



Co₃O₄ nanoparticles decorated Ag₃PO₄ tetrapods as an efficient visible-light-driven heterojunction photocatalyst

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ABSTRACT

Novel Ag₃PO₄ tetrapods with exposed {1 1 1} facets were synthesized via a facile precipitation method, and then Co₃O₄ nanoparticles were decorated on the surface of Ag₃PO₄ tetrapods using an impregnation method. On top of the superior photocatalytic performance of highly reactive {1 1 1} facets of Ag₃PO₄ tetrapods, the Co₃O₄/Ag₃PO₄ heterostructured photocatalyst exhibited further improved efficiency in photodegrading methyl blue (MB) under visible light irradiation (>400 nm). In addition, the Co₃O₄ content and calcination temperature had significant impacts on the photocatalytic activities of the samples. The highest efficiency was observed on the 2.0 wt% Co₃O₄/Ag₃PO₄ heterojunction calcined at 673 K. The improved photocatalytic performance could be mainly attributed to accelerated electron-hole separation by p–n junctions in Co₃O₄/Ag₃PO₄ heterojunction, and the enhanced structural stabilities may be due to the protection of insoluble Co₃O₄ and the effect of Ag⁰ on the surface of Ag₃PO₄. Moreover, h⁺ played the major role in the MB decolorization.

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1. Introduction

Semiconductor photocatalysis has attracted considerable attention attributing to the fact that it provides a new way to meet the challenges of environmental pollution and energy crises [1,2]. Unfortunately, most widely employed semiconductor photocatalysts are only active under UV-light irradiation, but photocatalysis using visible light could be highly economical compared to the process using an artificial UV-light source. Therefore, development of efficient visible light driven photocatalysts is a major challenge in this field. Recently, silver orthophosphate (Ag₃PO₄) has been reported as a promising photocatalytic material due to its very high photocatalytic activity under visible light irradiation [3]. This novel photocatalyst can achieve a quantum efficiency of up to 90% at wavelengths greater than 420 nm, which is significantly higher than the previous reported values. However, Ag₃PO₄ photocatalyst is still facing the same challenges encountered by most photocatalysts, such as the fast recombination of photo-generated charge carriers. Moreover, Ag₃PO₄ also suffers from stability issue in practical applications because it is photosensitive and slightly soluble in aqueous solution. Thus, diverse techniques have been proposed to

improve its activity and stability, i.e. morphology control, surface modification and element doping [4–13]. Very recently, coupling Ag₃PO₄ with other materials is regarded as a good strategy to design efficient and stable photocatalysts, such as, coupling with inorganic materials (TiO₂, SnO₂, ZnO, CeO₂, Fe₂O₃, AgX (X = Cl, Br, I), Bi₂WO₆, BiPO₄, BiOI, WO₃, Ag₂O, etc.) and organic materials (MoS₂, C₃N₄, graphene oxide, graphene, carbon nanotubes and carbon quantum dots, etc.) [14–29].

Co₃O₄ is a p-type semiconductor with the characteristics of high thermal and chemical stability, low solubility, interesting electronic, magnetic and catalytic properties [30], as well as narrow band gap (about 1.2–2.1 eV) [31,32]. Due to its excellent properties, Co₃O₄ can be applied as a photocatalyst or co-catalyst for the visible-light-driven photocatalytic reactions [33–35]. For example, Co₃O₄/BiOCl photocatalyst exhibited an enhanced photocatalytic activity under visible light in the decomposition of Rhodamine B (RhB) and methylenorange (MO) compared with pure BiOCl [36]. Because Ag₃PO₄ is suggested to be a n-type semiconductor as indicated by the positive photocurrent at anodic potential [3], and the valence band (VB) of Ag₃PO₄ (about 2.67 eV vs NHE) [37] is positive than that of Co₃O₄ (about 2.44 eV vs NHE) [31]. Therefore, the combination of Co₃O₄ and Ag₃PO₄ can easily form a p–n heterojunction and the photogenerated holes on the VB of the Ag₃PO₄ can be easily transferred to Co₃O₄, promoting the effective separation of photo-generated electrons and holes of Ag₃PO₄. Moreover, because of the

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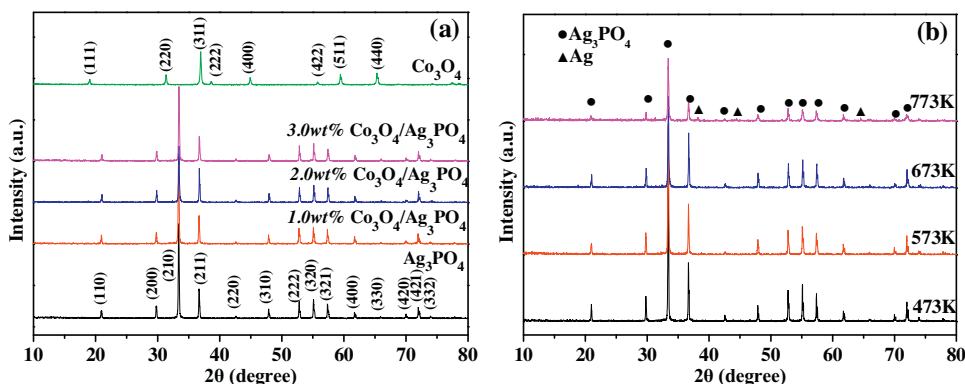


Fig. 1. XRD patterns of the samples: (a) Co_3O_4 , Ag_3PO_4 and $\text{Co}_3\text{O}_4/\text{Ag}_3\text{PO}_4$ composites with different Co_3O_4 content calcined at 673 K, (b) the 2.0 wt% $\text{Co}_3\text{O}_4/\text{Ag}_3\text{PO}_4$ composites calcined at different temperature.

chemical stability and low solubility of Co_3O_4 , loading Co_3O_4 on the surface of Ag_3PO_4 could effectively protect the Ag_3PO_4 from dissolution in aqueous solutions and enhance its stability during the photocatalytic process.

Evidenced by theoretical and experimental research, the {111} facets of Ag_3PO_4 are much more reactive than {110} and {100}. Zheng et al. [38] found the dispersion between the valence bands and conduction bands of the {111} surface was beneficial for the separation of photogenerated electrons and holes on the {111} surface, which improved the photocatalytic activity of the {111} surface. Martin et al. [39] attributed the excellent and reproducible performance of {111} terminated tetrahedrons of Ag_3PO_4 to a synergistic effect between high surface energy and a small hole mass, leading to high charge carrier mobility and active surface reaction sites. Given this, a cooperative effect of active facets and heterojunction may enhance the photocatalytic activity and stability of Ag_3PO_4 together.

In this paper, novel Ag_3PO_4 tetrapods with exposed {111} facets were synthesized by a facile precipitation method and then Co_3O_4 nanoparticles were decorated on the surface of Ag_3PO_4 tetrapods using an impregnation method. The photocatalytic performances were evaluated by photodegradation of methyl blue (MB) under the visible light irradiation. The effects of Co_3O_4 content and calcination temperature on photocatalytic activity were also investigated. In addition, the photodegradation mechanism on $\text{Co}_3\text{O}_4/\text{Ag}_3\text{PO}_4$ was also discussed.

2. Experimental

2.1. Preparation of Ag_3PO_4

The tetrapod-shaped Ag_3PO_4 microcrystals were prepared through a facile precipitation process. Typically, AgNO_3 (0.2 g) was dissolved in distilled water, and concentrated ammonia aqueous solution ($\text{NH}_3\text{H}_2\text{O}$, mass fraction 25–28%) was added to form a transparent solution. Then the above $[\text{Ag}(\text{NH}_3)_2]^+$ complex was directly poured into the aqueous solution containing the PEG (0.3 M) and Na_2HPO_4 (0.5 M) at 333 K. After stirring for 1 h, the products were collected by centrifugation, washed for several times and dried at 333 K overnight. For comparison, irregular Ag_3PO_4 crystals were synthesized by direct precipitation method as follows: Na_2HPO_4 solution was added drop by drop to the AgNO_3 solution under stirring. After stirring for 1 h, the above suspension experienced centrifugation, washing and drying.

2.2 Preparation of $\text{Co}_3\text{O}_4/\text{Ag}_3\text{PO}_4$ composites

The $\text{Co}_3\text{O}_4/\text{Ag}_3\text{PO}_4$ composites were prepared via a facile impregnation method. In a typical procedure, the as-prepared Ag_3PO_4 tetrapods were added into distilled water containing an

appropriate amount of $\text{Co}(\text{NO}_3)_2$. The suspension was sonicated for 0.5 h to completely disperse the Ag_3PO_4 crystals, followed by stirring until the water was volatilized completely at 333 K. The resulting powder was collected and calcinated at different temperature for 2 h in the air. The collected product was denoted as x wt% $\text{Co}_3\text{O}_4/\text{Ag}_3\text{PO}_4$, and the weight percentages of Co_3O_4 in the initial photocatalyst precursors were from 0 to 3.0 wt%. Co_3O_4 was prepared by calcining the $\text{Co}(\text{NO}_3)_2$ at 673 K for 2 h in the air.

2.2. Characterization

The X-ray diffraction (XRD) of the products was examined on a Rigaku-Dmax 3C diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The morphology of samples were observed by a JSM-6390A scanning electron microscope (SEM) and equipped with energy-dispersive X-ray (EDS). The surface area measurement was carried out by the N_2 adsorption isotherms conducted in the Quantachrome NOVA 2000e using the Brunauer-Emmette-Teller (BET) method. Fourier transform infrared (FT-IR) spectra were collected on PerkinElmer Frontier. Besides, UV–vis absorption spectra were recorded using a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer with BaSO_4 as a reference. X-ray photoelectron spectroscopy (XPS) data were collected from a Kratos AXIS NOVA spectrometer, and PL spectra were measured at room temperature on a Hitachi F-7000 fluorescence spectrophotometer.

2.3. Photocatalytic tests

The photocatalytic activities of samples were examined with visible light ($\lambda > 400 \text{ nm}$)-induced photodegradation of MB in an aqueous solution. In a typical photodegradation process, 40 mg photocatalysts were added into 50 mL MB solution (10 mg/L). Prior to irradiation, the suspensions were magnetically stirred in dark for 0.5 h to ensure the adsorption-desorption equilibrium of MB on the surface of photocatalysts. A 300 W Xe lamp (Beijing Perfect-light Technology Co. Ltd., China, Microsolar 300UV) with a 400 nm cut off filter was used as visible light source, which was positioned on the top of the reaction cell. The above suspension was stirred with bubbling of air throughout the tests at room temperature. The decolorization of MB was determined by measuring the absorbance of the solution at 664 nm using a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer.

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