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Ag₂O Nanoparticles Decorated Hierarchical Bi₂MoO₆ Microspheres for Efficient

Visible Light Photocatalysts

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Abstract

Nanosized Ag_2O decorated Bi_2MoO_6 hierarchical microspheres were successfully prepared and evaluated as efficient visible-light-responsive photocatalysts. X-ray diffraction (XRD) patterns confirmed that the formation of the Ag_2O and Bi_2MoO_6 composites while scanning electron microscopy (SEM) and energy dispersive X-ray spectrometer (EDX) results revealed the relatively uniform deposition of Ag_2O nanoparticles on the surface of Bi_2MoO_6 microspheres. The visible light photocatalytic activity of the composites was studied by photodegradation of methyl orange (MO) and the composite with Ag to Bi ratio of 1 : 1 shows the highest activity due to the effective separation of photocarriers. The photocatalytic mechanism study indicates photogenerated holes play a key role for the dye degradation.

Keywords: Photocatalyst; semiconductor composite; photodegradation; Bi₂MoO₆

1. Introduction

Semiconductor photocatalysts have attracted increasing attention for their potential applications in environmental remediation and energy conversion.[1-3] Bismuth-containing materials have been extensively studied efficient as photocatalysts chemical due to their good stability and high visible-light-responsibility.[2,3] Layered Bi₂MoO₆ is a n-type narrow band gap semiconductor (2.5~2.8 eV) which can utilize the visible light irradiation and would be a good candidate as photocatalysts.[4-5] Bi₂MoO₆ is characterized by alternative perovskite $(MoO4)^{2+}$ slaps and stacking of $(Bi_2O_2)^{2+}$ layers, which facilitates the effective separation of photoinduced electron-hole pairs, resulting in high photocatalytic activity.[3]

 Bi_2MoO_6 can degrade organic compounds under visible-light irradiation.[6] However, the photocatalytic efficiency of single Bi_2MoO_6 is still low, because of the rapid recombination of photogenerated electrons and holes. To improve the photocatalytic activity of Bi_2MoO_6 , some efforts have been made, such as rare earth elements doping, morphology control and formation of heterostructures.[7-11] It is well-known that the performance of photocatalysts is largely dependent on morphology, which can be obtained via controlled synthesis process. [12] Many kinds of Bi_2MoO_6 microstructures including nanofiber/wires, nanoplates, spheres and hierarchical architectures have been reported[13-16], among which 3D hierarchical structures exhibit the superior properties of dye absorption and light absorption via reflection.[16] Bi_2MoO_6 based spheres have been reported with high photocatalytic activity, such as Bi_2MoO_6 , Bi_2MoO_6/TiO_2 and Bi_2O_3/Bi_2MoO_6 [17-19], which were synthesized using hydrothermal, solvothermal or electrochemical methods. Rational design of heterostructures is another effective way to enhance the activity. Ag_2O is a p-type semiconductor with a narrow band gap about 1.46 eV. [20] Ag_2O/TiO_2 and Bi_2O_3/Ag_2O have been reported with improved activity in the decomposition of methyl orange (MO), [7,21,22] due to the inhibition of the recombination of photogenerated electrons and holes. In this study, the Ag_2O/Bi_2MoO_6 p-n heterojunction photocatalysts were synthesized through a chemical precipitation method using hierarchical Bi_2MoO_6 microspheres precursor. The composite with narrowed band gaps can inhibit the recombination of photogenerated electrons and holes, and exhibited higher photocatalytic activity. The relationship between the Ag_2O loading and the photocatalytic activity was studied and the possible enhanced mechanism was discussed also.

2. Experimental section

2.1 Preparation of the Bi₂MoO₆

The hierarchical Bi_2MoO_6 hollow spheres were prepared according to the following procedure. Briefly, $Bi(NO_3)_3 \cdot 5H_2O$ (1.6866 g) and $Na_2MoO_4 \cdot 2H_2O$ (0.4210 g) were dissolved separately in ethylene glycol (5 mL) under magnetic stirring to obtain the clarified solution. Then the two solution was mixed and added into ethyl alcohol (20 mL) with continuous stirring for 10 min. The mixture was poured in a 50mL Teflon-lined stainless steel autoclave and heated up to 160 °C for 20 h. After cooling down to the room temperature, the Bi_2MoO_6 precipitates were washed and dried at 60 °C.

2.2 Preparation of the Ag₂O/Bi₂MoO₆ composite photocatalysts

Taking the ion ratio $(Ag^+ : Bi^{3+})$ of 1 : 1 for example, 0.3048 g of Bi₂MoO₆ hollow spheres and 1 g of PEG-8000 were dissolved in 50 mL water and stirred for 5 min. Then 0.16987 g of AgNO₃ (\geq 99.8%) was added into the suspension with vigorous stirring for 10 min, and the pH value was adjusted to 12 by dropwise addition of NaOH (4 M) with vigorous stirring for 15 min. The resulting powder with black color was filtered and washed several times with deionized water and finally dried at 60 °C for 2 h. Similarly, pure Ag₂O nanoparticles were synthesized by the same procedure without Bi₂MoO₆. Other composite photocatalysts with Ag⁺ : Bi³⁺= 1 : 2, 2 : 1 and 3 : 1 were prepared by controlling the amount of AgNO₃ (0.08493, 0.33974 and 0.50961 g).

2.3 Characterization

X-ray diffraction (XRD) measurement was carried out by a Rigaku-D/max 2500 diffractometer with Cu-K α radiation ($\lambda = 0.15418$ nm) for phase identification. The morphology, particle size and chemical composition of the product were examined by a scanning electron microscopy (SEM, Hitachi S-4800) equipped with an energy dispersive X-ray spectrometer (EDX). The optical properties of the composites were determined by the UV-vis diffuse reflectance spectra (Cary 500 UV-vis-NIR spectrophotometer) over the wavelength range of 200 nm to 700 nm.

2.4 Photocatalytic activity evaluation

In a typical experiment, 0.02 g of Ag₂O/Bi₂MoO₆ composite was dispersed into 60

mL aqueous solution (0.005 g/L) stirred for 40 min in the darkness in order to reach an adsorption–desorption equilibrium between photocatalysts and the organic dye. Then the solution was exposed to visible light irradiation under vigorous stirring. A 300W Xe lamp (λ >400 nm) was used as the light source with a distance of 10 cm from the suspension. At a given time interval, 4 mL of suspension was taken and immediately centrifuged at 10000 rpm for 15 min. Then the concentration of MO solution without catalyst was determined by the absorption spectra at 446 nm using a specterometer (Perkin-Elmer Lambda-35 UV-vis spectrometer).

3.Results and discussion

3.1 Structure and morphology

The XRD patterns of the Bi₂MoO₆ and Ag₂O/Bi₂MoO₆ composites are shown in Fig. 1. As for pristine Bi₂MoO₆, the as-prepared powder is phase-pure orthorhombic structure, which is coincident with the standard JCPDS cards no. 84-787. After the introduction of Ag₂O, small peaks at ~33° and 38° become detectable and the newly-formed peaks can be perfectly indexed as Ag₂O phase (JCPDS cards no. 3-796). With the increasing of Ag⁺ content, the diffraction peaks of Ag₂O become much more stronger, indicating the increasing of Ag₂O deposition on Bi₂MoO₆ surface.

The morphology of the Bi_2MoO_6 and Ag_2O/Bi_2MoO_6 composites are shown in Fig. S1. The pure Bi_2MoO_6 in Fig. S1a exhibits a hierarchical sphere superstructure composed of many interleaving nanoflakes. For the Ag_2O/Bi_2MoO_6 composite, the spherical morphology was kept and lots of Ag_2O nanoparticles are sparsely deposited on the surface of Bi_2MoO_6 , as shown in Fig. S1b. In order to investigate the detailed surface composition, $Ag_2O/Bi_2MoO_6(1:1)$ was taken for energy dispersive X-ray spectroscopy (EDX), as shown in Fig. 2. The EDX-mappings demonstrate that Ag element is relatively uniformly distributed on the sphere, which also indicates the even deposition of Ag_2O on Bi_2MoO_6 sphere, in spite of several large Ag_2O nanoparticles.

3.2 Optical absorption property

The optical absorption properties are studied by the UV-vis DRS and typical absorption spectra are shown in Fig. 3. Obviously, Bi_2MoO_6 microspheres exhibit a sharp absorption edge located at about 423 nm. As for pure Ag₂O, a strong absorption band from the UV to visible light was observed. In comparison to Bi_2MoO_6 microspheres, the absorption of Ag₂O/Bi₂MoO₆(1:1) presents a slightly red-shifts at ~518 nm, revealing the absorption ability was greatly enhanced by the introduction of Ag₂O nanophase.

The band gap energy (E_g) of the composite plays a significant role in determining the photocatalytic performance. From the absorption spectra, the E_g of sample can be determined by the formula of $\alpha hv = A(hv - E_g)^n$, where α is absorption coeffcient, v is light frequency, A is proportionality constant [23]. E_g values of the pure Bi₂MoO₆ and Ag₂O/Bi₂MoO₆(1:1) composites are estimated as 2.78 and 1.94 eV, respectively. [24] The Ag₂O/Bi₂MoO₆(1:1) composites with a wide optical-response range are expected to show a better photocatalytic property than that of the Bi₂MoO₆.

3.3 Photocatalytic activity and the recycling performance

The photocatalytic activities of the Ag₂O/Bi₂MoO₆ composites with different ion ratios were estimated via photodegradation of MO under visible light irradiation (Fig.4). Bi₂MoO₆, Ag₂O and Ag₂O/Bi₂MoO₆ composites were all examined for comparison under the same testing condition. It can be seen that both Ag₂O and Bi₂MoO₆ present very weak photocatalytic activity. On the other hand, the photocatalytic activity of the Ag_2O/Bi_2MoO_6 composites show an obvious enhancing with the increase of Ag : Bi ratio from 1:2 to 3:1. As the ratio of Ag : Bi reaches at 1:1, the Ag₂O/Bi₂MoO₆ composite performed the best photocatalytic activity among all samples and the degradation rate is about 88% under visible-light irradiation in 80 min. According to the Langmuir-Hinshelwood (L-H) kinetics model, the photochemical reaction is a pseudo-first-order reaction and in line with the kinetics $\ln(C_0/C_t) = kt$, where C_0 is the initial concentration and C_t is the concentration at time t. The reaction rate constant k can be calculated and the results of Bi_2MoO_6 , Ag₂O/Bi₂MoO₆(1:1), (1:2), (2:1), (3:1) and Ag₂O are estimated to be 0.0001, 0.0257, 0.01694, 0.02029, 0.01499 and 0.0064 min^{-1} , respectively. The results show that the degradation rate of MO is dependent on the amount of Ag₂O loading and the best performance is obtained by $Ag_2O/Bi_2MoO_6(1:1)$.

The recycling usage of photocatalyst is an important criteria for the practical application of waste water purification. To investigate the stability of photocatalytic activity on $Ag_2O/Bi_2MoO_6(1:1)$ composite under visible light irradiation, the same samples are repeatedly used for five times after the separation via membrane filtration. The XPS spectra of the $Ag_2O/Bi_2MoO_6(1:1)$ composite after the photodegradation of

MO dye shows that Ag peak was observed, indicating the Ag^+ was partially reduced by the photogenerated electrons (Fig. S2). The recycling results (Fig. 5) show that after five cycling runs, the catalysts can also remains good activity, confirming that the $Ag_2O/Bi_2MoO_6(1:1)$ composite has good stability in activity and is easily to be used for recycling.

3.4 The mechanism of the photocatalytic decomposition of MO dyes

To further study the photocatalytic mechanism and identify the reactive species $(h^+, \cdot O_2^- \text{ or } \cdot OH)$ in decolorizing MO process over the Ag₂O/Bi₂MoO₆ composite, different scavengers were added during the photocatalytic process. In this study, ethylenediaminetetraacetate (EDTA), tert butyl alcohol (TBA) [25] and N₂ were respectively used as holes, hydroxyl radicals and superoxide radicals scavengers and their effects on the photocatalytic degradation of MO are shown Fig. 6. After bubbling N₂ in the photocatalytic system, the activity of catalyst was slightly quenched by the removal of O₂, indicating $\cdot O_2^-$ species take part in the photodegradation processes. While, as for the addition of TBA (\cdot OH quencher), the degrading rate of MO was obviously depressed, revealing the \cdot OH species are much more active than $\cdot O_2^-$ in the photodegradation process. Moreover, a serious quenching effect was observed after the adding of EDTA (h⁺ quencher), indicating holes play the dominate role in MO degradation. Thus, the effective inhibition of the recombination between electrons and holes would probably increased the photocatalytic activity.

On the basis of the above results, a possible mechanism for the photocatalytic degradation of MO by Ag_2O/Bi_2MoO_6 composites under the visible-light irradiation is

proposed (Scheme 1). When Bi_2MoO_6 complexed with Ag_2O , the Fermi energy levels would become balanced. And also both Bi_2MoO_6 and Ag_2O could be excited and corresponding photo-induced electron-hole pairs are generated (Eqs. 1-2).[26] The electrons on the CB of Ag_2O would be transferred to the CB of Bi_2MoO_6 according to the energy difference. Then, the accumulated photo-induced electrons on the CB of Bi_2MoO_6 would react with oxygen molecules on the surface and generate oxygen radicals • O_2^- (Eqs. 3). Considering the results of scavengers tests, it can be estimated that a small number of • O_2^- species are generated in the photocatalysis process. Meanwhile, the important role of holes can be observed in Fig. 6. The photo-induced holes located on the VB of Bi_2MoO_6 can be easily transferred onto the VB of Ag_2O inhibiting the recombination process. Further reactions would take place between holes and OH⁻, which can generate • OH (Eqs. 4) by the oxidation reaction towards the decomposion of MO dyes (Eqs. 5). Moreover, the dye also can be degraded through a direct hole oxidation reaction by holes (Eqs. 5).

$$Bi_2MoO_6 + h\nu \rightarrow Bi_2MoO_6(h^+) + e^-$$
(1)

$$Ag_2O + h\nu \rightarrow Ag_2O(h^+) + e^-$$
 (2)

$$e^{-} + O_2 \rightarrow \bullet O_2^{-}$$
(3)

$$h^+ + OH^- \rightarrow \bullet OH$$
 (4)

$$MO + h^{+} / \bullet OH / \bullet O_{2}^{-} \rightarrow degraded \ product \tag{5}$$

4. Conclusion

In summary, Ag₂O nanoparticles were successfully introduced on Bi₂MoO₆ the

surface of hierarchical microspheres through a chemical precipitation method. The formation of Ag_2O/Bi_2MoO_6 composites and the deposition of Ag_2O nanoparticles on Bi_2MoO_6 surface were confirmed by combined XRD, SEM and EDX mapping analysis. Ag_2O/Bi_2MoO_6 composites showed improved visible-light activity than that of Bi_2MoO_6 towards photocatalytic degradation of MO dye, and the best performance was obtained by $Ag_2O/Bi_2MoO_6(1:1)$. Scavenger quenching results revealed that holes play a dominate role in the photodegradation process. Our study demonstrates that Ag_2O decoration is very effective for the improvement of photo-catalytic activity of Bi_2MoO_6 , which may also apply to other photocatalysts.

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Fig. 1 XRD patterns of Bi_2MoO_6 and Ag_2O/Bi_2MoO_6 with different Ag to Bi ratios.



Scheme 1 Schematic illustration of the charge transfer pathway during the MO degradation process over Ag_2O/Bi_2MoO_6 under visible light irradiation



Fig. 2 (a) The SEM of Ag_2O/Bi_2MoO_6 and elemental distribution maps for (b) Ag, (c) Bi, (d) Mo, (e) O.



Fig. 3 (a) UV-visible diffuse reflectance spectra of the pure Bi_2MoO_6 , Ag_2O and $Ag_2O/Bi_2MoO_6(1:1)$ composite materials with different reaction time, (b) the estimated band gap energies of samples.



Fig. 4 (a) Photocatalytic degradation of MO over the Ag_2O/Bi_2MoO_6 composites with

different ion ratios of Ag and Bi under visible light.



Fig. 5 Cycling runs for the photodegradation of MO in the presence of Ag_2O/Bi_2MoO_6

(1:1) composite under visible light irradiation.



Fig. 6 Effects of EDTA, TBA and N_2 on the decomposition of MO in the presence of

Ag₂O/Bi₂MoO₆(1:1).

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- The Ag₂O/Bi₂MoO₆ composites were synthesized via a coprecipitation method.
- The photocatalytic activities of the composites with various weight ratio were evaluated using the degradation of methyl orange (MO) under visible light irradiation
- The Ag₂O/Bi₂MoO₆ composites exhibited enhanced photocatalytic performance.

