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Construction of an Ag_3PO_4 morphological homojunction for enhanced photocatalytic performance and mechanism investigation

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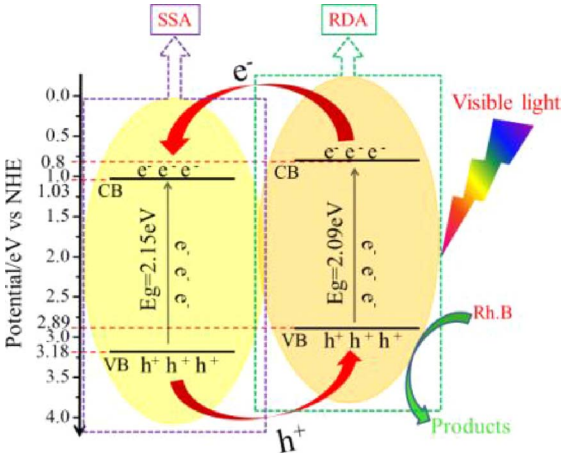
GRAPHICAL ABSTRACT

The acceleration of charge separation was achieved by the construction of morphological homojunction between Ag_3PO_4 semiconductors with different morphology.



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ABSTRACT

Homojunction construction is attractive for developing high-performance semiconductor photocatalysts. In this study, a facile combination process was employed for the first time to fabricate the Ag_3PO_4 morphological homojunction consisting of submicron spherical and rhombic dodecahedron particles, which could achieve morphology control and homojunction manipulation simultaneously. The enhancement of photocatalytic activity was attributed to that the formation of morphological homojunction which consists of rhombic dodecahedral Ag_3PO_4 (RDA) and submicron spherical Ag_3PO_4 (SSA) with different band structures, which promotes efficient separation of photogenerated electron-hole pairs and leads to high photocatalytic activity. The different band structures of Ag_3PO_4 indicate that morphology affects the valence and conduction band position of semiconductors, and further verifies the formation of morphological homojunction. The finding of our work illustrated that the fabrication of Ag_3PO_4 morphological homojunction was a promising strategy to be applied in photocatalysis and photoelectric conversion.

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1. Introduction

In recent years, silver phosphate (Ag_3PO_4) has attracted much attention for its narrow band gap structures, and it was considered as promising materials for photodegradation of organic pollutants [1,2]. Unfortunately, with further advances in Ag_3PO_4 research, an increasing number of disadvantages have been found. For instance, the quantum efficiency of Ag_3PO_4, including the generation and separation of photoinduced charges, was not satisfied [3–5]. Ag_3PO_4 semiconductor with different morphology showed an entirely different exposed facet. Controllable synthesis of Ag_3PO_4 photocatalysts with morphology-dependent photochemical performance was vital in improving the generation of photoinduced electron-hole pairs. Several papers reported the fabrication of Ag_3PO_4 with different morphology, such as cubic [6,7], rhombic dodecahedron [8], concave trisoctahedron [9,10], pine tree shaped [11], tetrapod [12], doughnut-like [13] and two-dimensional dendritic [14]. Also, Ye and coworkers reported that the Ag_3PO_4 with a highly exposed ratio of {110} facets exhibited enhanced photocatalytic activity, which may be because of the high surface energy of {110} facets [15]. All these semiconductors with different morphology showed an enhanced photocatalytic performance, which may be related to their surface area and surface energy [1,12,16].

Moreover, as a result for the enhanced separation and migration of photoinduced charge carriers, homojunction photocatalysts, constructed by the same semiconductor materials with different crystal phases, morphologies and exposing facets etc., is a promising strategy for both water splitting and wastewater purification [17,18], and a great deal of work has been done with respect to these purposes [19–21]. Compared with heterojunctions built from different components, the homojunction displays many advantages in the above-mentioned respects, and it also introduces an internal field between the two parts for retarding the recombination of photoinduced carriers and keeping the movement of charge carriers across the interface. Although the heterojunction construction received widespread attention for improving photocatalytic efficiency [22,23], the electron transfer behavior at the interface of different semiconductors still remain unclear, and a complex fabrication process was necessary for synthesis of heterojunctions. Hence, it is rational to construct a homojunction between the two same substances, which favors the controllable synthesis and mechanism investigation. Despite some previous papers reported that manipulation of surface homojunction with co-exposed reactive facet presented enhanced photocatalytic efficiency [24], the fabrication of Ag_3PO_4 based morphological homojunction has never been reported.

Considering the previous research results, our strategy is achieving morphology tunning and homojunction manipulation simultaneously for highly enhanced photo-oxidation capacity. Herein, in this paper, we report the fabrication of Ag_3PO_4 mophological homojunction photocatalysts for the first time. A series of Ag_3PO_4 mophological homojunction, which consisted of rhombic dodecahedral Ag_3PO_4 (RDA) and submicron spherical Ag_3PO_4 (SSA), was synthesized by using facile physical combination process. The basic physicochemical properties of Ag_3PO_4 morphological homojunction photocatalysts would be all well characterized. The photocatalytic activity of as-prepared catalysts was investigated by the photodegradation of Rh.B. The results showed that the photocatalytic activity was determined by the mass ratio of the RDA particle, and the sample 0.6% (formed by 0.6% of RDA and 99.4% of SSA in mass ratio) exhibited the highest photocatalytic activity among all samples. The mechanism for the enhancement of photocatalytic activity was also investigated in detail. Our work demonstrates a novel method for the fabrication of advanced catalytic materials.

2. Experimental section

2.1. Materials

Silver nitrate ($AgNO_3$, 99.8%), dibasic sodium phosphate ($Na_2HPO_4{\cdot}12H_2O$, 99%), absolute ethyl alcohol and deionized (DI) water were purchased from Sinopharm Chemical Reagent. Rhodamine B (Rh.B, AR) was obtained from Amethyst Chemicals. All chemicals were analytical grade and used as received without further purification.

2.2. Synthesis of the SSA particles and RDA particles

SSA particles were synthesized via precipitation. Adequate amounts of silver nitrate and dibasic sodium phosphate were dissolved in DI water respectively, and then the silver nitrate solution was dropped to the dibasic sodium phosphate solution under vigorous stirring. The products were collected after stirring for 120 min and washed with DI water and absolute ethanol several times, then dried under vacuum at 60 °C for 24 h in dark.

RDA particles were synthesized by using hydrothermal method. In a typical synthesis, adequate amounts of silver nitrate and dibasic sodium phosphate were dissolved in DI water, respectively. Then, the silver nitrate solution was dropped to the dibasic sodium phosphate solution under vigorous stirring. The suspension was added into a Teflon-lined stainless-steel autoclave with a volume capacity of 100 mL, which then was sealed and maintained at 180 °C for 36 h. After naturally cooling to room temperature, the products were collected by centrifugation, washed with distilled water and absolute ethanol several times, and then dried under vacuum at 60 °C for 24 h in dark for further characterization.

2.3. Synthesis of the Ag_3PO_4 morphological homojunction

The Ag_3PO_4 morphological homojunction photocatalysts, which consisted of SSA particles and RDA particles, were synthesized via a facile physical combination process. In a typical synthesis, adequate amounts of SSA particles were dissolved in absolute ethanol under vigorous stirring. After ultrasonic dispersion for 20 min, adequate amounts of RDA particles were added into above suspension under vigorous stirring. After ultrasonic dispersion for another 20 min, the suspension was dried under vacuum at 100 °C for 24 h in a vacuum drying oven to enhance the connection strength between SSA and RDA, and then the products were collected. Different contents (0.2%, 0.4%, 0.6%, 1.2%, 2%, 5%, and 10%) of RDA particles were prepared in the same manner, hereafter referred to as samples (0.2%, 0.4%, 0.6%, 1.2%, 2%, 5%, and 10%).

2.4. Characterization

The morphologies of the photocatalysts were investigated using scanning electron microscopy (SEM, JSM-7001F) equipped with EDS for elemental analysis. The crystal phases of the Ag_3PO_4 photocatalysts were analyzed using X-ray diffraction (XRD, Model XD-3) with Cu Kα radiation (λ = 1.54 Å) in the range of 10–80°. The chemical compositions of the samples were determined using X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi), and the resulting binding energies were calibrated to the C 1s (284.6 eV) peak. Diffuse reflectance spectra (DRS) were recorded using UV–vis spectroscopy (Carry 5000) in the range of 200–800 nm, and $BaSO_4$ was used as the reflectance standard material. The specific surface area of the Ag_3PO_4 photocatalysts was measured using BET (Autosorb-iQ2-MP). The PL spectra of the photocatalyst powders were recorded on an F-4600 system equipped with a solid sample holder at room temperature.

2.5. Photoelectrochemical performance measurement

The photoelectric conversion properties were investigated in a conventional three-electrode cell by using computer-controlled electrochemical workstation (CHI 660B). The working electrode was prepared according to the following process. 50 mg catalysts was suspended in 2 mL nafion aqueoussolution (1 wt%), the mixtures were