Synthesis of polyethylene/bismuth molybdate and its photocatalytic properties

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Abstract. Bismuth molybdate (Bi₂MoO₆) was synthesised by utilizing Bi(NO₃)₃·5H₂O and (NH₄)₆Mo₇O₂₄·4H₂O through hydrothermal method. Bi₂MoO₆ was loaded on polyethylene (PE) to prepare the film with photocatalytic properties. The product was characterised by XRD and UV DRS spectra and investigated photocatalytic degradation of sulfanilamide under solar light. The results confirmed a photocatalytic efficiency of 66%.

1. Introduction

Sulfonamides are one of the most widely used veterinary antibiotics[1]. There are only two ionic functional groups constitute their structure: aniline group and amide group. They have weak interaction with soil and minerals, and it is easy to migrate from the soil into the water environment system. These pollutants are relatively small in quantity, low in absolute concentration, difficult to enrich and dispose. It is of great potential harm, which has become an increasingly thorny environmental problem. The application of photocatalysis in the degradation of environmental pollutants has been widely valued by domestic and overseas researchers[2-4]. The "Green" is the great feature of the process of photocatalysis. The catalyst used is safe to the environment. The harm of intermediate degradation products to the environment is gradually lower than that of the degraded substances, and the final degradation products are harmless to the environment and human body.

Bismuth molybdate (Bi₂MoO₆) is non-toxic, high stability, suitable position of valence band and conduct band, which result in a narrow band gap (band gap is 2.70 eV). Bi₂MoO₆ can absorb visible light and photodegrade pollutants at higher utilization rate of sunlight. Bi₂MoO₆ has great potential in environmental purification and was mainly used for degradation of methylene blue, rhodamine B, crystal violet, methyl orange and other dyes.

In addition to exploring suitable methods to broaden the visible spectral response of Bi₂MoO₆[5-8], and to improve the separation efficiency of photogenerated electrons and holes, and improve the catalytic activity for photodegradation of sulfonamide antibiotic, the problems of catalyst agglomeration and recycling still need to be solved. It is a hot spot to use diatomite, zeolite, humus, activated carbon and other adsorption materials with high specific surface area as carriers, but such catalytic materials often sink in the water and have limited absorption of sunlight. In order to make full use of sunlight, we hope that the carriers loaded with Bi₂MoO₆ can float on the water surface, which is light, stable, cheap, easy to recycle and reuse.

Therefore, in this project, light weight modified polyethylene (PE) was used as carrier to load and disperse Bi₂MoO₆. This new composite material not only takes advantage of the excellent properties of Bi₂MoO₆ which can produce hydroxyl radical or peroxy radical with high oxidation ability under
illumination, but also takes advantage of the light weight of PE to avoid sedimentation, greatly enhancing the utilization of sunlight. At the same time, the composite material has low manufacturing cost and easy recovery. It should be a suitable choice for photodegradation of sulfanilamide antibiotics in water.

2 Experimental section

2.1 Preparation of Bi$_2$MoO$_6$

Bi(NO$_3$)$_3$·5H$_2$O and (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O have been procured from Changjiang huagong corp. without purification. Bi$_2$MoO$_6$ powder was prepared as followed. 5 mmol Bi(NO$_3$)$_3$·5H$_2$O was desoloved in 10 mL 2 mol/L HNO$_3$, corresponding stoichiometric (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O was dissolved in 10 mL 1 mol/L NaOH solution (Bi/Mo mole ratio was 4). 10 mL (NH$_4$)$_6$Mo$_7$O$_{24}$ solution was slowly dropped into Bi(NO$_3$)$_3$ solution under stirring, and 1:1 ammonia solution was added to adjust the pH value. The mixed solution was transferred to the PTFE lined autoclave. After heating for 4 hours, light yellow powder was then obtained.

2.2 Preparation of PE/Bi$_2$MoO$_6$ film

Polyethylene/bismuth molybdate (PE/Bi$_2$MoO$_6$) film was prepared by mixing polyethylene and xylene with bismuth molybdate powder in a certain mass ratio, stirring at 70 ℃ for 15 min, pouring it into a glassdish while hot, and drying at 130 ℃ for 2 h. The appearance of the film is light yellow with the increase of bismuth molybdate ratio. All films can float on the water. The size of the PE plastic fragment is about 2 cm$^2$.

2.3 Characterization

The crystalline structure of the prepared Bi$_2$MoO$_6$ powder was analyzed by X-ray diffractometer (XRD, DX-2700). The UV-diffuse reflectance spectroscopy (UV-DRS) was studied through Shimadzu UV-2550 spectrometer.

2.4 Photocatalytic test

The photocatalytic performance of the prepared sample was carried out by degradation of sulfanilamide. 0.1g of catalyst and 50 mL 10mg/L sulfanilamide solution was taken and stirred under dark condition for 30 min to achieve adsorption-desorption equilibrium. The solution was irradiated under solar light for 5 h and concentration was recorded at every 1 h intervals.

3 Results and discussion

3.1 Treatment of polyethylene in xylene

3.1.1 Optimum dissolution of PE in xylene. Polyethylene can be dissolved by xylene. A certain amount of PE plastic was added into xylene, heated at 70 ℃ to be dissolved, and then filtered to remove impurities. The best dissolution ratio was determined according to the dissolution rate.

| No. | xylene/mL | PE/g  | Dissolution time/s | Dissolution rate/g·s$^{-1}$ |
|-----|-----------|-------|-------------------|-----------------------------|
| 1   | 15        | 0.5290| 240               | 0.0022                      |
| 2   | 15        | 1.2421| 282               | 0.0044                      |
| 3   | 15        | 1.8006| 310               | 0.0058                      |
| 4   | 15        | 2.1982| 955               | 0.0023                      |
According to data No. 1-4 in table 1, the dissolution rate gradually increases and then decreases with the increase of the mass of polyethylene when xylene is 15 mL. The dissolution rate is higher when the mass of polyethylene is about 1.8 g. When the volume of xylene is increased to 30 mL and the mass of PE is 2.4 g-3.6 g, the dissolution rate is about 0.005 g·s⁻¹, as shown in table 1, list No. 5 and 6.

3.1.2 Volatilization temperature and time of xylene. A small amount of polyethylene-xylene solution was taken on the micro-melting-point meter to observe the foaming temperature and time of xylene. The investigation temperature was chosen as 130 °C and 150 °C, respectively, according to the boiling point of xylene which is between 137 °C and 140 °C. The phenomenon was listed in table 2 and table 3.

| T/°C | Time     | Phenomenon                                  |
|------|----------|---------------------------------------------|
| 130 °C | 17s      | The film melt and bubble gradually          |
|      | 6min     | The bubbles appear more dense and grow larger |
|      | 48min    | There are only a few bubbles                |
|      | 1h 2min  | The bubbles nearly disappeared              |

| T/°C | Time     | Phenomenon                                  |
|------|----------|---------------------------------------------|
| 150 °C | 3s       | A large number of bubbles appear rapidly    |
|      | 5min15s  | Small bubbles overlap gradually             |
|      | 40min    | A small amount of bubbles left              |
|      | 51min    | The bubbles nearly disappeared              |

According to the data in Table 2 and 3, when the xylene removal temperature is set at 130 °C-150 °C, the drying time should be more than 1 h.

3.2 XRD spectrum of Bi₂MoO₆

![XRD spectrum of Bi₂MoO₆](image)

Figure 1. XRD spectrum of Bi₂MoO₆.
The crystalline structure of the prepared Bi$_2$MoO$_6$ was analyzed by XRD spectrum as shown in figure 1. The obtained Bi$_2$MoO$_6$ was Orthorhombic phase $\gamma$-Bi$_2$MoO$_6$ (JCPDS No.51-0102).

### 3.3 UV-DRS analysis

![UV-diffuse reflectance spectroscopy of Bi$_2$MoO$_6$.](image)

The UV-diffuse reflectance spectroscopy (UV-DRS) was shown in figure 2. The bandgap is about 2.21 eV. According to the results of UV-Vis absorption, it can be inferred that the position of conduction band and valence band of Bi$_2$MoO$_6$, as shown in figure 3.

![Band gap position of Bi$_2$MoO$_6$.](image)
3.4 Photocatalytic performance of PE/Bi₂MoO₆ film

UV-Vis absorption of sulfanilamide solution under the irradiation of sunlight simulated by xenon light, as shown in figure 4a. After irradiation for 1 h, the absorption peak at 258 nm decreased obviously, and new absorption peaks appear at about 300 nm and 576 nm, respectively. The absorption peaks at 300 nm and 576 nm increased with the irradiation time extending.

It can be observed that the colorless sulfanilamide solution turns purple and then yellow gradually. This is due to the photodegradation of sulfanilamide to p-phenylenediamine, and the continuous oxidation of p-phenylenediamine to p-phenylenedione.

Add PE/Bi₂MoO₆ into sulfanilamide solution. The UV-Vis absorption spectrum after irradiation was shown in figure 4b. Compared to figure 4a, there is no absorption peak appear at 300 nm and 576 nm after irradiation. With the extension of irradiation time, the absorption peak of sulfanilamide at 258 nm gradually decreases, which indicates that PE/Bi₂MoO₆ can effectively degrade sulfanilamide under simulated sunlight, and the degradation rate is about 66%.

![Image](a) UV-Vis spectra of sulfanilamide solution under Xe lamp irradiation: (a) no catalyst (b) PE/Bi₂MoO₆ as catalyst.

4 Conclusion

In this project, Bi(NO₃)₃·5H₂O and (NH₄)₆Mo₇O₂₄·4H₂O were used as raw materials to synthesize Bi₂MoO₆ powder by hydrothermal method. The Bi₂MoO₆ powder was loaded on PE to compose PE/Bi₂MoO₆ film with photocatalytic performance. The film was floating on the water because of its lightweight during the whole process of photodegradation of sulfanilamide. It is easy to recover. The degradation of sulfanilamide was about 66% under irradiation after 5 h.

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