Hierarchical g-C₃N₄/BiOBr for Enhancing Photocatalytic Performance Under visible light

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Abstract. Hierarchical g-C₃N₄/BiOBr composite photocatalysts were successfully synthesized via a facile one-pot solvothermal method. Characteristics of the as-prepared photocatalysts were determined by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV–visible diffuse reflectance spectroscopy (UV-vis DRS). Removing performance of Rhodamine B (RhB) and tetracycline (TC) were also studied by the as-prepared photocatalysts under LED blue light irradiation. Results indicated that flower-like BiOBr hierarchical microspheres were successfully fabricated and interwoven by the flake-like g-C₃N₄, the photocatalysts showed highest photodegradation RhB and TC when the g-C₃N₄ attained 0.8% under LED blue light irradiation.

1. Introduction

Heterogeneous photocatalytic technique, which is environmentally friendly in removing organic contaminants, has attracted much attention over the past 30 years [1]. As the most widely used photocatalyst, TiO₂ can only be activated by UV light irradiation (accounting for just 4% of the solar irradiation) which hinders its practical application. As an emerging family of promising photocatalysts, Bismuth oxyhalides (BiOX, X = F, Cl, Br, I) exhibit excellent photocatalytic performance because of their layered tetragonal crystal structure and suitable band gaps [2]. Recently, much approaches has been done to improve the photocatalytic performance of BiOBr towards its application in water treatment. Typically, coupling it with other semiconductors to promote photoinduced electron-hole separation. It has been proved that BiOBr has a compatible band structure with g-C₃N₄, and many g-C₃N₄/BiOBr heterojunction have been constructed by different methods toward the enhanced photocatalytic performance [3]. In particular, owing to their improved catalytic capacity and a faster adsorption property, it have been reported three-dimensional (3D) hierarchical g-C₃N₄/BiOI were successfully designed and fabricated by virtue of their promising application in environmental remediation in recent years [4]. This inspired us to explore facile and efficient approaches to the fabrication of 3D hierarchical g-C₃N₄/BiOBr especially with unique properties. However, to the best of our knowledge, there have been few reports on the relative study.

Herein, for the first time, 3D hierarchical g-C₃N₄/BiOBr was assembled successfully between hierarchical BiOBr and flake g-C₃N₄ by a facile and one-pot solvothermal method. In addition, RhB and TC was selected as representative pollutant targets for degradation experiment. The photocatalytic
activity of the as-obtained novel photocatalysts was investigated by removal of RhB and TC under LED visible light irradiation ($\lambda = 450$ nm).

2. Experimental

2.1. Synthesis
All chemicals were of analytical grade purchased from the Shanghai Reagents Company (Shanghai, China), and were used without further purification. The g-C$_3$N$_4$ was prepared by thermal treatment of 20 g urea in a crucible with a cover under ambient pressure in air. The precursor was kept in a tube furnace heated to 550 °C for 4 h. The as obtained yellow powders were washed with deionized (DI) water and anhydrous ethanol, then dried at 65 °C for 12 h. The g-C$_3$N$_4$/BiOBr composites were synthesized by a one-pot solvothermal approach. In a typical synthesis, Bi(NO$_3$)$_3$$\cdot$5H$_2$O (2.8 mmol) and polyvinylpyrrolidone (PVP) (0.15 g) were dissolved completely in 50 mL of ethylene glycol (EG) with magnetic stirring at room temperature (25°C). NaBr (2.8 mmol) were added and stirred for 30 min. After this, different amounts of g-C$_3$N$_4$ were dispersed in the previous obtained solution and the mixture was stirred for 30 min. Subsequently, the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 160°C for 12 h and then cooled to room temperature naturally. Finally, the precipitates were filtered, washed thoroughly with (DI) water and anhydrous ethanol several times, and then dried in an oven at 65 °C for 6 h.

2.2. Characterization
The as-obtained powder samples were characterized by X-ray diffraction (XRD), Rigaku D/max-2550 diffractometer using filtered Cu-Kα radiation operating at an accelerating voltage of 40kV and current of 200 mA. The sample was scanned from 5° to 80°. Scanning electron microscopy (SEM) was performed using Quanta-250 field emission scanning electron microscope. UV–vis diffuse reflection spectra (DRS) were acquired using a Shimadzu UV-3100 UV–vis spectrophotometer equipped with an integrating sphere, using BaSO$_4$ as a reference.

2.3. Photocatalytic Evaluation
The photocatalytic experiments were carried out by using a 50 W blue LED lamp with a wavelength of 450 nm as the visible light source, which is placed about 5 cm from the surface of a liquid suspension of RhB or TC. All photocatalytic reactions were performed using the same initial conditions: 50 mL of TC (40 mg/L) or RhB (15 mg/L) was mixed with 20 mg catalyst under constant magnetic stirring. Prior to irradiation, the suspension was stirred for 30 min in the dark to reach adsorption-desorption equilibrium. At certain time intervals, approximately 2 mL of the suspension was sampled and the solids were subsequently removed from the solution through centrifugation (10,000 rpm, 10 min). Concentration of TC and RhB were determined by UV–vis spectroscopy (UV-1800, Shimadzu, Japan).

3. Results and discussions

3.1. XRD patterns
The XRD spectra of the BiOBr, g-C$_3$N$_4$ pure powders and 0.8%g-C$_3$N$_4$/BiOBr composite are presented in Fig. 1. For pure g-C$_3$N$_4$, the distinct diffraction peaks at 13.07°and 27.59°matched well with (100) and (002) diffraction planes (JCPDS 87-1526) were correspond to the characteristic interplanar stacking peaks of aromatic systems and interlayer structural packing, respectively [5]. In addition, it can be clearly seen that all the reflection peaks can be readily indexed into the tetragonal phase BiOBr of (JCPDS no. 09-0393) for pure BiOBr powder and 0.8%g-C$_3$N$_4$/BiOBr. However, no typical patterns of g-C$_3$N$_4$ (002) was observed in g-C$_3$N$_4$/BiOBr composite, which may due to the low g-C$_3$N$_4$ content in the g-C$_3$N$_4$/BiOBr and the g-C$_3$N$_4$ dispersed well in the composite material. The similar result can also be found in the previous works [6].
3.2. **SEM observation**

The SEM images of the pure BiOBr powder, g-$\text{C}_3\text{N}_4$ and g-$\text{C}_3\text{N}_4$/BiOBr composite are shown in Fig. 2. Fig. 2A present the SEM images of the BiOBr/FACs at low magnifications, it can be seen that the g-$\text{C}_3\text{N}_4$/BiOBr exhibit aggregated morphology and stacking pimple-like structure, in which these white small balls were BiOBr with a size of several micrometers interweaved by the cotton-like structure g-$\text{C}_3\text{N}_4$. From Fig. 2B, in the SEM images at high magnifications, it can be clearly seen that all these interwove BiOBr microspheres assembled from two-dimensional nanosheet and appeared as three-dimensional hierarchical microspheres with diameters ranging from 1 to 3 μm. After hybridized with the flake structure g-$\text{C}_3\text{N}_4$ polymer (Figure 2B), the BiOBr microspheres were well interwove among g-$\text{C}_3\text{N}_4$, forming a 3D hybridized structure, which would facilitate the transfer of photogenerated carriers and improve the photocatalytic performance.
3.3. DRS analysis

![Graph](image)

**Fig. 3.** The UV–Vis diffuse reflection spectra of the samples (A: BiOBr, B: 0.8%g-C₃N₄/BiOBr, C: g-C₃N₄)

The UV–vis diffuse reflectance spectra of pure BiOBr, g-C₃N₄ and g-C₃N₄/BiOBr are shown in Fig. 3. The absorption edge of the pure BiOBr was shorter than 420 nm, while the g-C₃N₄ exhibited an onset of absorption at 450 nm. Compared with pure BiOBr, the optical absorption for g-C₃N₄/BiOBr had no obviously change in the visible light region and shows a similar absorption edge with BiOBr. The band gap energy of as-synthesized samples could be calculated by the following formula [7, 8]:

\[
\alpha \gamma = A(\gamma - E_g)^{n/2}
\]

Where \( \alpha \) = the absorption coefficient, \( \gamma \) =light frequency, \( E_g \) = band gap, and \( A \) = constant, respectively. \( n \) depends on the characteristics of the transition in a semiconductor, including direct transitions (\( n = 1 \)) or indirect transitions (\( n = 4 \)). As previous reports indicated that BiOX (X = Br, I) was an indirect band gap material [9], the band gap energy could be estimated from a plot of \( (\alpha \gamma)^{1/2} \) vs. the photon energy (\( h\gamma \)). The x-axis intercept of the tangent to the plot approached the band gap energy of the sample. The evaluated band gap values are 2.75, 2.74 and 2.70 eV, corresponding to pure BiOBr, g-C₃N₄/BiOBr and g-C₃N₄, respectively. These results implied that the visible light response of the g-C₃N₄/BiOBr photocatalysts is improved by coupling of g-C₃N₄ with BiOBr and leaded to possible photoexcited charge separation between g-C₃N₄ and the BiOBr, which subsequently results in an enhanced photocatalytic activity [2].

3.4. Photocatalytic Evaluation

The photocatalytic activities of the pristine g-C₃N₄, BiOBr, and the g-C₃N₄/BiOBr composites were evaluated by the degradation RhB and TC under illumination of LED blue light (\( \lambda = 450 \) nm). As shown in Fig.4, pure BiOBr has a higher activity than g-C₃N₄, on which more than 92% of RhB could be removed by BiOBr, only 43% photocatalytic degradation rate was observed for g-C₃N₄ in the same condition. Obviously, almost all the g-C₃N₄/BiOBr composites with different proportions exhibit higher photocatalytic activity than the pristine g-C₃N₄ and BiOBr, indicating that the charge transfer was improved in g-C₃N₄/BiOBr composites. The 0.8% g-C₃N₄/BiOBr composite exhibits the highest photocatalytic activity, with the RhB degradation efficiency of 98% after visible-light irradiation for 50 min. Herein, g-C₃N₄/BiOBr composite was also used to photodegrade the TC under visible light irradiation, as shown in Fig. 4. It can be seen that 44% of TC was removed over g-C₃N₄ after 50 min visible light irradiation. It also indicates that BiOBr is an efficient photocatalyst for TC degradation. However, comparing with BiOBr and g-C₃N₄, the g-C₃N₄/BiOBr composite showed much higher
photocatalytic degradation activity under visible irradiation when the weight ratio was lower than 1.0%. The 0.8% g-C₃N₄/BiOBr composite showed best photocatalytic ability for the degradation of TC, but the photocatalytic activity of g-C₃N₄/BiOBr composite decreased with the increasing of weight ratio.

![Figure 4](image)

**Fig.4.** Photocatalytic degradation in the presence of g-C₃N₄, BiOBr, and g-C₃N₄/BiOBr under visible light irradiation (A: RhB; B: TC)

4. Conclusion
A series of novel g-C₃N₄/BiOBr composites with hierarchical structures were obtained via a facile solvothermal method. The 0.8% g-C₃N₄/BiOBr photocatalyst presented the highest visible light photocatalytic activity for RhB and TC removal. The efficient electron-hole separation was the main reason for the improved photocatalytic performance. Hence, g-C₃N₄/BiOBr composite is a promising visible light photocatalyst for water environment restoration.

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