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Short Communication

CuPc sensitized Bi_2MoO_6 with remarkable photo-response and enhanced photocatalytic activity

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ABSTRACT

Much enhanced photo-absorption of Bi_2MoO_6 was realized by introduction of an organic dye sensitizer, copper phthalocyanine (CuPc). The $CuPc/Bi_2MoO_6$ composite photocatalyst showed photo-response in the whole visible spectrum and even the near infrared region. As a result, it exhibited much higher photocatalytic activity than bare Bi_2MoO_6 in photo-degradation of RhB and phenol under simulated solar light. Moreover, the sensitization effect of CuPc was testified by photo-degradation of RhB under a red LED ($\lambda = 620$ nm) irradiation.

1. Introduction

Semiconductor-based photocatalysis under solar light irradiation has attracted much attention in the past few decades due to the urgent environmental concerns and increasing energy demand [1–5]. The most widely used semiconductor TiO_2 suffers from the drawback of narrow light-response range due to its large band gap, which is only active under ultraviolet light. In order to achieve efficient solar energy conversion, considerable research efforts have been directed toward exploring visible-light-induced photocatalysts [6–10]. Although many impressive photocatalytic materials have been explored and have shown exciting photo-activity under visible light, the red/near infrared region of the solar spectrum is scarcely exploited. How to take full advantage of the extraordinary amount of energy that the sun supplies us with remains a big challenge in the scientific research field.

Inspired by the dye-sensitized solar cells (DSSC), in which an organic dye sensitizer could act as a light-harvesting material to extend the absorption spectrum of the semiconductor electrode, we design a composite photocatalyst by introducing an organic dye sensitizer to the semiconductor. In this approach, the dye molecule can absorb visible light to produce a singlet or triplet state (dye*). An electron is then injected from excited state of the dye into the conduction band (CB) of the semiconductor. The injected electron can react with the adsorbed O_2 to yield strong oxidizing radicals (such as $O_2^{\bullet -}$ or OH•), which can degrade the organic pollutants. During the last few years a large number of new organic dyes have been developed, among which metallophthalocyanines (MPc) are particularly attractive due to their high stabilities toward heat and light, nontoxicity, semiconducting properties, and most importantly, intensive absorption in the red/near infrared region [11].

Bi_2MoO_6 is one of the simplest members of the Aurivillius oxide family which possesses many interesting physical and chemical properties such as ion conducting, dielectric properties, gas sensor, and catalytic behavior [12–16]. Recently, it was found to show good photocatalytic performance for water splitting and organic contaminants decomposing under visible light irradiation [17–25]. For example, Kudo et al. have reported that Bi_2MoO_6 showed high photocatalytic activity for O_2 evolution from an aqueous silver nitrate solution under visible light irradiation [23]. Fu et al. have synthesized Bi_2MoO_6 nanocrystalline by a solvothermal method and investigated its photocatalytic activity in degradation of RhB [24]. More recently, Huang et al. found that Bi_2MoO_6 nanobelts with dominant {010} facets exhibited facet-enhanced photocatalytic property for the photo-degradation of dye pollutants under visible light irradiation [25]. However, the absorption edge of bare Bi_2MoO_6 is till *ca.* 500 nm only, which occupies a small part of the solar spectrum. On the other hand, CuPc has a high absorption coefficient in the visible and even the near infrared region. Therefore, by combining Bi_2MoO_6 photocatalyst with CuPc, the visible and the near infrared region of the solar spectrum can be fully utilized.

In this study, a novel composite photocatalyst was designed using Bi_2MoO_6 as the inorganic semiconductor and CuPc as the organic sensitizer, which had a remarkable photo-response in the entire visible and even the near infrared region. The $CuPc/Bi_2MoO_6$ composite exhibited high photocatalytic activity under simulated solar light and a red LED ($\lambda = 620$ nm) irradiation.

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2. Experimental

2.1. Preparation of the photocatalyst

The Bi_2MoO_6 photocatalyst was prepared by a hydrothermal process according to our previous report [26].

Impregnation of the Bi_2MoO_6 substrate with the CuPc photosensitizer was carried out as follows: 10 μmol of CuPc was dissolved in 100 mL of ethylene glycol monomethyl ether to form a dark blue solution A. At the meantime, 1 mmol of Bi_2MoO_6 powder was dispersed in 20 mL of ethylene glycol monomethyl ether to form a suspension B. Then 100 μL of solution A was added into suspension B. Afterwards, the mixture was stirred at room temperature for 24 h. Finally, the products were collected by filtration, washed with distilled water for several times, and then dried at 60 °C in air for 12 h.

2.2. Characterization

The phase and composition of the as-prepared samples were measured by X-ray diffraction (XRD) studies using an X-ray diffractometer with Cu Kα radiation under 40 kV and 100 mA and with the 2θ ranging from 20° to 70° (Rigaku, Japan). The morphologies of the products were obtained by transmission electron microscopy (TEM) (FEI tecnai G2F30). UV–vis diffuse reflectance spectra (DRS) of the samples were recorded with a UV–vis spectrophotometer (Hitachi U-3010) using $BaSO_4$ as reference.

2.3. Photocatalytic degradation test

Photocatalytic activity of the CuPc/Bi_2MoO_6 composite was evaluated by the photocatalytic degradation of rhodamine B (RhB) and phenol under simulated solar light irradiation. A 500 W Xe lamp was used as the light source. The experiments were performed at room temperature as follows: 0.1 g of photocatalyst was added into 100 mL of RhB (10^{-5} mol/L) or phenol solution (20 mg/L). Prior to irradiation, the suspensions were magnetically stirred for an hour in the dark to ensure the adsorption/desorption equilibrium between photocatalyst powders and RhB or phenol. At given time intervals, 3 mL of suspensions were sampled and centrifugated to remove the photocatalyst powders. RhB concentration was analyzed through a UV–vis spectrophotometer (Hitachi U-3010) by recording the variations of the absorption band maximum (552 nm) and the concentration of phenol was obtained according to the linear relation between the absorbance (at 269 nm).

3. Results and discussion

3.1. Crystal structure of the products

The X-ray diffraction (XRD) patterns of bare Bi_2MoO_6 and CuPc/Bi_2MoO_6 composite were shown in Fig. 1. All the peaks could be indexed as orthorhombic Bi_2MoO_6 phase (JCPDS Card no. 77-1246) and no other peaks from possible impurities were detected. Compared to the XRD pattern of bare Bi_2MoO_6, no distinct difference was observed on the CuPc/Bi_2MoO_6 composite due to the low molar ratio of CuPc.

3.2. Morphology of the products

The morphology and microstructure of bare Bi_2MoO_6 and CuPc/Bi_2MoO_6 composite were revealed by the transmission electron microscope (TEM) images. The TEM image in Fig. 2(A) showed that bare Bi_2MoO_6 possessed a two-dimensional plate-like structure with a lateral size of *ca.* 100 nm. For the CuPc/Bi_2MoO_6 composite, a thin CuPc layer could be observed on the surface of Bi_2MoO_6 nanoplate (Fig. 2(B)). The close contact between Bi_2MoO_6 and CuPc is beneficial to promoting the charge separation in the composite system, thus leading to an enhanced photocatalytic activity.

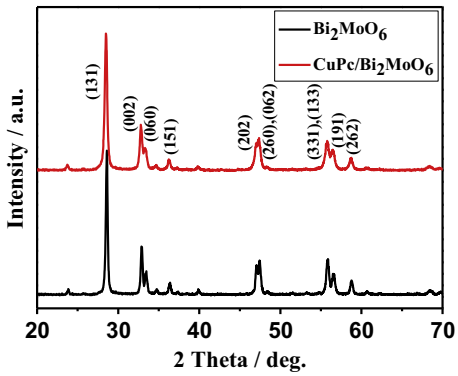

Fig. 1. XRD patterns of the as-prepared products.

3.3. Optical properties of the products

Fig. 3 shows the UV–vis diffuse reflection spectrum (DRS) of bare Bi_2MoO_6 and the CuPc/Bi_2MoO_6 composite. As observed in Fig. 3, the diffuse reflectance spectrum of bare Bi_2MoO_6 only exhibited the fundamental absorption band from the UV light region to visible light with the wavelength shorter than *ca.* 500 nm. CuPc showed a broad absorption band in the wavelengths of 500–800 nm. This absorption band might be attributed to the Q-band of CuPc, which arises from the π–π* transition of monomer from the HOMO to the LUMO of the Pc^{-2} ring [27,28]. Therefore, after the introduction of CuPc, the photo-response property of Bi_2MoO_6 was enhanced greatly. As shown in Fig. 3, the CuPc/Bi_2MoO_6 composite showed an intense absorption band from 500 to 800 nm. Furthermore, two splitting absorption bands were observed around 620 and 710 nm, which were likely ascribed to the vibronic coupling in the excited state of CuPc [29,30]. Therefore, the introduction of CuPc sensitizer could effectively enhance the photoabsorption of Bi_2MoO_6, thus significantly increasing the utilization rate of solar energy.

3.4. Photocatalytic activity

The photo-degradation of RhB and phenol were carried out to investigate the sensitization effect of CuPc on the photocatalytic activity of Bi_2MoO_6. A 500 W Xe lamp was used as the light source to simulate the solar light. As observed in Fig. 4, the degradation of RhB was negligible in the absence of the photocatalyst after 15 min of irradiation, indicating that RhB exhibited little photolysis under simulated solar light. Obviously, the introduction of CuPc into Bi_2MoO_6 could significantly enhance the photocatalytic activity. RhB could be degraded completely after 15 min of simulated solar light irradiation in the presence of the CuPc/Bi_2MoO_6 composite, whereas only 67.4% of RhB was degraded by bare Bi_2MoO_6 within the same time period.

Furthermore, the photocatalytic activity of the CuPc/Bi_2MoO_6 composite was compared with bare Bi_2MoO_6 by photo-degradation of a colorless pollutant phenol, thus the photo-sensitization effect could be excluded. The photo-degradation efficiencies of phenol as a function of irradiation time in the presence of CuPc/Bi_2MoO_6 composite compared to bare Bi_2MoO_6 was plotted in Fig. 5(A). It could be seen that the CuPc/Bi_2MoO_6 composite exhibited better photocatalytic performance than bare Bi_2MoO_6, which could degrade 100% and 89.8% of phenol in 2.5 h, respectively. The above results demonstrated that modification of CuPc was an effective way to enhance the photocatalytic activity of Bi_2MoO_6.

In order to check the stability of the composite photocatalyst, the circulating runs in the photocatalytic degradation of phenol were performed. As shown in Fig. 5(B), after four recycles for the photodegradation of phenol, the photocatalytic activity of the composite photocatalyst remained almost unchanged, confirming the CuPc/