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Controlled synthesis of $Ag_3PO_4/BiVO_4$ composites with enhanced visible-light photocatalytic performance for the degradation of RhB and 2, 4-DCP

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ABSTRACT

$Ag_3PO_4/BiVO_4$ composites were fabricated by in-situ precipitation method. Results showed that $Ag_3PO_4/BiVO_4$ composites exhibited higher photocatalytic activity than that of pure $BiVO_4$ and Ag_3PO_4 sample under visible light irradiation. The effect of Ag_3PO_4:$BiVO_4$ ratio on the photocatalytic activity was systemically studied and the optimum molar ratio of Ag_3PO_4:$BiVO_4$ was 1:5. The $Ag_3PO_4/BiVO_4$-5 exhibited excellent photocatalytic activity for the degradation of Rhodamine B (ca. 92% in 30 min) and 2, 4-dichlorophenol (ca. 84% in 180 min) under visible light irradiation. The enhanced photocatalytic activity could be mainly ascribed to the suitable $Ag_3PO_4/BiVO_4$ heterojunction interface and the smaller particles of Ag_3PO_4 compared to pure Ag_3PO_4 particles which could promote the separation of photoinduced electron-hole pairs. The $Ag_3PO_4/BiVO_4$ composite can significantly reduce the silver consumption compared to the pure Ag_3PO_4. It is worth noting that $Ag_3PO_4/BiVO_4$ composite can act as a high performance and low cost visible-light-driven photocatalyst for environmental remediation.

1. Introduction

Semiconductor photocatalysts have attracted considerable attention for their potential applications in environmental remediation and energy production [1–3]. Among all the semiconductor-based photocatalysts, TiO_2 has become an ideal photocatalyst because of its nontoxicity, higher chemical stability and oxidization features [4,5]. However, TiO_2 can only respond to the UV light due to its wider bandgap (3.2 eV), which restricts its practical application. Therefore, the development of efficient visible-light-driven photocatalysts is becoming more and more attractive and a great deal of effort has been devoted into this research field.

$BiVO_4$ with a bandgap of 2.4 eV has been recognized as one of the visible-light responsive photocatalysts. Many studies have verified that $BiVO_4$ exhibits promising visible light photocatalytic activity in splitting water and decomposing pollutants [6–9]. However, the photocatalytic activity of pure $BiVO_4$ is low owing to the higher recombination rate of photoinduced electron-hole pairs; poor charge transport characteristic and weak surface adsorption property. Therefore, it is desirable to find a more effective way to improve the photocatalytic activity of $BiVO_4$. In recent years, several strategies have been devoted to improving the photocatalytic activity of $BiVO_4$ photocatalyst, such as metal and nonmetal atoms doping [10,11], constructing heterojunction [12–14] and surface modification [15]. Coupling of two semiconductors with variable bandgaps to form heterojunction has been proven to be a feasible approach to enhance the separation efficiency of photo-induced electrons and holes. Many types of heterojunction, e.g. $WO_3/BiVO_4$ [16], $CuO/BiVO_4$ [17], $Bi_2S_3/BiVO_4$ [18], $Co_3O_4/BiVO_4$ [19] and $BiOCl/BiVO_4$ [14] have been successfully fabricated and applied in photocatalysis. In spite of these, it is still necessary to explore suitable semiconductors to couple with $BiVO_4$ and remarkably improve the photocatalytic activity.

In recent years, Ag_3PO_4 has been recognized as a novel promising photocatalyst with excellent visible-light photocatalytic activity [20,21]. It has been proved that the photocatalytic activity of Ag_3PO_4 is significantly higher than that of currently known visible light photocatalysts, for instance, $BiVO_4$, Bi_2WO_6 or N-doped TiO_2. However, it usually suffers from photocorrosion and leaching in aqueous solutions under light irradiation, which limits its extensive utilization. Furthermore, the consumption of a

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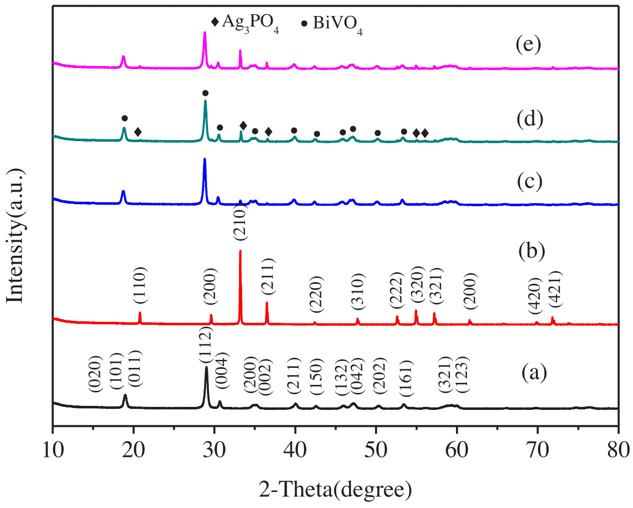

Fig. 1. XRD patterns of the prepared $BiVO_4$ (a), Ag_3PO_4 (b), $Ag_3PO_4/BiVO_4$-10 (c), $Ag_3PO_4/BiVO_4$-5 (d) and $Ag_3PO_4/BiVO_4$-3 (e).

large amount of silver, also strongly limits its practical applications in photocatalysis field [22–24].

Based on the above discussion, Ag_3PO_4 can be considered to be an appropriate sensitizer to improve the photocatalytic activity of $BiVO_4$ under visible light driven by fabricating the $Ag_3PO_4/BiVO_4$ system. Furthermore, reducing the consumption of silver on the basis of higher visible light photocatalytic activity is also a key factor for the practical application of Ag_3PO_4 based photocatalyst. Herein, we report a successful attempt at the fabrication of $Ag_3PO_4/BiVO_4$ composite photocatalysts via an in-situ precipitation method to enhance the photocatalytic performance. The photocatalytic activity of the composite photocatalysts was investigated by the degradation of Rhodamine B (RhB) and 2, 4-dichlorophenol (2, 4-DCP) under visible light irradiation. The effect of Ag_3PO_4 content on the degradation rate of RhB under visible light irradiation ($\lambda > 400$ nm) in the $Ag_3PO_4/BiVO_4$ composites system was investigated. Meanwhile, the possible mechanism for the enhanced photocatalytic activity of $Ag_3PO_4/BiVO_4$ composite photocatalysts was also discussed.

2. Experimental section

2.1. Preparation of $BiVO_4$

The $BiVO_4$ sample was synthesized via a simple hydrothermal method. In a typical procedure, 10 mmol Bi $(NO_3)_3{\cdot}5H_2O$ was fully dissolved in 30 mL solvent (deionizer water: ethylene glycol = 1:1, V/V) with the addition of 3 mL HNO_3 solution (67%) to form solution A. Simultaneously, 10 mmol NH_4VO_3 was fully dissolved in 30 mL the same above solvent with the addition of 2.2 mL ethylenediamine solution in another beaker to form solution B. Then the solution B was slowly dropped into the solution A. After magnetic stirring for 30 min, the suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave to perform hydrothermal process at 160 °C for 16 h. Subsequently, the autoclave was cooled to room temperature naturally. The obtained sample was filtered, washed with deionized water and absolute ethanol for several times and then dried at 80 °C for 12 h in air.

2.2. Preparation of $Ag_3PO_4/BiVO_4$ composite photocatalyst

The $Ag_3PO_4/BiVO_4$ composite photocatalysts were prepared by a simple in-situ precipitation method. In the typical process, 2 mmol as-prepared $BiVO_4$ was dispersed in 50 mL distilled water and the solution was sonicated for 20 min. Then, a certain amount of $AgNO_3$ was added to the above homogeneously dispersed solution under violent stirring to dissolve $AgNO_3$ completely. Subsequently, a stoichiometric calculation amount of $Na_2HPO_4{\cdot}12H_2O$ previously dissolved in 50 mL distilled water was added dropwise into the above solution. Then, the solution was kept stirring violently for 5 h in a dark condition. The obtained sample was filtered, washed with deionized water and absolute ethanol for several times and then dried at 70 °C for 12 h in air. The molar ratio of Ag_3PO_4 to $BiVO_4$ for the $Ag_3PO_4/BiVO_4$ composite photocatalysts is 1:15, 1:10, 1:5, 1:4 and 1:3. We designated the $Ag_3PO_4/BiVO_4$ composite photocatalysts with different molar ratio of Ag_3PO_4 to $BiVO_4$ as $Ag_3PO_4/BiVO_4$-x (x = 15, 10, 5, 4, 3, x represents the molar ratio of Ag_3PO_4 to $BiVO_4$). For comparison, the pure Ag_3PO_4 photocatalyst was prepared under the same condition. The physical mixture sample was prepared by grinded the Ag_3PO_4 and $BiVO_4$ mixture in the agate mortar according to the 1: 5 molar ratio mingle.

2.3. Characterization

The crystal structure of the samples was determined by X-ray diffraction (XRD, Bruker D8 Advance, Germany) using Cu Kα and the scanning range was 10–80° (2θ). The morphologies and microstructures of as-prepared samples were observed by Transmission electron microscopy (TEM, JEOL JEM-2100F, Japan) and scanning electron microscopy (SEM, FEI NOVA NANOSEM-450, America). The structure of the as-fabricated samples was measured by Fourier transform infrared spectrometer using pressed KBr pellets method (FTIR, FTIR-8400S SHIMADZU, Japan). The specific surface areas of the samples were determined by a volumetric adsorption apparatus (ASAP2010M + C, USA). The optical absorption spectra of the samples were recorded by ultraviolet–visible spectrophotometer (UV–vis, SHIMADZU UV-2550, Japan) using $BaSO_4$ as a reference. The photogenerated electron-hole pair separation efficiency of the samples was evaluated by fluorescence spectrophotometer (SHIMADZU RF-5301, Japan).

2.4. Photocatalytic test

Photocatalytic activities of the as-fabricated photocatalysts were evaluated by the degradation of RhB and 2, 4-DCP aqueous

Table 1
The BET surface areas and the reaction rate constant of the samples.

Sample name	Molar ratio of Ag_3PO_4 to $BiVO_4$	BET surface areas ($m^2\,g^{-1}$)	Reaction rate constant (κ, min^{-1})
$BiVO_4$	–	6.30	0.0098
Ag_3PO_4	–	0.39	0.055
$Ag_3PO_4/BiVO_4$-10	1:10	4.25	0.052
$Ag_3PO_4/BiVO_4$-5	1:5	4.92	0.087
$Ag_3PO_4/BiVO_4$-3	1:3	4.65	0.098