After the start of the experiment, for a certain time period, about 3 ml suspensions were collected and centrifuged to wipe off the photocatalysts. The concentrations of residued MO were then monitored by a UV–vis spectrometer at a wavelength of 463 nm.

3. Results and discussions

3.1. Characterization

Figure 1 shows the XRD patterns of the as-prepared samples. The pure g-C₃N₄ sample shows two diffraction peaks at 12.97°and 27.93°, corresponding to the (100) and (002) planes, which are attributed to the periodic arrangement of the basic structural units in the g-C₃N₄ and the interlayer build-up of the cyclic aromatic substance [6]. For pure Bi₂WO₆, there is a series of narrow and pointed diffraction peaks, which are in good agreement with the orthorhombic phase of Bi₂WO₆ (JCPDS 39-0256) without any impurity. After the two materials are compounded, the g-C₃N₄-Bi₂WO₆ composite was similar to the pure Bi₂WO₆ diffraction pattern. This phenomenon can be ascribed to two aspects: one is that the (002) of g-C₃N₄ and (131) of Bi₂WO₆ diffraction peaks were located in a similar position (approx. 28°),
Figure 1. XRD patterns of as-synthesized g-C₃N₄, Bi₂WO₆ and g-C₃N₄-Bi₂WO₆ photocatalysts.

Figure 2. (a–b) FT-IR spectra of the as-synthesized g-C₃N₄, Bi₂WO₆ and g-C₃N₄-Bi₂WO₆.

and the other is that the g-C₃N₄ layer was too thin, thus the diffraction intensity is relatively weak with respect to those of Bi₂WO₆ which make g-C₃N₄ diffractions invisible in the composite [21].

The FT-IR spectra of g-C₃N₄, Bi₂WO₆ and g-C₃N₄-Bi₂WO₆ photocatalysts are shown in figure 2a. The absorption peaks at 3428 cm⁻¹ and 1628 cm⁻¹ in the spectrum of pure Bi₂WO₆ are attributed to the stretching vibration and bending vibration of the O–H, respectively. For g-C₃N₄ sample, the 3155 cm⁻¹ band can be attributed to the N–H stretching mode. The enlarged spectrum from 400 to 1600 cm⁻¹ is shown in figure 2b. The main absorption peaks at 400–800 cm⁻¹ in pure Bi₂WO₆ sample correspond to Bi–O, W–O stretching and W–O–W bridging stretching modes [22]. In the case of pure g-C₃N₄, the intense band at 808 cm⁻¹ belongs to the characteristic breathing mode of s-triazine, and the strong bands in the 1200–1600 cm⁻¹ region with peaks at 1243, 1324, 1401 and 1569 cm⁻¹ correspond to typical stretching vibration modes of C=N and C–N heterocycles [23,24]. All these peaks can be found in g-C₃N₄-Bi₂WO₆ photocatalyst, indicating the presence of g-C₃N₄ and Bi₂WO₆ components in composite photocatalysts.

The elemental composition of the samples was measured by XPS. We can see that the g-C₃N₄ mainly consisted of C, N and a little amount of O elements (figure 3a). The O element that appeared here may be ascribed to O₂ adsorbed on the surface during polymerization process, which usually occurs in synthetic g-C₃N₄ materials [25]. As shown in figure 3b, two peaks at 157.58 and 162.88 eV can be attributed to Bi 4f/2 and 4f/2 of Bi³⁺ ions. The XPS of W 4f electrons is shown in figure 3c, indicating the +6 valence of...
Figure 3. XPS spectra of the photocatalysts: (a) whole XPS spectra of g-C₃N₄ and 8:2 g-C₃N₄-Bi₂WO₆ composite, (b) Bi 4f and (c) W 4f of 8:2 g-C₃N₄-Bi₂WO₆ composite, and (d) N 1s of g-C₃N₄ and 8:2 g-C₃N₄-Bi₂WO₆ composite.

Figure 4. (a, b) UV–vis DRS of the as-synthesized g-C₃N₄, Bi₂WO₆ and g-C₃N₄-Bi₂WO₆ photocatalysts.

W element [26]. Figure 3d shows high-resolution N 1s spectra of the samples. The N 1s spectrum could be fitted into four peaks, corresponding to four binding energies of sp2-bonded nitrogen in C–N=C (ca 398.7 eV), nitrogen in tertiary N–(C)₃ groups (ca 400.3 eV), amino groups C–N–H (ca 401.4 eV) caused by imperfect polymerization and π-excitations (ca 404.3 eV) [27,28]. All of these results further confirmed the coexistence of g-C₃N₄ and Bi₂WO₆ in g-C₃N₄-Bi₂WO₆ composite photocatalysts.

The band structures of as-prepared samples were evaluated by the UV–vis DRS technique. As shown in figure 4a, the pristine Bi₂WO₆ has an absorption edge of approximately 443 nm, which corresponds to a band gap of approximately 2.80 eV [17,29]. The absorption edge of pure g-C₃N₄ was at about 457 nm, corresponding to the band gap of 2.71 eV, which is consistent with the reported values in the
literature [30]. After combining the two semiconductors, a gradual red shift appeared as the amount of g-C3N4 increased; this should be the result of the interaction between g-C3N4 and Bi2WO6 in the heterojunction [31,32]. The band-gap values were also estimated from the intercept of tangents to plots of (Ahv) 1/2 versus photon energy [31], as shown in figure 4b. It is worth noting that the g-C3N4-Bi2WO6 composite shows narrower band gap in comparison with pure g-C3N4 and Bi2WO6. The results indicate that the g-C3N4-Bi2WO6 heterojunction complex photocatalyst has a good visible light response, which can enhance its photocatalytic activity.

As seen from the SEM image of figure 5a, g-C3N4 has a hierarchical flower-like morphology, which was assembled by many nanoflakes with a thickness of only a few nanometres. The nanoflake structure was further characterized by TEM observation. As shown in figure 5c, a typically two-dimensional lamellar structure with a thickness of several nanometres of g-C3N4 nanoflakes was observed, which is similar to the reported reference [33]. The SEM image of 8:2 g-C3N4-Bi2WO6 composite is exhibited in figure 5b. Clearly, with the coupling of Bi2WO6 nanoparticles, the hierarchical structures of g-C3N4 were disassembled into discrete nanoflakes. With the increase of Bi2WO6 content, the g-C3N4 nanoflake was

**Figure 5.** Characterization of the as-synthesized Bi2WO6 and g-C3N4 photocatalyst: (a) g-C3N4 and (b) 8:2 g-C3N4-Bi2WO6 composite of SEM images, (c) g-C3N4, (d) Bi2WO6 and (e) 8:2 g-C3N4-Bi2WO6 sample of TEM images, (f) HR-TEM image of the 8:2 g-C3N4-Bi2WO6 heterostructure.
Figure 6. (a) Absorption spectra of MO with irradiation time over 8 : 2 g-C3N4-Bi2WO6 composite photocatalyst. (b) Degradation rates of MO under visible light irradiation without catalyst and in the presence of g-C3N4, Bi2WO6 and g-C3N4-Bi2WO6 samples.

completely covered by Bi2WO6 nanoparticles, which would have a negative effect on the photocatalysis because of the decrease in photocatalytic reaction site on the g-C3N4 nanoflake surface. Figure 5d shows the TEM image of pure Bi2WO6 sample. It can be observed that Bi2WO6 formed irregular nanoparticles with a mean size of approximately 30 nm. From the TEM image of the 8 : 2 g-C3N4-Bi2WO6 sample (figure 5e), we know that Bi2WO6 nanoparticles were closely covered on the g-C3N4 nanosheet surface. The HR-TEM image of figure 5f shows lattice fringe spacing of 0.316 and 0.273 nm, which belongs to (113) and (060) lattice planes of cubic Bi2WO6. Because of low crystallinity of the g-C3N4, it is hard to find the lattice fringe of g-C3N4 [23]. The result obviously shows that g-C3N4 nanosheets form a close heterogeneous contact with Bi2WO6. This close contact interface accelerates the migration of photogenerated electrons and holes between g-C3N4 and Bi2WO6, inhibiting the recombination of photogenerated electron-hole pairs and improving the photocatalytic activity.

3.2. Photocatalytic performance

Based on the above conclusions, we evaluated the photocatalytic activity of the synthesized samples by degrading methyl orange under visible light irradiation. As shown in figure 6a, the highest degradation rate of 95.88% after 120 min irradiation was obtained over 8 : 2 g-C3N4-Bi2WO6 composite sample. Meanwhile, no other peaks in the UV region indicate the full decomposition of aromatic component. To compare the photocatalytic performance of different photocatalysts, the degradation rate of MO was determined by the characteristic absorption peak of methyl orange at 463 nm. The C/C0 versus irradiation time is plotted in figure 6b. The concentration of MO solution without photocatalyst did not change after 120 min degradation, indicating that methyl orange is quite stable, and ruled out the possibility of the occurrence of its self-degradation. As the Bi2WO6 sample has a relatively high photogenerated electron-hole pairs recombination rate, the pure Bi2WO6 sample exhibits its low photocatalytic activity. Similarly, only 68.8% of MO was degraded by the g-C3N4 sample for the same irradiation time. It was expected that the construction of proper heterojunction can enhance the photocatalytic activity through effective separation of photogenerated electron-hole pairs. As proved in this paper, all the g-C3N4-Bi2WO6 composite photocatalysts present enhanced photocatalytic ability for the degradation of MO compared to pure Bi2WO6 and g-C3N4. Besides, the highest activity was obtained over 8 : 2 g-C3N4-Bi2WO6 composite, and its degradation rate was 1.4 and 3.2 times higher than that of pure g-C3N4 and Bi2WO6, respectively. It should be noted that too much Bi2WO6 content in composite photocatalyst (such as 2 : 8 g-C3N4-Bi2WO6) would distinctly reduce the photocatalytic activity of the composite. Previous research also pointed out that the dispersion and size of deposited nanoparticles could influence their photocatalytic efficiency [34,35]. On g-C3N4 nanosheets, Bi2WO6 nanoparticles with smaller size and favourable dispersibility meant higher photocatalytic activity. The smaller size and higher dispersibility of Bi2WO6 on the g-C3N4 sheets meant higher photocatalytic activity. But if the loading density of Bi2WO6 nanoparticle was too high, the photocatalytic site on the g-C3N4 sheet surface will be covered, which would damage the heterojunction structure and reduce synergistic effect between the two components [36]. As a result, only Bi2WO6 nanoparticles coated on g-C3N4 with proper size and
dispersion would enhance the photocatalytic activity of composite photocatalyst. In this work, it was found the 8:2 g-C₃N₄-Bi₂WO₆ composite sample displayed the highest catalytic performance due to the optimal structure.

The kinetics of photocatalytic degradation of methyl orange reflects the reaction rate of the photocatalyst. The change of methyl orange concentration can be obtained by the first-order kinetic equation \( \ln(C_0/C_t) = kt \) to obtain the corresponding apparent degradation rate constant \( k \), where \( C_0 \) and \( C \) are the concentrations of pollutant in solution at time \( t_0 \) and \( t \), respectively, and \( k \) is the apparent first-order rate constant [37]. As shown in figure 7a, all fitting curves of \( t \) for \( \ln(C_0/C_t) \) are approximated by a straight line, and thus the corresponding kinetic constants \( k \) are calculated. Observably, the rate constant \( k \) is calculated to be 0.00999, 0.01104, 0.0166, 0.02659 and 0.00313 min⁻¹ for pure g-C₃N₄, 2:8 g-C₃N₄-Bi₂WO₆, 5:5 g-C₃N₄-Bi₂WO₆, 8:2 g-C₃N₄-Bi₂WO₆ and pure Bi₂WO₆ samples, respectively (figure 7b). That is, 8:2 g-C₃N₄-Bi₂WO₆ catalyst has the best photocatalytic activity, the degradation rate of methyl orange is almost 2.7 and 8.5 times higher than that of either individual g-C₃N₄ or Bi₂WO₆. The above results show that the introduction of Bi₂WO₆ could effectively enhance the visible light photocatalytic activity of g-C₃N₄.

Apart from the photocatalytic performance, the stability of photocatalysts in the practical application also has a very important significance. The g-C₃N₄-Bi₂WO₆ composite photocatalyst was cycled four times under the same conditions. After every cycle, the sample was centrifuged, washed and dried at 60°C. After four cycles, the degradation rate of methyl orange was still 84.26% (figure 8), which shows a high photocatalytic stability of the composite after four recycling runs. Thus, the stability and recyclability of g-C₃N₄-Bi₂WO₆ composites are excellent.

Figure 7. (a) The first-order kinetics plot and (b) the kinetic constants for the photodegradation of MO under visible light irradiation (λ > 420 nm) by g-C₃N₄, Bi₂WO₆ and g-C₃N₄-Bi₂WO₆ samples.

Figure 8. Cycling runs for the photocatalytic degradation of MO over 8:2 g-C₃N₄-Bi₂WO₆ composite sample under visible light irradiation.
3.3. Possible photocatalytic mechanism

It can be seen from the photocatalytic experiments that the novel g-C$_3$N$_4$-Bi$_2$WO$_6$ composite has shown a good photocatalytic effect for degrading the MO under visible light. On the basis of the above experimental results, a possible mechanism for the g-C$_3$N$_4$-Bi$_2$WO$_6$ composite photocatalyst is proposed. The process of electron-hole separation and transport in interface is shown in figure 9. It is known from the literature that the band-gap positions of g-C$_3$N$_4$ were determined at −1.13 and +1.58 eV [4], while those of Bi$_2$WO$_6$ were estimated at 0.46 and +3.26 eV. Once the composite photocatalyst is irradiated by visible light, both g-C$_3$N$_4$ and Bi$_2$WO$_6$ can be stimulated and generate photogenerated electron-hole pairs. Because it has a well-matched staggered band-gap structure and a close interface, the electrons on the conduction band of g-C$_3$N$_4$ will be transferred to the conduction band of Bi$_2$WO$_6$. At the same time, holes on the VB of Bi$_2$WO$_6$ reversely transfer to the VB of g-C$_3$N$_4$. This process effectively facilitates the separation of photogenerated electron-holes, thereby inhibiting the recombination of photogenerated electron-hole pairs separation effectively and decrease the possibility of photogenerated charge recombination greatly. Therefore, Bi$_2$WO$_6$ nanoparticles and g-C$_3$N$_4$ nanosheet in the g-C$_3$N$_4$-Bi$_2$WO$_6$ complex material could form the optimal heterojunction structures, which result in the improvement of the photocatalytic activity.

As we know, photogenerated holes, ·OH radicals and ·O$_2^-$ are the three main major active species in the degradation process [13,38]. Therefore, to study the role of these reactive groups in the photocatalytic process, a series of free radicals capture experiments were conducted by using ethylenediaminetetraacetate (EDTA, 6 mmol l$^{-1}$), benzoquinone (BQ, 0.5 mmol l$^{-1}$) and tert-butanol (TBA, 6 mmol l$^{-1}$) as effective scavengers for holes, ·O$_2^-$ and ·OH radicals respectively [39]. In the free radicals capture experiments (figure 10a), when TBA was added to the system, the degradation efficiency of MO was reduced from 95.89% to 80.53% compared with the photocatalytic experiment without the capture agent, indicating that the photogenerated holes are not the primary active group for the degradation of methyl orange, and they are also not the sources of ·OH radicals. It is worth noting that the degradation of MO is slightly enhanced when the hole trapping agent EDTA was added, which means that the hole is not the active group for degrading the MO, and the reason for the increase in catalytic activity is that EDTA is a capture agent, so that the photogenerated electron-hole could be effectively separated. However, when BO was added, the degradation rate of MO was only 45.02%, which demonstrates that the main active species should be ·O$_2^-$ in the degradation of MO [40,41].

For further insight into photogenerated electron-hole pair behaviour of the g-C$_3$N$_4$-Bi$_2$WO$_6$ composite and to verify the above-mentioned mechanism, PL spectra of the as-prepared photocatalysts were obtained. Generally, in semiconductor materials, the migration and separation of photogenerated carriers lead to the generation of fluorescence spectra [42,43]. Figure 10b presents the PL spectra of pure g-C$_3$N$_4$, pure Bi$_2$WO$_6$ and 8:2 g-C$_3$N$_4$-Bi$_2$WO$_6$ composite samples excited with a 365 nm light. At room temperature, the luminescent characteristic peaks of pure g-C$_3$N$_4$ are centred at 440 nm, which is attributed to the radiation recombination process of self-trapped excitations [44]. Compared with those of pure g-C$_3$N$_4$, the position of the emission peaks of the 8:2 g-C$_3$N$_4$-Bi$_2$WO$_6$ sample was almost unchanged, but the intensity was greatly reduced, which indicates that the photogenerated charges recombination rate was controlled in the heterojunction semiconductors. The PL results support the above discussion on the photocatalytic experiments and proposed mechanism strongly. Over all, the
g-C3N4-Bi2WO6 composite photocatalysts can effectively separate photogenerated electron-hole pairs and inhibit recombination of the charges, which has a very promising application in environmental purification.

4. Conclusion

In conclusion, the g-C3N4-Bi2WO6 composite photocatalyst with a heterojunction structure was prepared by a simple solvothermal method. This novel g-C3N4-Bi2WO6 composite catalyst exhibits outstanding visible light response photocatalysis, attributing to the effective separation of electron-hole pair at heterojunction interfaces. Among the as-prepared various weight ratios of g-C3N4-Bi2WO6 samples, the 8:2 g-C3N4-Bi2WO6 sample displayed best photocatalytic activity because of its optimum structure. The investigation of the photocatalytic mechanism showed that the degradation of methyl orange by the g-C3N4-Bi2WO6 sample is mainly through ·O2⁻ radicals, and ·OH was verified to be inappreciable. We believe this work provides some new insights for fabrication of highly efficient heterojunction photocatalysts for environmental remediation.

Data accessibility. This paper does not contain any additional data.

Authors’ contributions. H.L., N.L., M.W. and F.L. conceived and designed the study; H.L., N.L. and B.Z. performed the experiments and collected data; H.L. and N.L. analysed the data and wrote the paper. All authors gave final approval for publication.

Competing interests. The authors declare no competing interests.

Funding. This research was supported by Guangxi Natural Science Foundation (2015GXNSFAA139278) and the Program for New Century Excellent Talents in University (no. NCET-12-0655).

Acknowledgements. We thank test support of laboratory staff in the test of Materials Science and Engineering, Guilin University of Technology.

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