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Visible-light-driven Ag_2MoO_4/Ag_3PO_4 composites with enhanced photocatalytic activity

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ABSTRACT

Novel Ag_2MoO_4/Ag_3PO_4 (AgMoP) composites were synthesized by a facile precipitation method. The composition, structures and optical properties of as-prepared catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), UV–vis diffused reflectance spectra (UV–vis DRS). The photocatalytic activities were evaluated by the degradation of rhodamine B (RhB), methylene blue (MB) and methyl orange (MO) under visible light irradiation ($\lambda \geq 420$ nm). 5% AgMoP composite showed the best photocatalytic performance, and its degradation rate constants were 2.8, 2.4, 4.6 times higher than pure Ag_3PO_4 for the degradation of RhB, MB, MO, respectively. Particularly, its photocatalytic property can be maintained even after four degradation cycles. Additionally, based on UV–vis DRS and active species trapping, the photocatalytic mechanism for the enhanced photocatalytic performance of Ag_2MoO_4/Ag_3PO_4 was proposed.

1. Introduction

Semiconductor photocatalysis technology can serve as a promising, cost-effective and environmentally friendly approach to cope with the environment pollution and energy crises [1–4]. In order to achieve the prospective application of photocatalysis, it is imperative to design and prepare efficient visible-light-driven photocatalysts. In general, there are three basic principles for the development of high-efficient photocatalysts: (i) the high utilization of visible light; (ii) efficient separation and migration of electron-hole pairs; (iii) suitable redox potential to trigger the photocatalytic reaction [5–8]. On the basis of these principles, the fabrication of novel photocatalysts with high visible-light activity has been intensively developed in recent years.

To date, Ag-based photocatalysts, such as AgX (X = Cl, Br, I), Ag_2S, Ag_2O, Ag_2CO_3 and Ag_3PO_4, have been extensively studied due to their excellent photocatalytic properties under visible light illumination [9]. Among these photocatalysts, Ag_3PO_4 has been reported as a promising photocatalyst for photooxidation of water and decomposition of organic pollutants due to its excellent photooxidative capabilities with quantum efficiency up to 90% at wavelengths longer than 420 nm [10,11]. According to first-principles calculations, the superior photocatalytic performance of Ag_3PO_4 can be ascribed to the highly dispersive conduction band and PO_4^{3-} electrostatic induction, which facilitates the separation of photogenerated electrons and holes [12]. Although pure Ag_3PO_4 displays highly efficient photocatalytic performance, the inevitable photodecomposition and inferior structural stability restrain the practical application of Ag_3PO_4. Thus, many attempts have been made to solve these problems, including morphological modulation, ion doping and heterojunction fabrication [13–15]. Among them, the semiconductor heterojunction structure is regarded as a direct and simple strategy to design the efficient and stable Ag_3PO_4-based photocatalysts. Generally, the heterojunction systems composed of different semiconductors with suitable band structures are in favor of achieving the efficient separation of photogenerated electron-hole pairs, and thus indeed benefit the photocatalytic activity and stability [15,16]. Accordingly, various composite photocatalysts have been developed to overcome the shortcomings of Ag_3PO_4, such as AgX/Ag_3PO_4 (X = Cl, Br, I), Co_3O_4/Ag_3PO_4, MoS_2/Ag_3PO_4, Ag_3PO_4/grapheme, Ag_3PO_4@mpg-C_3N_4 and so on [17–21].

Silver molybdate (Ag_2MoO_4) is another important semiconductor with controllable morphology structures, including nanoparticles, cube-like, flower-like, and wire-like nanostructures [22–25]. At present, it has attracted intensive attentions in the field of gas-sensing and photoswitch devices, photoluminescence, antibacterial materials due to the easily controllable morphology

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[25–27]. However, it is worth noting that pure Ag_2MoO_4 semiconductor suffers from the low utilization of visible light because of its wide band gap energy, which restricts its application in photocatalysis [28]. Recently, some efforts have been devoted to design Ag_2MoO_4-based composites to improve the photocatalytic performance of Ag_2MoO_4 under visible light illumination. For example, Bai et al. [29] synthesized Ag@Ag_2MoO_4-AgBr composite through in-situ anion-exchange method. Compared with pure AgBr and Ag_2MoO_4, the composite exhibited high photocatalytic activity and stability in the degradation of various organic dyes under visible light irradiation. Li et al. [23] prepared the cube-like Ag-Ag_2MoO_4 composite by a microwave-assisted hydrothermal process. The catalyst showed good visible-light-responsive photocatalytic activity since the localized surface plasmon resonance of Ag^0 particles can promote the absorption of visible light. Based on the analyses, coupling Ag_2MoO_4 with Ag_3PO_4 could be an enormous potential to enhance the photocatalytic activity and stability of individual component. To the best of our knowledge, Ag_2MoO_4/Ag_3PO_4 composite has not been reported previously.

In the present work, we developed a novel Ag_2MoO_4/Ag_3PO_4 composite photocatalyst by a facile precipitation method. The structures, morphologies and optical properties have been discussed in detail. Three different kinds of organic dyes, rhodamine B (RhB), methylene blue (MB) and methyl orange (MO) were chosen as model pollutants to evaluate the photocatalytic performance of as-prepared catalysts under visible light irradiation. The experimental results indicated that the Ag_2MoO_4/Ag_3PO_4 composite exhibited much higher photocatalytic activity and stability than pure Ag_3PO_4. In addition, the possible photodegradation mechanism of Ag_2MoO_4/Ag_3PO_4 was also discussed.

2. Experimental

2.1. Catalyst preparation

All reagents were of analytical grade and used without further purification. Ag_2MoO_4 was prepared by a simple precipitation method. Na_2MoO_4 solution (0.025 M, 40 mL) was added drop by drop into $AgNO_3$ solution (0.05 M, 40 mL) with constant stirring. After stirring for 4 h in the dark, the obtained white precipitate of Ag_2MoO_4 was separated by centrifugation, washed with deionized water and ethanol for several times, then dried at 60 °C for 6 h.

The preparation of Ag_2MoO_4/Ag_3PO_4 composite was also carried out through a facile precipitation process. In a typical procedure, 2 mmol $AgNO_3$ was dissolved in 40 mL of distilled water with constant stirring. A certain amount of $Na_2MoO_4{\cdot}2H_2O$ was first added into the above solution to generate a certain white precipitate. Then, 40 mL of Na_2HPO_4 solution (0.0167 M) was added drop by drop into the above suspension. After continually stirring for 4 h in the dark, the obtained yellow precipitate of Ag_2MoO_4/Ag_3PO_4 (AgMoP) was separated by centrifugation, washed with deionized water and ethanol for several times, then dried at 60 °C for 6 h. To investigate the effect of Ag_2MoO_4 contents, three AgMoP samples were prepared by adjusting the added amount of $Na_2MoO_4{\cdot}2H_2O$. The actual weight percentages of Ag_2MoO_4 in Ag_3PO_4 were 2.1 wt%, 5.4 wt% and 7.8 wt%, respectively, according to the analyses of inductively coupled plasma-atomic emission spectroscopy (ICP-AES). For convenience, the different Ag_2MoO_4/Ag_3PO_4 composites were denoted as 2, 5, 8% AgMoP. In addition, pure Ag_3PO_4 was prepared by similar procedure without the addition of $Na_2MoO_4{\cdot}2H_2O$.

2.2. Characterization

The as-prepared samples were characterized by a X-ray diffraction (XRD; Bruker D8 Advance diffractometer) with Cu-Kα radiation ($K\alpha_1$ = 1.5406 Å, $K\alpha_2$ = 1.5444 Å) in the range of $2\theta = 10°–80°$ at room temperature. X-ray photoelectron spectroscopy (XPS) analyses were obtained by a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer with Al Kα radiation. The actual contents of Ag_2MoO_4 in the AgMoP composites were determined by ICP-AES on an Agilent 725ES instrument. The surface morphologies of photocatalysts were observed by a field-emission scanning electron microscopy (FE-FEM, NanoSEM 450) equipped with an energy X-ray dispersive spectrometer (EDS). The Brunauer-Emmett-Teller (BET) specific surface areas of the prepared samples were analyzed by nitrogen adsorption/desorption isotherms at liquid nitrogen temperature with Micromeritics ASAP 2010 instrument. UV–Vis diffuse reflectance spectra (DRS) were performed on a Shimadzu UV-2450 spectrophotometer in a wavelength range of 200–800 nm, using $BaSO_4$ as a reference.

2.3. Photocatalytic activity test

The photocatalytic activities of as-prepared photocatalysts were tested by the degradation of RhB, MB and MO solutions under visible light irradiation ($\lambda \geq 420$ nm). A 350 W xenon lamp with a 420 nm ultraviolet filter was used as the visible light source. In a typical experiment, 50 mg of photocatalyst was added into 100 mL of 10 mg/L dye aqueous solution and then ultrasonicated for 10 min. The suspension liquid was magnetically stirred in dark for 30 min to establish the adsorption-desorption equilibrium between the photocatalyst and dye molecules prior to light irradiation. During illumination, 4.0 mL of suspension was collected at the regular intervals and centrifuged to remove the catalyst. The residual concentration of dye solutions was analyzed via a PerkinElmer Lamda 35 UV–Vis spectrophotometer.

3. Results and discussion

3.1. Catalyst characterization

The crystal structures of as-prepared catalysts were investigated by XRD analyses, as shown in Fig. 1. The sharp and strong diffraction peaks of pure Ag_3PO_4 (Fig. 1a) can be readily indexed to the body-centered cubic structure of Ag_3PO_4 (JCPDS No. 06-0505) with high crystallinity. For pure Ag_2MoO_4 (Fig. 1e), the diffraction patterns can be assigned to the cubic phase of Ag_2MoO_4 crystal (JCPDS No. 08-

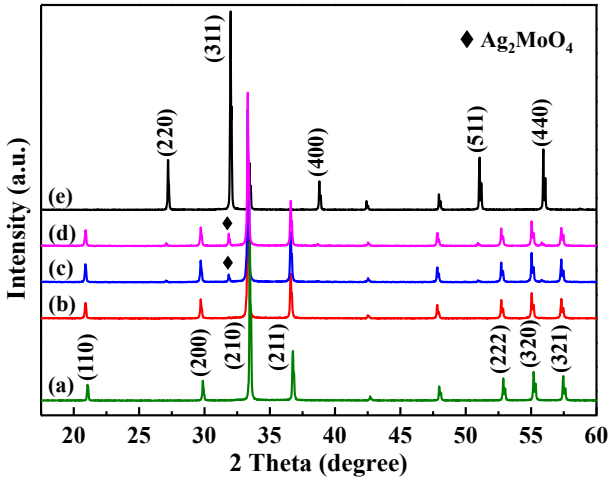

Fig. 1. XRD patterns of (a) pure Ag_3PO_4, (b) 2% AgMoP, (c) 5% AgMoP, (d) 8% AgMoP, and (e) pure Ag_2MoO_4 catalysts.