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Ultra-low loading of Ag_3PO_4 on hierarchical In_2S_3 microspheres to improve the photocatalytic performance: The cocatalytic effect of Ag and Ag_3PO_4

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ABSTRACT

Ag_3PO_4/In_2S_3 composite photocatalysts with ultra–low loading of Ag_3PO_4 (0.017 ~ 4.89 wt %) were prepared by a facile precipitate method and characterized by XRD, SEM, TEM, HRTEM, BET, DRS and XPS techniques. The as–obtained composites were employed to degrade different kinds of organic pollutants (dyes and colorless pollutants) in aqueous solution under visible light irradiation. The Ag_3PO_4/In_2S_3 composites exhibited excellent adsorption capacity and photocatalytic activity. The optimal composite with 0.086 wt % Ag_3PO_4 content exhibited the highest photocatalytic activity, which could degrade almost all dyes (MO, MB and RhB) within 7 min of light irradiation and more than 50% of phenol and salicylic acid after 3 h of irradiation. Recycling experiments confirmed that the Ag_3PO_4/In_2S_3 catalysts had superior cycle performance and structural stability. The photocatalytic activity enhancement of Ag_3PO_4/In_2S_3 composites could be mainly attributed to the efficient separation of photogenerated charge carriers through a Z–scheme system composed of Ag_3PO_4, Ag and In_2S_3, in which Ag nanoparticles acted as the charge transmission bridge. The high photocatalytic stability was ascribed to the successful inhibition of the photocorrsion of both In_2S_3 and Ag_3PO_4 by transferring the photogenerated holes and electrons from them to Ag, respectively. This study indicated the application of Ag–Ag_3PO_4 as cocatalyst and provided a new way to design and prepare high–efficiency and stable photocatalysts for photocatalytic decontamination of organic pollutants.

1. Introduction

Semiconductor photocatalysis has been considered as an effective and most promising strategy to address the environmental crises and energy shortage issues [1,2]. In view of the efficient utilization of solar energy, numerous attempts have been made in recent years to develop different visible light–active photocatalysts. Among them, sulfide photocatalysts including binary sulfides (e.g., CdS, In_2S_3, SnS_2, Cu_2S) and ternary chalcogenides (e.g., $ZnIn_2S_4$, $CdIn_2S_4$, $SnIn_4S_8$) with narrow band gaps, have been proved to be good candidates for photocatalytic hydrogen evolution from water and photocatalytic degradation of organic pollutants under visible light irradiation [3–9]. However, these sulfide photocatalysts are still facing the same challenges encountered by most photocatalysts, such as limited photocatalytic efficiency associated with the fast recombination rate of photogenerated electron–hole pairs and photocorrsion issue due to the oxidation of S–metal bond by photogenerated holes. Traditionally, for improving the photocatalytic efficiency of sulfide photocatalysts, cocatalysts are usually involved to load on base photocatalysts. The introduction of cocatalysts not only effectively separates the electron–hole pairs but also provides more active sites to facilitate the adsorption and oxidation/reduction reactions. For instance, Zong et al. reported the enhancement of photocatalytic H_2 evolution on CdS by loading MoS_2 or WS_2 as cocatalyst under visible light irradiation [10,11]. Shen and co-workers observed that dual cocatalysts consisting of noble metals (Pt) and transition-metal sulfides (Ag_2S, SnS, CuS) played a crucial role in achieving very high efficiency for H_2 evolution over $ZnIn_2S_4$ photocatalyst [12]. Although

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many other cocatalysts such as $Co(OH)_2$ and graphene oxide have been explored and found to be effective for facilitating the activity of sulfide photocatalysts [13,14], the development of novel cocatalysts to fulfill the high photocatalytic activity is still concerned.

On the other hand, fabrication of heterogeneous–type photocatalytic system is an effective strategy to suppress the photocorrsion because it allows the prompt migration of photogenerated charges [15]. Silver phosphate (Ag_3PO_4) has been reported as a promising photocatalyst with wonderful photocatalytic activity under visible light irradiation since the pioneer work by Ye et al. in 2010 [16]. Due to the outstanding photosensitive and photocatalytic characteristics, Ag_3PO_4 photocatalysts have afterward be used to fabricate heterogeneous composite photocatalysts such as $Ag_3PO_4/In(OH)_3$ [17], AgX/Ag_3PO_4 (X = Cl, Br, I) [18], $SrTiO_3/Ag_3PO_4$ [19], Ag_3PO_4/TiO_2 [20], $Ag_3PO_4/g\text{–}C_3N_4$ [21,22], Ag_3PO_4/WS_2 [23], Ag_3PO_4/MoS_2 [24], $Ag_3PO_4/InVO_4/BiVO_4$ [25], and so on, in which the photogenerated electron–hole pairs can be separated effectively and the photocatalytic activity and stability of separate component is highly improved. However, the above studies have mainly focused on fabricating Ag_3PO_4–based composite photocatalysts, in which precious Ag_3PO_4 takes up the major component, to some extent restricting the practical use of such heterogeneous photocatalysts. Our recent study reported a low–cost and efficient Ag_3PO_4/SiO_2 complex photocatalytic system by grafting few Ag_3PO_4 photocatalysts onto inexpensive SiO_2 supporting material [26]. An improved photocatalytic activity could be achieved for the decomposition of methyl orange (MO) under visible light irradiation even when the Ag_3PO_4 content decreased to 15 wt% in the Ag_3PO_4/SiO_2 composite photocatalysts.

For the purpose of further decreasing the Ag_3PO_4 content and designing novel high–efficiency and stable photocatalysts, in this study, Ag_3PO_4 as a novel cocatalyst with ultra–low loading amount (0.017–4.89 wt %) was anchored onto In_2S_3 hierarchical microspheres to synthesize Ag_3PO_4/In_2S_3 composites. The photocatalytic performance was evaluated by the degradation of dyes and colorless organic pollutants under visible light irradiation. The Ag_3PO_4/In_2S_3 composites exhibited excellent photocatalytic activity and stability. The reaction mechanism of the improved photocatalytic performance of Ag_3PO_4/In_2S_3 composites was also investigated. This work may provide new insights for the design and preparation of new high–efficiency and stable visible–light–driven photocatalysts.

2. Experimental Section

2.1. Materials

All of the reagents used in this experiment were analytical reagent grade and without further purification. Indium chloride tetrahydrate ($InCl_3 \cdot 4H_2O$), L–cysteine, sodium hydroxide (NaOH), disodium hydrogen phosphate ($Na_2HPO_4 \cdot 12H_2O$), silver nitrate ($AgNO_3$), commercial Al_2O_3, methyl orange (MO), nitroblue tetrazolium (NBT) and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used throughout the work.

2.2. Sample preparation

2.2.1. Synthesis of pure In_2S_3

Pure In_2S_3, with a typical flowerlike structure, was synthesized by a hydrothermal method. In a typical synthesis, 0.5 mmol $InCl_3 \cdot 4H_2O$ and 2 mmol L–cysteine were firstly dissolved in 80 mL of distilled water to form a homogeneous solution under constant vigorous stirring. The pH of the solution was adjusted to 8 by dropwise addition of a 1 M solution of NaOH. After further stirring for 30 min, the resulting solution was transferred into a Teflon–lined stainless autoclave and then heated at 180 °C for 10 h. The obtained products were washed several times with water and ethanol, and the yellow precipitate was dried in an oven at 60 °C. $ZnIn_2S_4$ hierarchical microspheres were synthesized by a similar hydrothermal method.

2.2.2. Synthesis of Ag_3PO_4/In_2S_3 composite

For preparation Ag_3PO_4/In_2S_3 composite photocatalysts, 0.1 g of In_2S_3 powder was dispersed in a set volume of Na_2HPO_4 solution (0.1 M) and ultrasonicated for 0.5 h. A certain amount of $AgNO_3$ solution was then dropped into the solution under vigorous stirring. After stirring for 1 h, the resulting solid product was collected by centrifugation, washed with distilled water, and dried in an oven at 60 °C. In this manner, different weight contents (0.017∼4.89 wt%) of Ag_3PO_4 in Ag_3PO_4/In_2S_3 composite samples were obtained and denoted as AI–1, AI–2, AI–3, AI–4, AI–5 and AI–6, respectively. Pure Ag_3PO_4 and Ag_3PO_4/Al_2O_3 samples were respectively prepared using the same procedures as AI–2 except that no In_2S_3 was added and In_2S_3 was replaced by commercial Al_2O_3. Pt/In_2S_3 was synthesized by impregnating the In_2S_3 catalysts with an aqueous H_2PtCl_6 solution followed by reduction using $NaBH_4$ as reduction reagent. The initial ratio of Pt to In_2S_3 was fixed at 0.086 wt %.

2.3. Sample Characterizations

X–ray diffraction patterns (XRD) were collected on a Rigaku MinFlex II equipped with Cu Kα irradiation. The morphology of the samples was investigated with field emission scanning electron microscope (FESEM) (Hitachi SU-8000). The high–resolution transmission electron microscopy (HRTEM) measurement was conducted using a JEM–2010 microscope working at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was conducted on an ESCALAB 250 photoelectron spectroscope (Thermo Fisher Scientific) at 3.0×10^{-10} mbar with monochromatic Al Kα radiation (E = 1486.2 eV), the binding energy was corrected with reference to the C 1 s peak (284.6 eV) for each sample. BET surface area was performed on an ASAP2020 M apparatus (Micromeritics Instrument Corp., USA). For BET surface area analyses, the samples were degassed in vacuum at 200 °C for 10 h and then measured at 77 K. UV−visible diffuse reflectance spectra (DRS) of the powders were obtained for the dry-pressed disk samples using a Cary 500 Scan Spectrophotometer (Varian, USA) over a range of 200–800 nm. $BaSO_4$ was used as a reflectance standard in the UV−visible diffuse reflectance experiment. The photoluminescence (PL) spectra were obtained by using a F-4600 Fluorescence spectrophotometer with an excitation wavelength of 216 nm. Photoelectrochemical measurements were conducted with an epsilon (BAS) electrochemical workstation. A 300W Xe–arc lamp equipped with cutoff filters (400 nm < λ < 800 nm) was used as a visible light source. A standard three-electrode cell with a work electrode (as-prepared photocatalyst), a platinum wire as counter electrode, and a standard calomel electrode as reference electrode were used in the photoelectric studies. 0.1 M Na_2SO_4 was used as the electrolyte solution. All electrochemical potentials are reported vs. NHE.

2.4. Evaluation of Photocatalytic Activity

Photocatalytic experiments were performed in an aqueous solution at ambient temperature. A 300 W Xe–arc lamp equipped with cutoff filters (400 nm < λ < 800 nm) was used as the visible light source. The system was cooled by a fan and circulating water to maintain at room temperature. Briefly, 80 mg of photocatalyst was suspended in 80 mL dye solution (MO, RhB and MB, 10 ppm), phenol solution (10 ppm) or salicylic acid solution (10 ppm). Prior to irradiation, the suspension was magnetically stirred in dark for 1 h