The influence of g-C₃N₄ loading on the photocatalytic activity of Bi₁₂O₁₇Br₂/Bi₂O₃ composite in the phenol red degradation

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Abstract In this work, the influence of graphite-like C₃N₄ (g-C₃N₄) loading on the photocatalytic performance of Bi₁₂O₁₇Br₂/Bi₂O₃ composite was studied. The results indicated that g-C₃N₄-Bi₁₂O₁₇Br₂/Bi₂O₃ photocatalysts displayed much higher photocatalytic efficiency for the phenol red degradation than the bare Bi₂O₃ and Bi₂O₃/Bi₁₂O₁₇Br₂ composite under visible light illumination. The best photocatalytic performance of the composite sample with almost 100% phenol red degradation located at g-C₃N₄-Bi₁₂O₁₇Br₂/Bi₂O₃-50 under visible light illumination for 80 mins. This excellent photocatalytic performance was displayed according to the efficient separation and transportation of the photogenerated charges, which was resulted from the coupling of C₃N₄ and Bi₁₂O₁₇Br₂/Bi₂O₃.

1. Introduction

Photocatalysis has become an ideal method for producing clean sources of energy and environmental pollution treatment [1-3]. The crucial step for its application is to develop new, efficient, and clean catalysts [4-10]. Recent years, bismuth-based semiconductor photocatalysts such as Bi₂O₃ [11,12], BiVO₄ [13-15], Bi₂MoO₆ [16-18], BiOX (X = Cl, Br, I) [19], and Bi₂WO₆ [20] have attracted much attention because of their attractive photocatalytic activities under visible light irradiation. Bi₂O₃ has been broadly used in photocatalysis filed due to its perfect optical and photocatalytic properties [21-23]. Furthermore, Bi₂O₃ is also a material, which has a narrow band gap (2 to 3.9 eV) all of which make Bi₂O₃ to degrade dyes under UV and visible-light illumination [11,12]. Results come to that nanometer structures of Bi₂O₃ can improve the stability of metastable Bi₂O₃ at low temperature, which in return can also enhance the photocatalytic activities [24]. However the photodegradation activity isnot so active. To resolve these issues, great efforts have been made on heteronanostructures to enhance the separation of photogenerated charges, for further improving the photocatalytic performance [24-26].

Herein, the ternary heterostructured g-C₃N₄-Bi₁₂O₁₇Br₂/Bi₂O₃ composite photocatalysts were successfully synthesized for the first time. The phenol red was employed as a mode to study the photocatalytic performances of the ternary heterostructured composites. The results reveal that
compared with pure Bi$_2$O$_3$ and Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$ composite, the ternary heterostructured g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$ composite have a marked enhanced phenol red photodegradation efficiency under visible-light. The g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-50 catalyst performed the best in the degradation of phenol red. Moreover, the possible photocatalysis mechanism of the g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$ nanoheterostructure was also studied.

2. Experimental

2.1. Preparation of samples

2.1.1 Preparation of g-C$_3$N$_4$. In a typical step, dicyandiamide (2.0 g) was heated to 550 °C (with a rate of 2.3 °C/min), after that, it was still heated at the tempered of 550 °C for 2 hs [26-28]. The product was collected for later use.

2.1.2 Preparation of g-C$_3$N$_4$-Bi$_2$O$_3$/Bi$_{12}$O$_{17}$Br$_2$ photocatalysts. Different mass ratios g-C$_3$N$_4$-Bi$_2$O$_3$/Bi$_{12}$O$_{17}$Br$_2$ composites were prepared via hydrothermal method. As 50% g-C$_3$N$_4$-Bi$_2$O$_3$/Bi$_{12}$O$_{17}$Br$_2$ for example, in a typical procedure, 100 mg g-C$_3$N$_4$, 100 mg Bi(NO$_3$)$_3$·5H$_2$O, and 30 mg sodium dodecyl benzene sulfonate (SDBS) were mixed in 10 mL ethylene glycol. The mixture was vigorously stirred for 10 mins, and then 30 mL ethanol was added and vigorously stirred for around 10 mins, and heat treated at 160 °C for 12 hs in an oven. At last, the obtained 50wt% g-C$_3$N$_4$-Bi$_2$O$_3$/Bi$_{12}$O$_{17}$Br$_2$ powder was washed with distilled water twice, and dried. Different concentrations of g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$ composites at 10wt%, 30wt%, 70wt% and 90wt% were synthesized (denoted as g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-10, g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-30, g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-70, and g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-90, respectively).

2.2. Characterization of samples

The structures of the as-fabricated samples were tested by X-ray diffraction (XRD). A scanning electron microscopy (SEM, Japan JEOL, JSM-6510) was used to study the microstructure of the photocatalysts. The chemical compositions of the as-synthesized samples were tested through scanning electron microscope-X-ray energy dispersion spectra (SEM-EDX, JSM-6510). The diffuse reflectance spectra (DRS) were studied through a UV-vis spectrometer (UV-2550, Shimadzu).

2.3. Photocatalytic activities

The photocatalytic performances of the as-fabricated samples were studied by using phenol red photocatalytic degradation tests. The phenol red solution containing 50 mg of catalyst was mixed. A 300 W Xe lamp (λ > 420 nm) was used to offer visible light illumination. Before visible light illumination, the phenol red solution was vigorously stirred in the dark (60 mins). At 20 mins intervals, 4 mL of the phenol red solution was collected and measured.

3. Results and discussion

From Fig. 1a, it can be observed that the bare g-C$_3$N$_4$ has two peaks of around 13.0° and 27.3° respectively [27]. And the Bi$_2$O$_3$/Br$_2$/Bi$_2$O$_3$ composite shows a coexistence of Bi$_2$O$_3$ phase (JCPDS No. 41-1449) and Bi$_{12}$O$_{17}$Br$_2$ phase (JCPDS No. 37-0701), revealing that the mixture of Bi$_2$O$_3$ and Bi$_{12}$O$_{17}$Br$_2$ are the main existing forms of the sample. For g-C$_3$N$_4$- Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$ composites, similar diffraction peaks to the Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$ are detected [28].

In the FT-IR spectrum (Fig. 1b) of bare g-C$_3$N$_4$, three absorption peaks in the region of 800–4000 cm$^{-1}$ can be observed [27]. The broad absorption band at 3000–3500 cm$^{-1}$ is resulted from the stretching vibration of O–H and the stretching vibration of N–H [27]. The strong peaks of 1200-1700 cm$^{-1}$ (centered at 1243, 1335, 1411, and 1649 cm$^{-1}$) are due to the vibration of CN heterocycle [27].
The peak of 802 cm$^{-1}$ is ascribed to the mode of N≡H units [27]. All the peaks of g-C$_3$N$_4$ appear in the g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$ samples, revealing the existence of g-C$_3$N$_4$.

Figure. 1 (a) XRD patterns of the as-fabricated samples: (a) g-C$_3$N$_4$, (b) Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$, (c) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-10, (d) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-30, (e) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-50, (f) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-70, (g) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-90. (b) IR spectra of the as-obtained photocatalysts: (a) g-C$_3$N$_4$, (b) 10% g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-10, (c) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-30, (d) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-50, (e) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-70, (f) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-90, (g) Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$.

Figure. 2 SEM images of the as-fabricated photocatalysts: (a) g-C$_3$N$_4$, (b) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-10, (c) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-30, (d) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-50, (e) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-70, (f) g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-90, (g) Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$, and EDS elemental mapping maps of g-C$_3$N$_4$-Bi$_{12}$O$_{17}$Br$_2$/Bi$_2$O$_3$-50 sample (g-l).
The SEM images of bare g-C₃N₄ and g-C₃N₄-Bi₁₂O₁₇Br₂/Bi₂O₃ are revealed in Fig. 2. From Fig. 2(a), pure g-C₃N₄ particles are big irregular crystals (average diameter of 1–2 μm). After g-C₃N₄ loading, g-C₃N₄ particles were deposited on the Bi₁₂O₁₇Br₂/Bi₂O₃ samples, leading to the formation of g-C₃N₄-Bi₁₂O₁₇Br₂/Bi₂O₃ heterostructure (Fig. 2b-f). The formation of the g-C₃N₄-Bi₁₂O₁₇Br₂/Bi₂O₃ nanoheterostructure was illustrated through the elemental mapping of the as-fabricated g-C₃N₄-Bi₁₂O₁₇Br₂/Bi₂O₃-50 sample (Fig. 3g-l). Images of Bi–M, Br–L, O–K, N–K, and C–K show the Bi, O, N, C, and Br signals, respectively, further revealing the existence of g-C₃N₄, Bi₂O₃, and Bi₁₂O₁₇Br₂ in the g-C₃N₄-Bi₁₂O₁₇Br₂/Bi₂O₃-5 sample.

Fig. 3a shows the comparison of photocatalyticgradation rates of phenol red over different catalysts under visible light illumination. From the catalytic experiments, g-C₃N₄-Bi₁₂O₁₇Br₂/Bi₂O₃ samples were found to be more photactive towards phenol red than bare g-C₃N₄, Bi₂O₃, and Bi₁₂O₁₇Br₂/Bi₂O₃ sample. As can be seen in Fig. 3b, visible light illumination of phenol red by the g-C₃N₄-Bi₁₂O₁₇Br₂/Bi₂O₃-50 sample resulted in the apparent decrease in absorption.
The photocatalysis mechanism of the g-C\(_3\)N\(_4\)-Bi\(_{12}\)O\(_{17}\)Br\(_2\)/Bi\(_2\)O\(_3\) was studied, as revealed in Fig. 3c. The CB levels and VB levels of g-C\(_3\)N\(_4\), Bi\(_{12}\)O\(_{17}\)Br\(_2\), and Bi\(_2\)O\(_3\) were obtained from the reported works [24,27]. The g-C\(_3\)N\(_4\)-Bi\(_{12}\)O\(_{17}\)Br\(_2\)/Bi\(_2\)O\(_3\) hybrid catalysts demonstrate much higher photocatalytic performance than bare g-C\(_3\)N\(_4\) and Bi\(_{12}\)O\(_{17}\)Br\(_2\)/Bi\(_2\)O\(_3\), which shows that photogenerated charges separate more efficiently in the g-C\(_3\)N\(_4\)-Bi\(_{12}\)O\(_{17}\)Br\(_2\)/Bi\(_2\)O\(_3\) composite. When the ternary heterostructured samples are irradiated, g-C\(_3\)N\(_4\), Bi\(_{12}\)O\(_{17}\)Br\(_2\), as well as Bi\(_2\)O\(_3\) can be excited and produce photogenerated charges. Most of charges recombine easily, thus the bare sample has a respectively low photocatalytic efficiency [29-37]. For the ternary heterostructured g-C\(_3\)N\(_4\)-Bi\(_{12}\)O\(_{17}\)Br\(_2\)/Bi\(_2\)O\(_3\) sample, at first, when the ternary heterostructured composite is excited by visible light illumination, the electrons in the CB of g-C\(_3\)N\(_4\) can migrate to the CB of Bi\(_{12}\)O\(_{17}\)Br\(_2\) because of the CB of g-C\(_3\)N\(_4\) is more negative than that of Bi\(_{12}\)O\(_{17}\)Br\(_2\). In addition, the holes on the Bi\(_{12}\)O\(_{17}\)Br\(_2\) can move to g-C\(_3\)N\(_4\). Second, the CB of Bi\(_{12}\)O\(_{17}\)Br\(_2\) is more negative than that of Bi\(_2\)O\(_3\) can account for the fact that the photogenerated electrons in the CB of Bi\(_{12}\)O\(_{17}\)Br\(_2\) can migrate to the CB of Bi\(_2\)O\(_3\). The holes on the Bi\(_2\)O\(_3\) surface can transfer to Bi\(_{12}\)O\(_{17}\)Br\(_2\). The electrons in the CB of g-C\(_3\)N\(_4\) can directly migrate to the CB of Bi\(_{12}\)O\(_{17}\)Br\(_2\). These charge transfer can improve the charges separation, thus enhancing the photocatalytic efficiency.

4. Conclusions

In short, ternary heterostructured g-C\(_3\)N\(_4\)-Bi\(_{12}\)O\(_{17}\)Br\(_2\)/Bi\(_2\)O\(_3\) composite photocatalysts were successfully synthesized, and the composite samples showed excellent photocatalytic performance. And g-C\(_3\)N\(_4\)-Bi\(_{12}\)O\(_{17}\)Br\(_2\)/Bi\(_2\)O\(_3\)-50 composite performed best.

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