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Full Length Article

# Synthesis of C@$Bi_2MoO_6$ nanocomposites with enhanced visible light photocatalytic activity

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ABSTRACT

Carbon–coated $Bi_2MoO_6$ (C@BM) composites have been successfully synthesized via two–step hydrothermal method. The morphology, structure and photocatalytic performance of the composites in the degradation of Rhodamine B (Rh B) are characterized. The results show that the C@BM composites exhibit enhanced photocatalytic performance in the degradation of Rh B with maximum degradation rates of 90% (210 min) under visible light irradiation. 1.0%C@BM sample shows the highest photocatalytic activity, and the improved photocatalytic performance is mainly ascribed to the formation of Mo—O—C and Bi—O—C bonds. The bonds could promote electron transfer from $Bi_2MoO_6$ to carbon layer and inhibit the recombination of electron–hole pairs with the presence of carbon layer in the composites. Moreover, the carbon layer on $Bi_2MoO_6$ could enhance the absorption in the visible light region. In the photocatalytic degradation process, $^{\bullet}O_2^{-}$ and holes are the predominant active species for the decomposition of Rh B.

## 1. Introduction

In recent years, the environmental problem has become increasingly serious, and water pollution caused by the expansion of chemical and textile industries has also turned into one of the issues need to be solved. As an environmentally and friendly method, semiconductor photocatalysts has drawn much attention which can harvest sunlight as an energy source to degrade pollutants [1–5]. Titanium dioxide ($TiO_2$) has been extensively investigated for air and water purification [6,7], and it shows some advantages over other semiconductors such as excellent activities and long–term stability against photo and chemical corrosion [8–10]. $TiO_2$ is only excited under ultraviolet (UV) light irradiation because of its wide band gap (3.2 eV for anatase). However, UV light accounts for only 4% of the whole solar spectrum [9]. Therefore, it is very important to develop a new visible light driven photocatalyst which can efficiently utilize solar light.

In the past few years, mental oxide photocatalysts like bismuth compounds have attracted intense research interest because of their excellent light sensitivity and high photocatalysts activity. Among bismuth compounds, $Bi_2MoO_6$ is the simplest member of the layered Aurivillius–related oxide family, and consists of $[Bi_2O_2]^{2+}$ layers sandwiched between $MoO_4^{2-}$ slabs. As Bi–based ternary metal oxide photocatalyst, it usually exhibits excellent photocatalytic activity under visible light irradiation [11–13]. $Bi_2MoO_6$ attracts lots of interests due to its unique advantage, and has narrow band gap (2.3 eV–2.8 eV) and corresponds well with visible light [14]. However, the recombination of photo–generated electrons and holes still exists in $Bi_2MoO_6$, which decreases its photocatalytic performance [15]. Thus, it is a challenge to modify $Bi_2MoO_6$ to improve photocatalytic activity. Researchers have tried various strategies including precious metal deposition, metal ion doping and semiconductor composites [16–18]. Recently, coating with a thin layer of amorphous carbon on the surface of photocatalyst gains lots of attentions, which is an effective method to stabilize the surface and enhance the photocatalytic activity. For instance, Chen et al. [19] have successfully synthesized C–coated $ZnIn_2S_4$ nanocomposites and discovered that carbon coating remarkably improved the photocatalytic efficiency. Thus, amorphous carbon–coated photocatalyst holds great potential for improving the photocatalytic activity. Meanwhile, carbon–coated photocatalyst can be obtained through the inexpensive and environmental processes using glucose as precursor.

In this study, a facile route for hydrothermal preparation of carbon–coated $Bi_2MoO_6$ (C@BM) nanocomposites was employed by adding glucose as the precursor. The C@BM nanocomposites distinctly improves the photocatalytic activity under visible light. It is attributed to the intimate interfacial contacts between $Bi_2MoO_6$ and carbon layers, which leads to higher separation efficiency of

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photogenerated electrons and holes pairs and longer lifetime of photogenerated carriers.

## 2. Experimental section

### 2.1. Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3·5H_2O$, 99%) was purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China), and glucose anhydrous ($C_6H_{12}O_6$) was obtained from Shanghai Bio Science & Technology Co. Ltd. (Shanghai, China). Ammonium molybdate tetrahydrate(($(NH_4)_6Mo_7O_{24}·4H_2O$, 99%) was acquired from Aladdin Chemistry Co. Ltd. (Shanghai, China). Ammonium hydroxide ($NH_3·H_2O$, 99.5%) was obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China). Nitric acid ($HNO_3$, 98%) was obtained from Aladdin Chemistry Co. Ltd. (Shanghai, China). All the chemicals were used as received without further purification, and deionized water was used throughout the experiments.

### 2.2. Synthesis of photocatalysts

#### 2.2.1. Preparation of $Bi_2MoO_6$

Pure $Bi_2MoO_6$ photocatalyst was prepared by a hydrothermal method. The 2.0 mmol of $Bi(NO_3)_3·5H_2O$ and 0.143 mmol of $(NH_4)_6Mo_7O_{24}·4H_2O$ were placed into 10 mL (2 mol/L) $HNO_3$ and 10 mL deionized water under stirring, respectively. After stirring for 20 min, $Bi(NO_3)_3·5H_2O$ solution was added into $(NH_4)_6Mo_7O_{24}·4H_2O$ solution dropwise under constant stirring. The obtained suspension was stirred 60 min, and adjusted pH to 7 by $NH_3·H_2O$. The obtained homogeneous suspension was then transferred into a Teflon–lined stainless steel autoclave (100 mL) and maintained 180 °C for 12 h by were filtered, The products were washed with distilled water and ethyl alcohol several times, and dried in vacuum at 60 °C for 8 h. Then the pure $Bi_2MoO_6$ photocatalyst was obtained.

#### 2.2.2. Preparation of C@BM

A certain of glucose was dissolved into 20 mL of distilled water, then 0.1 g of $Bi_2MoO_6$ was added to the glucose solution slowly under vigorous stirring. After stirring for 30 min, the mixture was transferred into Teflon–lined autoclave, and heated at 180 °C for 6 h. The product was washed with distilled water and absolute ethanol for several times, and dried in an oven at 60 °C for 8 h. Finally, the C@BM composites were obtained. The weight percentages of carbon to $Bi_2MoO_6$ were controlled to be 0, 0.2 wt%, 0.4 wt%, 1.0 wt%, 2.0 wt%, 4.0 wt% and 10 wt% by changing the weight of glucose.

### 2.3. Characterization

X–ray Powder Diffractometer (XRD) was performed on a Bruker D8 Advance diffract meter (Bruker, Germany) using Ni–filtered Cu K α radiation (=1.5418 Å) at 60 kV and 60 mA over the 2θ range of 10°–80°. The surface morphologies and compositions of photocatalysts were examined using a scanning electron microscope (SEM, JEOL 7500F) combined with energy dispersive X–ray spectrometer (EDX). The ultra–structure of each sample was observed by high–resolution transmission emission microscopy (HRTEM, JEOL, JEM 2100). Thermogravimetric analysis (TGA) was carried out on a STD Q600 TA instrument in air flow at a heating rate of 10 °C/min. X–ray photoelectron spectroscopy (XPS) measurements were obtained using an ESCALAB 250 spectrometer (Thermo Fisher Scientific, UK) with non–monochromatic Al K X–rays (1486.6 eV). The binding energy was calibrated by taking the C 1s peak of contaminant carbon as a reference at 284.6 eV. Infrared spectra were recorded by a Fourier transform infrared spectrometer (FTIR, Nicolet Avatar 370). The *Brunauer–Emmett–Teller* (BET) specific surface area was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P0) range of 0.05–0.3. Photoluminescence (PL) spectra of the samples were obtained using a fluorescence spectrometer (Hitachi F–4600). UV–vis diffuse reflectance spectra (DRS) were carried out with a UV–vis spectrophotometer (TU–1901) using $BaSO_4$ as reference. The electron spin resonance (ESR) spectrometer was used to detected radical species by on Bruker EMX EPR spectromemter. In detail, the sample (1.0 mg) was dispersed in 1.0 mL of Rh B, into which 40 mmol/L of 5,5-dimethyl-L-pyrroline-N-oxide (DMPO)/benzyl alcohol solution (1:10, v/v) was added. The mixture was oscillated to obtain well-blending suspension, and the irradiation source (>420 nm) was Xe lamp system. The parameters for the ESR spectrometer were as follows: center field was 3367 G, and microwave power was 21.45–21.95 mW.

### 2.4. Evaluation of photocatalytic activity

The photocatalytic activities of as-prepared were evaluated in terms of the photocatalytic degradation of Rh B, which was carried out at ambient temperature in a continuous flow reactor. A 500 W Xe lamp was used as visible light source, and the UV light portion was filtered by a 420 nm cut–off filter. The distance between the Xe lamp and the reactor was 25 cm 0.1 g photocatalyst was put into 100 mL Rh B solution (5 mg/L). After dispersing in ultrasonic bath for 10 min, the mixture was stirred in the dark for 60 min to obtain the equilibrium adsorption–desorption. At certain time, a certain of suspension was taken out from the mixture and immediately centrifuged. The obtained solution was analyzed by the spectrophotometer at 554 nm to determine Rh B concentration. To detect the active species during photocatalytic reactivity, sacrificial agents were used to capture different active species. The hole, electron, hydroxyl radical ($^•OH$) and superoxide radical ($^•O_2{}^-$) were captured by sodium oxalate (5 mmol/L), Cr (VI) (0.5 mmol/L), isopropanol (IPA, 5 mmol/L) and 4–Hydroxy–2,2,6,6–tetramethylpiperidinyloxy (TEMPOL, 2 mmol/L), respectively.

## 3. Results and discussion

### 3.1. Crystal structure and morphology

XRD patterns of $Bi_2MoO_6$ and C@BM composites are shown in Fig. 1. The high crystallinity of $Bi_2MoO_6$ can be obtained by the hydrothermal method, and the main diffraction peaks of samples can be well indexed to orthorhombic $Bi_2MoO_6$ (JCPDS No. 76–2388) [20]. The main diffraction peaks of C@BM composites were obviously influenced by the amount of carbon layer on the surface. As the amount of carbon is 1.0%, the diffraction peaks become shaper and stronger compared with other samples, indicating that 1.0%C@BM has the best crystallization. The peaks of carbon are not observed in XRD patterns of the C@BM samples, which suggests the presence of carbonaceous materials rather than crystalline carbon in these composites [21].

The morphologies of $Bi_2MoO_6$ and C@BM are observed by SEM. As shown in Fig. 2a–d, the $Bi_2MoO_6$ and C@BM composites show the irregular platelike nanosheets with the thickness of about 20–70 nm. Many cracks are found on the surface of the $Bi_2MoO_6$, but the cracks are disappeared with the addition of carbon layer in C@BM composite. It indicates that $Bi_2MoO_6$ nanosheets are coated by carbon, and the carbon nanoparticles gradually grow to fill the cracks. With the increasing of coated carbon, the surface of the C@BM exhibits much rough. The EDX spectra of composites linked to SEM show that carbon element has existed in the C@BM