



Improving the photocatalytic performance of silver phosphate by thermal annealing: Influence of acetate species



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ABSTRACT

Two Ag_3PO_4 photocatalysts were prepared using different silver precursors (CH_3COOAg and AgNO_3) and then thermally annealed in air at various temperatures. The surface chemistry of the pristine Ag_3PO_4 photocatalysts was quite different: the Ag_3PO_4 sample (AP-C) prepared from CH_3COOAg possessed excessive acetate species on its surface while that (AP-N) derived from AgNO_3 showed a clean surface. The residual acetate species played crucial role in the thermally excited decomposition of Ag_3PO_4 into metallic Ag and the simultaneous formation of Ag vacancies. The photocatalytic activity of the pristine AP-C sample was greatly improved after thermal treatment due to the synergistic effect of Ag vacancies and metallic Ag, which contributed to the efficient separation of photogenerated charge carriers. On the contrary, for the AP-N sample, the photocatalytic activity was largely weakened upon thermal annealing because the negative changes in textural structures. Of importance, after impregnation of AP-N in acetic acid solution and annealing, the photocatalytic activity was largely improved.

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1. Introduction

Semiconductor-mediated photocatalysis has attracted considerable attention because of its potential applications in environmental purification and solar energy conversion. Till now, much effort has been devoted to the design and development of photocatalysts capable of using visible light, which accounts for more than 43% of the abundant solar light. Two strategies have been employed in the design of visible-light-driven photocatalysts. One strategy involves the chemical modifications on a UV-active photocatalyst like TiO_2 , including doping of foreign elements or coupling with a narrow band gap semiconductor [1–5]. The other strategy has been focused on the exploration new and efficient photocatalytic materials that are sensitive to visible light for improving photocatalytic performances [6–8].

In recent years, silver phosphate (Ag_3PO_4) has been reported as a new type of photocatalyst that is highly effective in visible light

[9–12]. Ye and co-workers demonstrated the novel use of Ag_3PO_4 semiconductor to oxidize water as well as decompose organic contaminants under visible light irradiation [9,10]. They further investigated the effects of morphology and facet on the photocatalytic properties of Ag_3PO_4 [11]. Teng et al. have recently synthesized polypod-like Ag_3PO_4 particles and applied them in pollutant degradation under natural indoor weak light irradiation [13]. Many researchers have also focused on fabricating of semiconductor composites such as $\text{AgX}/\text{Ag}_3\text{PO}_4$ ($X = \text{Cl}, \text{Br}, \text{I}$) [14–16], $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ [17,18], $\text{Ag}_3\text{PO}_4/\text{SnO}_2$ [19], $\text{Ag}_3\text{PO}_4/\text{In}(\text{OH})_3$ [10], $g\text{-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$ [20,21], $\text{Ag}_3\text{PO}_4/\text{BiVO}_4$ [22], $\text{Ag}_3\text{PO}_4/\text{graphene}$ [23], $\text{Ag}_3\text{PO}_4/\text{BiOI}$ [24], $\text{NiFe}_2\text{O}_4/\text{Ag}_3\text{PO}_4$ [25] and *etc.* to further improve the photocatalytic activity and structural stability of bare Ag_3PO_4 . Recently, we have also successfully grafted active Ag_3PO_4 photocatalysts onto uniform SiO_2 supporting materials to achieve highly efficient and stable performance towards degradation of dyes under visible light irradiation [26].

Deposition of noble metals onto semiconductors has been extensively studied and viewed as a promising approach to improve the photocatalytic performance. Inspiration by the photosensitive characteristic of Ag-based photocatalysts [8,27], a simple photoreduction route has been developed to prepare $\text{Ag}/\text{Ag}_3\text{PO}_4$ heterostructures in aqueous solution under light irradiation

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[28]. However, the dynamics of such photoreduction is uncontrollable and Ag_3PO_4 could be completely decomposed into metallic Ag if no electron acceptor was supplied [29]. Our recent work demonstrated the fabrication of $\text{M}/\text{Ag}_3\text{PO}_4$ ($\text{M} = \text{Pt}, \text{Pd}, \text{Au}$) Schottky-type heterostructures by a chemical deposition route using NaBH_4 as a reduction agent [30]. The metallic nanoparticles deposited on Ag_3PO_4 could promote the transfer of photo-generated electrons, which inhibited the recombination of electrons and holes effectively and suppressed the photocorrosion of Ag_3PO_4 , leading to a significant increase in photocatalytic activity and stability. Many other synthetic routes have also been developed to construct $\text{Ag}/\text{Ag}_3\text{PO}_4$ heterostructure photocatalysts in view of the rational tailor of the interface interaction between Ag and Ag_3PO_4 . For example, Bi and co-workers developed novel $\text{Ag}/\text{Ag}_3\text{PO}_4$ heterostructures by selective growth of Ag_3PO_4 crystals on Ag nanowires or growth of metallic Ag on Ag_3PO_4 cubes to improve the contact between Ag nanoparticles and Ag_3PO_4 semiconductor [31,32]. By introducing some reducing agents like pyridine, ethylene glycol and glucose, $\text{Ag}/\text{Ag}_3\text{PO}_4$ heterostructure photocatalysts have been successfully obtained through solution-based synthetic routes [33–35]. More recently, Botelho and co-workers employed a microwave–hydrothermal method to grow Ag nanoparticles onto the surface of Ag_3PO_4 crystals without use of any other reducing agents, suggesting that Ag_3PO_4 could be partially converted into metallic Ag when exposed to thermal energy radiation [36]. However, scientific studies on the thermal treatment of solid Ag_3PO_4 by simple high-temperature annealing in atmosphere condition are not found in the literature.

In this work, we report the thermal annealing of Ag_3PO_4 solid powders in air at various temperatures and investigate the effect of surface species on the thermal decomposition mechanism of Ag_3PO_4 . Two pristine Ag_3PO_4 samples prepared from CH_3COOAg or AgNO_3 having quite different surface characteristics were selected. The variations of microstructures and photocatalytic activities of Ag_3PO_4 upon annealing were investigated in detail. Furthermore, a feasible strategy, namely carbon–thermal reduction, by impregnation of Ag_3PO_4 in acetic acid solutions followed by thermal annealing in air was proposed to improve the photocatalytic activity of Ag_3PO_4 .

2. Experimental

2.1. Preparation

All the chemicals were purchased from Shanghai Reagent Company. All the chemicals and solvents were used without further purification. The pristine Ag_3PO_4 samples were prepared by an ion-exchange method. In a typical synthesis, 0.02 mol NaH_2PO_4 and 0.06 mol CH_3COOAg or AgNO_3 were dissolved in 100 mL of distilled water, respectively. The above solutions were mixed under constant stirring for 30 min. The as-obtained yellow precipitates were washed and kept in an oven at 60 °C for 3 h. After that, the dried samples (named as AP-C or AP-N) were calcined in a muffle furnace at 200, 400 and 700 °C in air for 4 h. The resultant samples are denoted as A200-C, A400-C and A700-C, or A200-N, A400-N and A700-N, respectively. All the Ag_3PO_4 -based composite photocatalysts such as $\text{Ag}_3\text{PO}_4/\text{In}(\text{OH})_3$ (AP/ $\text{In}(\text{OH})_3$), $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ (AP/ TiO_2) and $\text{Ag}_3\text{PO}_4/\text{SnO}_2$ (AP/ SnO_2) were prepared according to the literature [10,17,19].

2.2. Characterization

Infrared spectra of the samples were recorded on a Perkin-Elmer IR spectrophotometer using a KBr pellet technique (2 mg sample, 200 mg KBr). X-ray diffraction patterns (XRD) were collected on a

Rigaku MinFlex II equipped with $\text{Cu K}\alpha$ irradiation. Morphologies of the samples were observed by field emission scanning electron microscopy (FE-SEM) (Hitachi SU-8000). A Varian Cary 500 Scan UV/vis system was used to obtain the optical absorption spectra of the samples over a range of 200–800 nm. The specific surface areas of the samples were determined from the nitrogen adsorption data at liquid nitrogen temperature using the Barrett–Emmett–Teller (BET) technique on a Micromeritics ASAP 2000 surface area analyzer. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250 photoelectron spectroscope (Thermo Fisher Scientific) with monochromatic $\text{Al K}\alpha$ radiation ($E = 1486.2$ eV).

2.3. Photocatalytic activity

Photocatalytic experiments were performed in an aqueous solution at ambient temperature. A 300 W halogen lamp (Philips Electronics) equipped with a composited cut-off filter ($400 \text{ nm} < \lambda < 800 \text{ nm}$) 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 aqueous solution of MO (10 ppm). Prior to irradiation, the suspension was magnetically stirred in dark for 0.5 h to establish an adsorption–desorption equilibrium. A 3 mL aliquot was taken at several minutes intervals during the experiment and centrifuged to remove the powders. The residual concentration of dye was analyzed on a Shanghai Youke UV756CRT spectrophotometer. The degradation percentage is reported as C/C_0 , where C_0 is the concentration of initial MO, and C represents the corresponding concentration at a certain time interval. To test the stability, the sample was recycled and reused five times in the decomposition of MO under the same conditions. After each photocatalytic reaction, the aqueous solution was centrifuged to recycle the solids that were then dried at 353K in vacuum for another test.

3. Results and discussion

The Ag_3PO_4 samples in the present study were prepared by a simple ion-exchange method using CH_3COOAg and AgNO_3 as different silver precursors. As the precursor composition greatly affects the surface chemistry of catalysts, the FTIR spectra of pristine Ag_3PO_4 samples as well as the annealed samples are shown in Fig. 1. For comparison, the spectrum of pure CH_3COOAg or AgNO_3 is also given. For both pristine Ag_3PO_4 samples, the strong band featured at 1011 cm^{-1} (or 1015 cm^{-1}) is assigned to the asymmetric stretching of P–O–P groups, while the weak peak at 559 cm^{-1} corresponds to O=P–O bending vibration [14,20,37,38]. In addition, the broad absorption band within $3000\text{--}3700 \text{ cm}^{-1}$ is ascribed to the O–H stretching vibration of adsorbed water molecules [20]. Except for the peaks coming from Ag_3PO_4 , two characteristic peaks located at about 1577 and 1413 cm^{-1} are observed in the FTIR spectrum of AP-C, corresponding to the asymmetric and symmetric stretching vibrations of C=O and C–O–C bands, respectively [39,40]. This indicates the existence of CH_3COO^- species on the surface of Ag_3PO_4 crystals [14]. In contrast, the AP-N sample displays a clean surface as no obvious NO_3^- species are found at 1385 cm^{-1} . These observations demonstrate that the Ag_3PO_4 samples prepared from different silver precursors exhibit distinct surface characteristics. Upon annealing, the intensities of the CH_3COO^- species gradually decrease with elevating temperature to 200 and 400 °C and the organic species almost disappear after 700 °C annealing in air. It should also be noted that some new peaks attributing to C–H stretching vibrations appear between 2700 and 3000 cm^{-1} in A200-C [41]. This suggests that the acetates species may be initially decomposed into some intermediate organic species at temperature above 200 °C and further be

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