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Photochemical synthesis and enhanced photocatalytic activity of $MnO_x/BiPO_4$ heterojunction

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Abstract: Monoclinic $BiPO_4$ with rod-like shape was prepared via a CTAB-assisted hydrothermal route. MnO_x nanoparticles were loaded on the surfaces of $BiPO_4$ rods by a photo-deposition process to form $MnO_x/BiPO_4$ heterojunctions. The as-prepared samples were characterized by XRD, SEM, TEM, XPS, FL, and UV-Vis diffuse reflectance measurements. The results showed that MnO_x nanoparticles were strongly anchored to the surfaces of $BiPO_4$ rods when the mole ratio of Mn to Bi was controlled at a low level, forming $MnO_x/BiPO_4$ heterojunctions with effective and sound interfaces. The $MnO_x/BiPO_4$ heterojunctions exhibited higher photoactivity than pristine $BiPO_4$ for photodegradation of methyl blue under UV irradiation, which could be attributed to the efficient charge transfer at the heterojunction interfaces. The higher light absorption ability of $MnO_x/BiPO_4$ in the range of 300−420 nm compared with pristine $BiPO_4$ was also responsible for the enhanced photocatalytic activities of $MnO_x/BiPO_4$ heterojunctions.
Key words: $BiPO_4$; photocatalysis; hydrothermal method; MnO_x; heterojunction; photodeposition

1 Introduction

Semiconductor photocatalysis is expected to be a very promising technology to address problems in environmental remediation and energy utilization [1,2]. Recently, many Bi-based semiconductors, such as $BiVO_4$ [3], Bi_2MoO_6 [4], $BiWO_6$ [5,6], and $BiPO_4$ [7], have been applied as photocatalysts. Among these photocatalysts, $BiPO_4$ has attracted more and more attention. $BiPO_4$ mainly exists in three crystalline phases: monoclinic structure, monoclinic monazite structure, and hexagonal structure. Among them, the monoclinic $BiPO_4$ shows the best photocatalytic activity due to its high photocatalytic activity, excellent absorption of UV, strong oxidation ability and chemical stability in aqueous solution, while that of the hexagonal $BiPO_4$ is the worst [7]. It was reported that the photocatalytic activity of monoclinic $BiPO_4$ is much better than that of Degussa P25 TiO_2 [8]. However, monoclinic $BiPO_4$ still suffers from its wide bandgap (4.2 eV), poor adsorptive performance, and large size [9], which limits the utilization of visible light and the separation of photoinduced charge carriers, hindering further improvement of photocatalytic activity. Therefore, it is highly necessary to develop an effective method to solve those problems.

Combining with a cocatalyst, such as a noble metal or another semiconductor, to form heterojunction is an effective way to broaden the light absorption range and promote the separation of photoinduced charge carriers of a photocatalyst. Noble metals, such as Ag, Pt, and Au, are deriving-electron type cocatalysts, while some semiconductors, such as MnO_x, PbO_x, and Ag_3PO_4, are deriving-hole-type cocatalysts [9−11]. It was reported that both Ag and Ag_3PO_4 could enhance the separation efficiency of the photoinduced holes and electrons of $BiPO_4$, improving the photocatalytic activity [11,12]. MnO_x is a photocatalyst with high activity owe to its small particle size, strong adsorptivity, and excellent absorption of visible light [10]. So, anchoring MnO_x on the surface of $BiPO_4$ to form a stable heterojunction may cover the shortage of $BiPO_4$. In addition, photo-induced holes are the main active species of $BiPO_4$ for dye degradation [10]. Therefore, deriving-hole-type MnO_x may effectively improve the separation efficiency of the

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photoinduced charge carriers of $BiPO_4$. However, to our best knowledge, there are no reports about deposition of MnO_x on $BiPO_4$.

Herein, monoclinic $BiPO_4$ rods were prepared via a hydrothermal approach, MnO_x nanoparticles were then loaded on the surface of $BiPO_4$ rods by a photo-deposition process to form a novel $MnO_x/BiPO_4$ heterojunctions. The photoactivities of the as-prepared samples were evaluated by degradation of methyl blue (MB) under UV irradiation.

2 Experimental

2.1 Preparation of $BiPO_4$

All reagents were of AR grades and used without further purification. Deionized water was used in all experiments. $BiPO_4$ was synthesized as follows: 1.15 g of $Na_3PO_4·12H_2O$ and 0.25 g of CTAB were dissolved into 15 mL of deionized water, while 1.46 g of $Bi(NO_3)_3·5H_2O$ was dissolved into 15 mL of HNO_3 solution (1 mol/L). The two solutions were then mixed up. NaOH solution (2 mol/L) was dropwise added to tailor the pH of the mixture under magnetic stirring. The obtained suspension was fixed to 40 mL by adding deionized water. After being stirred for 30 min, the suspension was transferred into a 50 mL Teflon-lined autoclave stainless steel autoclave. The autoclave was heated at 140 °C for 15 h, and then cooled to room temperature naturally. The product was collected, washed with deionized water and absolute alcohol three times, respectively, and finally dried at 80 °C for 20 h to obtain $BiPO_4$ powders.

2.2 Preparation of $MnO_x/BiPO_4$ heterojunctions

$MnO_x/BiPO_4$ heterojunctions were synthesized by photo-deposition. 1 g of $BiPO_4$ was ultrasonically dispersed into 100 mL deionized water, then a certain amount of $MnSO_4·H_2O$ was dissolved into the suspension (the mole ratios of Mn to Bi were controlled at 0.05, 0.08, and 0.15, respectively). The mixture was magnetically stirred for 24 h in the dark, and then irradiated for 3 h under UV light. The product was collected and thoroughly washed with deionized water and ethanol respectively, and finally dried at 80 °C for 20 h to obtain $MnO_x/BiPO_4$ heterojunctions. The as-prepared samples were characterized and confirmed for the Mn to Bi mole ratio via atomic absorption spectroscopy (AAS) using Chem. Tech Analytical 2000 spectrophotometer.

2.3 Characterization

The crystalline structure of the sample was analyzed by a Rigaku D/Max 2500 powder diffractometer (XRD) with Cu K_α radiation (λ=1.5406 Å). The morphology of the as-prepared samples was investigated by transmission electron microscopy (TEM, Philips Tecnai20G2S-TWIN) and environmental scanning electron microscope (ESEM, FEI QUANTA 250). X-ray photoelectron spectroscopy (XPS) data of the samples were determined with a K-Alpha 1063 electron spectrometer from Thermo Fisher Scientific using 72 W Al K_α radiation. UV-Vis diffuse reflectance spectra were measured with a Specord 200 UV spectrophotometer. Photoluminescence spectroscopy analysis (PL) of the samples was carried out on a Hitachi F−4500 fluorescence spectrophotometer.

2.4 Photocatalytic test

The photocatalytic properties of $MnO_x/BiPO_4$ heterojunctions were assessed by photodegradation of MB aqueous solution under ultraviolet irradiation with a 45 W ultraviolet lamp. 0.2 g of photocatalyst was mixed with 100 mL of 10 mg/L methyl orange aqueous solution. The mixture was ultrasonically dispersed for 10 min and then magnetically stirred in dark for 30 min before commencing the photocatalytic reactions to allow the system to reach an adsorption/desorption equilibrium. All photocatalytic reactions were carried out in a laboratory constructed photoreactor. 3 mL of sample solution was taken at given time intervals and separated through centrifugation. The concentrations of MB solution were evaluated by an UNICO UV−2100 spectrophotometer at 660 nm.

3 Results and discussion

3.1 Structure and morphology of $BiPO_4$

Figure 1 shows the XRD patterns of the products prepared at different pH values. It can be found that all the diffraction peaks of the samples prepared at pH 1 and 2 are readily indexed to a pure phase of monoclinic $BiPO_4$ (JCPDS No. 15−0767), while those of the sample prepared at pH 4 are indexed to a pure phase of hexagonal $BiPO_4$ (JCPDS No. 45−1370). The strong and sharp diffraction peaks indicate that these three samples are highly crystalline. When the pH is tailored to 6, the characteristic diffraction peaks corresponding to both monoclinic $BiPO_4$ and hexagonal $BiPO_4$ are found in the XRD pattern, indicating the coexistence of monoclinic $BiPO_4$ and hexagonal $BiPO_4$. Moreover, the diffraction peak intensity decreases obviously compared with that of the other samples. It can be deduced that pH plays a key role in the crystal phases of the products in the present case, and strong acid condition favors the growth of monoclinic $BiPO_4$, which was reported to show the highest photocatalytic activity among the three crystalline phases of $BiPO_4$ [7].

Figures 2(a) and (b) show the SEM images of the