Study on a Novel Compound of BION / BMO Enhancing Photocatalytic Activity under Visible Light

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Abstract. A composite photocatalytic material had been designed in this paper by one-step hydrothermal method. With tetracycline as the target pollutant, Bi₂O₂(OH)(NO₃)/Bi₂MoO₆₋₁ (mole ratio, labelled BION/BMO-1) showed the best photocatalytic performance among these catalysts. Through the morphological characterization of SEM, BION/BMO-1 complex is closely bonded by the flaky structure to form flower-like structure. XPS analysis shows that there is a strong interaction between Bi₂O₂(OH)(NO₃) and Bi₂MoO₆ interface. Through BET result, BION/BMO-1 had the largest specific surface area, which enhanced its adsorption performance and ability of degradation pollutants.

1. Introduction

As a clean and efficient treatment method, semiconductor photocatalytic materials have attracted extensive attention in the treatment of organic polluted wastewater in recent years [1]. However, many single-component photocatalysts are limited in application due to their low charge separation efficiency [2,3]. Therefore, there are many improvement methods, such as semiconductor composite, ion doping, precious metal deposition and morphology regulation, etc, which greatly improve the photocatalytic activity of materials [4,5].

Bi₂MoO₆ and Bi₂O₂(OH)(NO₃) has been studied by many scholars. Li [6] et al. synthesized CeO₂/Bi₂MoO₆ compound, and enhanced the degradation effect of organic pollutant in visible light. Wu [7] et al. designed Pt@C@Bi₂MoO₆ composite for enhanced 2,4–dibromophenol degradation under visible–light irradiation. Hao [8] et al. studied multifunctional Bi₂O₂(OH)(NO₃) nanosheets with {001} active exposing facets on dye-sensitization. Li [9] et al. synthesized Bi₂O₂(OH)(NO₃)·1.5H₂O/BiOCl heterojunction to highly enhanced photocatalytic activity. But there is no report about the Bi₂O₂(OH)(NO₃)/Bi₂MoO₆ composite.

In this paper, we synthesized Bi₂O₂(OH)(NO₃)/Bi₂MoO₆ composite by one-step hydrothermal method, and analyzed the microstructure of element, composition of the sample and surface chemical state by BET, XPS and photodegradation of organic pollutant (TC). Some external factors affecting the photocatalytic efficiency as well as catalyst's stability were investigated.
2. Introduction

2.1. Preparation of photocatalysts

The Bi$_2$O$_2$(OH)(NO$_3$)/Bi$_2$MoO$_6$ was synthesized by a one-step solvothermal reaction [10]. Firstly, 2 mmol Bi (NO$_3$)$_3$·5H$_2$O (0.97 g) and 0.5 mmol Na$_2$MoO$_4$·2H$_2$O (0.121 g) were dissolved in 70 mL of deionized water, stirring 30 min. After that, the mixture was transferred to a 100 mL polytetrafluoroethylene high pressure reactor, maintained at 120 °C for 24 h. After cooling to room temperature, the products were collected by centrifuging, washed with deionized water and anhydrous ethanol three times respectively, dried at 60 °C for 6 h in vacuum oven. The final products were labeled BION/BMO-1 (mole ratio).

Other proportions of samples were prepared by adjusting the dosage of Na$_2$MoO$_4$·2H$_2$O. Among the samples prepared, the dosage of Na$_2$MoO$_4$·2H$_2$O was 0.0605 g, 0.1815 g and 0.2420 g respectively, and marked as BION/BMO-3, BION/BMO-0.33 and BMO. Without Na$_2$MoO$_4$·2H$_2$O, BION was made.

2.2. Characterization

Powder X-ray diffraction (XRD) was carried out using a RU-200B (Japan), employing a scanning rate of 0.2 ° s$^{-1}$ and 2θ ranges from 5 ° to 70 °. X-ray photoelectron spectroscopy (XPS) was performed on a G Multilab (USA). The C 1s peak at 284.8 eV was used to calibrate peak positions. Morphologies were examined with a Supra 55 field emission-scanning electron microscope (SEM) (JSM-IT300). Specific surface areas was probed by measuring volumetric N2 adsorption–desorption isotherms at liquid nitrogen temperature, using an ASAP 2020 HD88 instrument (Micromeritics, USA).

2.3. Visible-light-driven photocatalytic performance

To evaluate the photocatalytic activity of compound catalyst, the Tetracycline (TC, 20 mg/L) was selected as the target pollutant. In a typical experiment, 0.02 g photocatalysts were dispersed in 50 mL tetracycline (20 mg/L), stirred for 30 min in dark to achieve adsorption equilibrium. The 300 W xenon lamp, fitted with light filter, provided the light source for 120 min, 5 ml solution was taken out every 30 minute. Solution was the centrifugal to remove photocatalysts, spectrophotometer to measure the absorbance at 357 nm. The degradation efficiency is calculated by the following formula:

\[
\text{Degradation (\%)} = \left( \frac{A_0 - A}{A_0} \right) \times 100\% = \left( \frac{C_0 - C}{C_0} \right) \times 100\% \tag{1}
\]

Where $A_0$ and $A$ are the absorbance of pollutant solutions before and after light irradiation, $C_0$ and $C$ are assigned to the corresponding concentrations of pollutants.

3. Result and discussion

3.1. Morphological and structural analysis

The crystalline phase of Bi$_2$O$_2$(OH)(NO$_3$), Bi$_2$MoO$_6$ and their composite catalyst samples were analyzed by the X-ray diffraction patterns, which are shown in Figure 1. The diffraction peaks of all the Bi$_2$O$_2$(OH)(NO$_3$) and Bi$_2$MoO$_6$ samples could be indexed to the orthorhombic Bi$_2$O$_2$(OH)(NO$_3$) (ICSD 15-4359) and Bi$_2$MoO$_6$ (JCPDS No.21-0102), and there are no other peaks, showing the BION and BMO were pure, and BION/BMO was synthesized successfully.
Figure 1. XRD patterns of BMO, BION and BION/BMO.

Figure 2 shows the morphology and particle size of BION, BMO and BION/BMO-1. As shown in figure 2a and b, the pure BION sample obtained by hydrothermal method is a layered structure composed of a large number of smooth nanoparticles. The pure BMO sample is also lamellar, but its thickness is smaller than that of BION sample. From figure 2c, the composite sample BION/BMO-1 is a flower-like structure, which is formed by the close adhesion of the lamellar structure, and the thickness of this flower-like structure is thinner.

Figure 2. SEM images of (a) BION, (B) BMO, and (C) BION/BMO-1.

The chemical composition and surface state of BION/BMO-1 were studied by X-ray photoelectron spectroscopy (XPS). As shown in the figure 3, the constituent elements Bi, Mo, O, N and C can be accurately detected, and the C peak should be attributed to the XPS instrument itself. Figure 3 b-d is the high-resolution XPS spectrum of Bi 4f, Mo 3d and O 1s, respectively. As shown in figure 3b, the peaks
of the binding energy of 159.0 eV and 164.3 eV belong to Bi 4f, indicating that the Bi$^{5+}$ exists in complex BION/BMO-1. The two analytical peaks at 232.2 eV and 235.4 eV are from the Mo$^{6+}$ of BMO in figure 3c. Compared with BMO, BION/BMO-1 complex Mo 3d is offset, which may be caused by an interface action between complexes. In figure 3d, the analytical peaks of 529.8 eV and 530.2 eV come from Bi-O in BION and Mo-O in BMO respectively, while the analytical peaks of 532.2 eV should be adsorbed oxygen come from NO$_3$- and H$_2$O.

![Figure 3. XPS spectra of the BION, BMO and BION/BMO-1: (a) survey, (b) Bi 4f, (c) Mo and (d) O 1s.](image)

The specific surface areas of BION, BMO, and BION/BMO-1 were tested, as shown in the figure 4. The specific surface areas of BION, BMO, and BION/BMO-1 were calculated to be 1.45, 19.34 and 39.78 m$^2$/g, respectively. BION/BMO-1 had the largest specific surface area.

![Figure 4. N2 adsorption-desorption curves of BION, BMO and BION/BMO-1.](image)
3.2. Photocatalytic performance

In order to evaluate the catalytic effect of BION/BMO composite, tetracycline (TC) was selected as the pollutant. As shown in the figure 5a, TC solution was hardly degraded with the BION sample, indicating that BION had scarce photocatalytic degradation effect on TC under visible light. When BMO was added alone, the photocatalytic degradation rate of tetracycline was 46.58 % after 120 min of visible light. The photocatalytic degradation effect of tetracycline was improved when BION/BMO composite photocatalyst was added. After 120 min of visible light irradiation, the photocatalytic degradation rates of TC in samples BION/BMO-3, BION/BMO-1 and BION/BMO-0.33 were 70.10 %, 81.85 % and 71 % respectively, all higher than the photocatalytic degradation rates of BION alone and BMO alone. From figure 5b, it can be seen from the results that after 5 cycles, the degradation effect of BION/BMO-1 on tetracycline reduced a little due to the loss of samples in the process of sample recovery. However, the degradation effect of tetracycline after 5 cycles is more than 70 %, indicating that the catalyst has good stability.

![Figure 5](image)

**Figure 5.** (a) Photocatalytic degradation curves of TC solution by different photocatalysts, (b) Degradation percentage of TC solution by BION/BMO-1 in cycle experiments.

4. Conclusion

BMO/BION composite was synthesized by a simple hydrothermal method, and was proved by SEM, BET, XPS and other characterization methods. With tetracycline as the target pollutant, the degradation effect of BION/BMO-1 is 5.46 times that of BION and 1.76 times that of BMO under visible light, indicating the photocatalytic performance of material greatly improved.

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