



Silver-decorated orthophosphate@bismuth molybdate heterostructure: An efficient photocatalyst with two visible-light active components

Mingyi Zhang, Lu Li, Ying Liu, Lingling Xu, Xitian Zhang*

Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of Physics and Electronic Engineering, Harbin Normal University, Harbin 150025, PR China



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ABSTRACT

In this paper, decorating Ag₃PO₄/Bi₂MoO₆ heterostructures with uniformly dispersed ultrafine Ag nanoparticles are obtained by a combination of solvothermal technique, deposition–precipitation method and in situ photoreduction process. Two visible-light active components (Ag₃PO₄, Bi₂MoO₆) and the electron-transfer system (Ag) are spatially fixed in this heterostructures system. The photocatalytic studies revealed that the heterostructures system exhibits enhanced photocatalytic activity than the Bi₂MoO₆ and Ag₃PO₄/Bi₂MoO₆ heterostructures under visible light. The enhanced photocatalytic activity can be attributed to the effective separation of photogenerated carriers driven by the matching band potentials between Ag₃PO₄ and Bi₂MoO₆, as well as the good electron trapping role of Ag nanoparticles in situ formed on the surfaces of Ag₃PO₄ particles during the photocatalytic reaction.

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1. Introduction

During the past decades, advances in heterogeneous photocatalysis have received considerable attention focused on the viewpoint of environment pollution and energy shortage. To date, the semiconductor TiO₂ has undoubtedly proven to be one of the most excellent photocatalysts for the oxidative decomposition of many organic compounds [1–3]. Unfortunately, anatase TiO₂ can only be excited by ultraviolet (UV) radiation ($\lambda < 400$ nm) because of its large band gap energy of 3.2 eV [4]. To utilize solar energy more effectively, the development of efficient visible-light-driven (VLD) photocatalysts has attracted worldwide attention. As we know, essentially two main strategies have been used for the preparation of VLD photocatalysts until now: (1) extend the photoresponse of anatase TiO₂ to the visible region by doping of a non-metal or a transition metal such as TiO_{2-x}N_x, TiO_{2-x}S_x and Fe/TiO₂ [5–7]. However, this way is not so effective because dopants will also serve as a sites for electron–hole recombination to decrease photocatalytic activity. (2) Exploiting novel VLD photocatalysts such as simple/complex oxides and sulfides [8–15]. Although efforts have been made to prepare many kinds of single-component VLD

photocatalysts, its practical application is still limited because of a bottleneck caused by the rapid recombination of photoinduced electrons and holes.

Recently, the coupling of semiconductors photocatalysts with metal and/or other semiconductors has been reported to greatly improve their photocatalytic performances. For example, the deposition of a metal, such as Ag and Au, on the surface of semiconductors photocatalysts highly improved its photocatalytic efficiency through the Schottky barrier conduction band electron trapping and surface plasmon resonance [16–18]. In our previous work, we have prepared some bicomponent heterostructure VLD photocatalysts, such as TNCuPC/TiO₂, ZnO/ZnS, Bi₂MoO₆/ZnTiO₃, etc. [19–26]. It has been proven that those heterostructure display the excellent photocatalytic performance because of the extended absorption in the visible light region resulting from the VLD component and the good separation of photoexcited electrons and holes. Teng et al. prepared ternary Ag–Ag₃PO₄–TiO₂ as VLD photocatalyst for the decomposition of 2-chlorophenol under visible light irradiation, where Ag₃PO₄ is the only VLD component and the metal Ag specie on the surface is probably contributing to enhancing the electron–hole separation and interfacial charge transfer [27]. These works imply that the development of better VLD photocatalysts depends on a wide range of visible-light photo-responses and highly effective interfacial charge transfers.

* Corresponding author. Tel.: +86 451 88060349; fax: +86 451 88060349.
E-mail address: xtzhangzhang@hotmail.com (X. Zhang).

In our present work, in order to broaden the range of visible-light photo-response and improve the separation of photoexcited electrons and holes simultaneously, we construct the ternary Ag/Ag₃PO₄/Bi₂MoO₆ heterostructure system, where both Ag₃PO₄ and Bi₂MoO₆ are photochemical systems that can be excited by visible light, while Ag is used as the electron-transfer system. This tricomponent heterostructure system with double visible-light active component exhibited higher catalytic activity than the bicomponent heterojunction system of Ag₃PO₄/Bi₂MoO₆, because of their high separation efficiency of photoinduced electro-hole pairs caused by the photosynergistic effect between the three components.

2. Experimental

2.1. Fabrication of Bi₂MoO₆

First, the Bi₂MoO₆ was prepared by the solvothermal method [28]. In a typical case, 0.05 mol of Bi(NO₃)₃·5H₂O and 0.025 mol Na₂MoO₄·2H₂O was dissolved in 5 mL of ethylene glycol (EG) under magnetic stirring, respectively. The two solutions were mixed together, and then, 30 mL ethanol was slowly added into the above solution. The mixture was stirred at room temperature for 30 min until the solution presented the homogeneous phase and then transferred into the 50 mL Teflon-lined stainless steel autoclave and kept at 160 °C for 24 h. Finally, the precipitate was centrifuged, washed with ethanol and deionized water for three times until there were no other possible impurities in the product. The resulting product was dried at 60 °C for 2 h and denoted as BMO.

Then, Ag/Ag₃PO₄/Bi₂MoO₆ composites were prepared by deposition-precipitation and photoreduction process. Briefly, 1.0 g Bi₂MoO₆ was added to 40 mL of distilled water, and the suspension was stirred magnetically for 30 min. Then, 20 mL AgNO₃ aqueous solution (15 mM) was added into the suspension and stirred for another 30 min. After that, a certain amount of NH₃·H₂O (2 wt% NH₃) was added to make sure that Ag⁺ reacts with NH₃. Then, 20 mL of Na₂HPO₄·12H₂O aqueous solution (5 mM) was added dropwise into the suspension, and stirred for 60 min. The resulting suspensions were stirred for 2 h. All the above processes were carried out at ambient temperature. The products were filtered, washed by deionized water, and then dried at 70 °C for 12 h. The as-fabricated sample was denoted as APO/BMO.

Finally, the Ag₃PO₄/Bi₂MoO₆ sample was irradiated using a 300 W Xe lamp for 3 min to convert some Ag⁺ ions on the surfaces of Ag₃PO₄/Bi₂MoO₆ to Ag⁰ species. The solution color changed to dark brown, indicating that silver nanoparticles appeared and the ternary Ag/Ag₃PO₄/Bi₂MoO₆ photocatalysts were prepared. The as-fabricated sample was denoted as Ag/APO/BMO. For comparison, Ag₃PO₄ samples were also prepared by a similar process in the absence of Bi₂MoO₆, denoted as APO.

2.2. Characterization

A field emission scanning electron microscope (FE-SEM; SU-70, Hitachi, Japan) equipped with energy dispersive X-ray (EDX) spectrometer was used to observe the morphology of the samples. The crystalline structures of the samples are characterized by X-ray powder diffraction (XRD, D/max2600, Rigaku, Japan) and transmission electron microscopy (TEM; FEI, Tecnai TF20). UV-vis diffuse reflectance spectra (DRS) of the samples are obtained by using a UV-vis spectrometer (PerkinElmer, Lambda 850) used polytetrafluoroethylene (PTFE) as a reference and is converted to the absorbance by the Kubelka-Munk method. Fourier transform infrared (FT-IR) spectra are obtained on Magna, a 560 FT-IR spectrometer with a solution of 1 cm⁻¹. X-ray photoelectron spec-

troscopy (XPS) measurement was performed on a VG-ESCALAB LKII instrument with Mg KR ADES ($h\nu = 1253.6$ eV) source at a residual gas pressure of below 1×10^{-8} Pa.

The photocurrent was conducted by using an electrochemical analyzer (CHI660E, ChenHua Instruments, Shanghai, China) with a standard three-electrode configuration, which employed a Pt wire as a counter electrode, a saturated calomel electrode as a reference electrode and fluorine-doped tin oxide (FTO) as working electrode. 10 mg of sample powder was dispersed into 2 mL of *N,N*-dimethylformamide under ultrasonication for 10 min to obtain slurries. The as-prepared slurries were spread onto the surface of FTO glasses to obtain sample films with the region of 1×1 cm. These as-prepared FTO glasses electrodes were dried at 100 °C for 60 min under ambient conditions to improve adhesion. The 50 mL 0.5 M Na₂SO₄ (pH 6.8) was used as the electrolyte solution. A 300 W Xe lamp with a 420 nm cut-off filter was employed as a visible light photosource.

2.3. Photocatalytic test

The degradation of rhodamine (RhB) was carried out in a 200 mL beaker containing 100 mL RB with a concentration of 1×10^{-5} mol/L and 50 mg of the as-prepared Ag/Ag₃PO₄/Bi₂MoO₆ photocatalysts with vigorous magnetic stirring at room temperature under visible light irradiation of a 300 W Xe lamp with a cut-off glass filter transmitting $\lambda > 420$ nm. The solution was stirred in the dark for 30 min to obtain a good dispersion and reach adsorption-desorption equilibrium between the organic molecules and the catalyst surface. The concentration of RhB was measured by UV-vis spectrophotometer at given intervals during the degradation process of RhB.

3. Results and discussion

The X-ray diffraction (XRD) patterns of the as-prepared pure Bi₂MoO₆, Ag₃PO₄/Bi₂MoO₆ and Ag/Ag₃PO₄/Bi₂MoO₆ are shown in Fig. 1. The XRD pattern of the Bi₂MoO₆ could be indexed well with the pure phase of monoclinic Bi₂MoO₆ (JCPDC no. 76-2388). Comparison with the pure Bi₂MoO₆, it shows that the Ag₃PO₄/Bi₂MoO₆ heterostructure is well crystallized and all the diffraction peaks can well be indexed to the monoclinic Bi₂MoO₆ and cubic structure of Ag₃PO₄ (JCPDS 06-0505), respectively. No characteristic peaks for impurities, suggesting that the heterostructure is composed of Ag₃PO₄ and Bi₂MoO₆. After an in situ reduction processing,

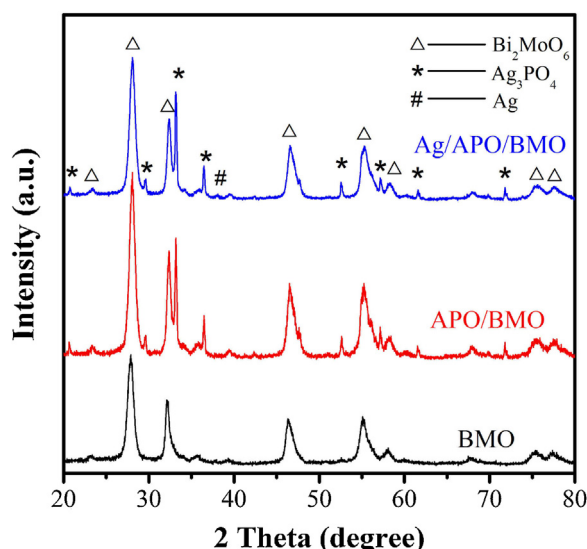


Fig. 1. XRD diffraction patterns taken from the BMO, APO/BMO and Ag/APO/BMO.

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