Research Article
Synthesis and Photocatalytic Activity of Ag₃PO₄ Triangular Prism

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Ag₃PO₄ triangular prism was synthesized by a facile chemical precipitation approach by simply adjusting external ultrasonic condition. The as-synthesized Ag₃PO₄ triangular prism was characterized by X-ray diffraction pattern (XRD), field emission scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectra, and ultraviolet-visible diffuse reflectance (UV-vis DRS) absorption spectra. The photocatalytic activity of Ag₃PO₄ triangular prism was evaluated by photodegradation of organic methylene blue (MB), rhodamine B (RhB), and phenol under visible light irradiation. Results showed that Ag₃PO₄ triangular prism exhibited higher photocatalytic activity than N-doped TiO₂ and commercial TiO₂ (P25) under visible light irradiation.

1. Introduction

Photocatalysis technology is considered as an efficient, stable, and environmentally friendly method for controlling environmental pollutions [1]. In the past years, the discovery of new efficient visible-light-driven photocatalysts attracts much attention. It is noted that a breakthrough on visible-light active photocatalysts was made by Yi et al.’s research team, who reported the use of Ag₃PO₄ as an active visible-light-driven photocatalyst for oxidation of water and photodecomposition of organic compounds [2]. This research finding is considered as a breakthrough in the field of visible-light active photocatalysts. Hence, investigation of the basic principles and application of Ag₃PO₄ photocatalyst is a hot topic. Up to now, various methods have been proposed to further enhance the visible-light-driven photocatalytic activity. One of the methods is the coupling of Ag₃PO₄ with other semiconductors or noble metals to promote the charge separation efficiency of Ag₃PO₄ and then enhancing of the photocatalytic activity. Some composite samples such as Ag₃PO₄/TiO₂ [3], AgBr@Ag₃PO₄/Fe₂O₃ [4], Ag₃PO₄/graphene oxide [5], Ag₃PO₄/TiOF₂ [6], Ag₃PO₄/Ag [7], Ag₃PO₄/ZnO [8], Ag₃PO₄/BiOCl [9], Ag₃PO₄/reduced graphite oxide sheets [10], and g-C₃N₄/Ag₃PO₄ [11] have recently been developed to enhance the photocatalytic activity of Ag₃PO₄. Another method is the synthesis of Ag₃PO₄ with various new morphologies. In addition, it is known that the morphologies and microstructures of functional materials affect the physical and chemical properties [12, 13]. The morphology control of photocatalysts was considered to be one of the most promising avenues to improve the photocatalytic properties [14]. Therefore, further studies on Ag₃PO₄ crystals with new morphologies and structures will be of great value. In recent years, some morphologies of Ag₃PO₄ have been reported [15–21]. For example, Bi et al. fabricated the single-crystalline Ag₃PO₄ rhombic dodecahedrons with {110} facets exposed and cubes bounded entirely by {100} facets, and they found that both of these samples exhibited higher photocatalytic activity than the microsized spherical Ag₃PO₄ particles [15]. Our research group prepared Ag₃PO₄ nanorods with enhanced photocatalytic activity [16]. Wang et al. synthesized the tetrahedral Ag₃PO₄ crystals exposed with {111} facets [17]. Liang et al. synthesized hierarchical Ag₃PO₄ porous microcubes with enhanced photocatalytic
property [18]. Up to now, synthesis of Ag₃PO₄ crystals with novel morphologies or microstructures is still an important and challenging research field.

To the best of our knowledge, there is no research on the synthesis of Ag₃PO₄ triangular prism. Herein, we controllably prepared Ag₃PO₄ triangular prism via a facile and efficient synthesis process in the mixture solvent of DMF and H₂O at room temperature. Meanwhile, the photocatalytic activity was investigated in this paper.

2. Experimental

In a typical preparation procedure, 10 mL of N,N-dimethylformamide (DMF) and 10 mL of deionized water (H₂O) were mixed together to form transparent solvent. Then, 3 mmol of AgNO₃ was dissolved into the mixture solvent. Subsequently, H₃PO₄ (1 mL, 85%) was added dropwise into the above solution under ultrasonic condition (ultrasonic reactor, KQ-100B, 40 kHz, 120 W/cm², Kunshan Co., China). After this process, the ultrasonic condition was maintained for 4 h. The obtained precipitation was separated by centrifuge and followed by washing with ethanol and deionized water for 3 times, respectively, to remove the DMF and other residues. Finally, the product was dried at 60°C. For comparison purpose, N-doped TiO₂ was synthesized by a reported method [22]. The commercial TiO₂ (P25) was purchased from Degussa.

X-ray diffraction (XRD) experiment was carried out with a D/max-2400 diffractometer (Rigaku, Japan) using Cu-Kα radiation. The morphologies of the sample were examined by scanning electron microscopy (SEM, Hitachi S-4800). Fourier transform infrared (FTIR) spectrum of the sample was recorded between 400 and 4000 cm⁻¹ on a Nicolet NEXUS 670 FTIR spectrometer. Ultraviolet-visible diffuse reflectance (UV-vis DRS) absorption spectrum was measured using a Perkin Elmer 950 spectrometer, while BaSO₄ was used as a reference.

The photocatalytic activity of sample was measured by decomposition of methylene blue (MB) and rhodamine B (RhB) in a reactor at room temperature. In a typical process for degradation of a dye, 50 mg of photocatalyst was suspended in the dye solution (10 mg/L, 60 mL). Before irradiation, the suspensions were stirred in the dark for 60 min to ensure the establishment of adsorption-desorption equilibrium. A 350 W Xe lamp with a cutoff filter of 420 nm was employed for the visible-light irradiation source and positioned 20 cm away from the reactor to trigger the photocatalytic reaction. A certain volume of suspension was withdrawn at selected times for analysis. After recovering the photocatalyst by centrifugation, the concentration of dye
solution was analyzed by measuring the light absorption of the clear solution at 664 nm (λ_max for MB solution) or 555 nm (λ_max for RhB solution) using a Perkin Elmer 950 spectrometer. The percentage of degradation was calculated by C/C_0. Here, C is the concentration of remaining dye solution at each irradiated time interval, while C_0 is the initial concentration. Furthermore, a colorless compound, phenol, was also chosen as a model pollutant since phenol shows no absorption in the visible region. The concentration of phenol solution was analyzed by measuring the light absorption of the clear solution at 270 nm (λ_max for phenol solution).

To test the stability of Ag_3PO_4 triangular prism, the cycling runs in photocatalytic degradation of MB in the presence of Ag_3PO_4 triangular prism were measured. After one cycle, the photocatalyst was filtrated and washed thoroughly with deionized water, and then fresh MB solution (10 mg/L) was added to the photocatalyst to begin the next cycling run. Five consecutive cycles were completed and each cycle lasted for 60 min.

3. Results and Discussion

The SEM images of as-prepared sample were displayed in Figures 1(a)–1(c). It is observed that more than 80% of the product could be assigned to the triangular-prism-shaped morphology in this sample. Moreover, the lengths of bottom and chamfered edges are up to several micrometers. The XRD pattern of as-prepared triangular-prism-shaped sample was shown in Figure 1(d). All the diffraction peaks could be indexed to the cubic Ag_3PO_4 phase (JCPDS number 06-0505). Combining the SEM results, a conclusion that Ag_3PO_4 triangular prism was obtained can be drawn. The synthesis mechanisms of Ag_3PO_4 triangular prism could be explained as follows: the ultrasound assisted method could accelerate solid particles to high velocities via creating cavitation and shock waves, which leads to interparticle collision and effective fusion at the point of collision [23, 24]. This kinetic process speeds up the diffusion of Ag_3PO_4 nuclei in the reaction system, resulting in the formation of unique triangular-prism-shaped morphology, which can be attributed to the Ostwald ripening progress.

The chemical compositions of as-prepared Ag_3PO_4 triangular prism were examined by means of FTIR method. Figure 2(a) shows the FTIR spectrum of Ag_3PO_4 triangular prism. A strong and broad absorption around 3200 cm^{-1} and as sharp band at 1670 cm^{-1} are observed, which could be attributed to the stretching vibration of O–H and the bending vibration of H–O–H of residual water molecules, respectively. Besides that, two strong absorption bands are observed at 1012 and 560 cm^{-1}, which can be assigned to the molecular
vibrations of phosphate (PO$_4^{3-}$) [25, 26]. This result confirms that there are no DMF molecules adsorbed on the surfaces of Ag$_3$PO$_4$ triangular prism. The UV-vis absorption spectrum of as-prepared Ag$_3$PO$_4$ triangular prism is displayed in Figure 2(b). It reveals that the absorption edge of Ag$_3$PO$_4$ triangular prism is around 525 nm, which means that it could strongly absorb a large part of visible light (400–525 nm).

Figure 3 shows the adsorption-desorption isotherms of as-prepared Ag$_3$PO$_4$ triangular prism, N-doped TiO$_2$, and commercial TiO$_2$ (P25) in the dark. It is found that most of the adsorption of dyes occur within 40 min, and the adsorption-desorption equilibrium can be achieved within 60 min. Moreover, it is observed that the adsorption affinity follows the order N-doped TiO$_2$ > commercial TiO$_2$ (P25) > Ag$_3$PO$_4$ triangular prism. Clearly, the Ag$_3$PO$_4$ triangular prism shows lower adsorption affinity for MB compared to the N-doped TiO$_2$ and commercial TiO$_2$ (P25), which could be associated with the size of samples. The size of Ag$_3$PO$_4$ triangular prism is around several micrometers, while the size of N-doped TiO$_2$ and commercial TiO$_2$ (P25) is about 20–50 nanometers. Larger size of Ag$_3$PO$_4$ triangular prism leads to the poor adsorption of MB molecules on the surfaces of Ag$_3$PO$_4$ triangular prism, resulting in the lower adsorption affinity.

The photocatalytic activity of samples was then investigated after reaching the adsorption-desorption equilibrium in the dark. Figure 4 shows the photocatalytic degradation behavior. From Figures 4(a) and 4(b), it can be seen that self-degradation of MB and RhB was not obvious under visible-light irradiation, indicating that MB and RhB can be used as
the targeted pollutants. It is noted that the percentage of photocatalytic degradation of MB for Ag₃PO₄ triangular prism, N-doped TiO₂, and commercial TiO₂ (P25) is 93%, 58%, and 5%, respectively. Accordingly, the percentage of photocatalytic degradation of RhB for Ag₃PO₄ triangular prism, N-doped TiO₂, and commercial TiO₂ (P25) is 90%, 40%, and 5%, respectively. Therefore, the percentage of photocatalytic degradation of MB and RhB for the samples follows the following order: Ag₃PO₄ triangular prism > N-doped TiO₂ > commercial TiO₂ (P25). This result clearly indicates that the Ag₃PO₄ triangular prism shows higher photocatalytic activity under visible-light irradiation, which could attribute to the strong visible-light absorption of Ag₃PO₄ triangular prism. In contrast, N-doped TiO₂ could absorb a small part of visible light, and commercial TiO₂ (P25) cannot make use of visible light because of a large band gap (3.2 eV). Since the MB and RhB dyes may absorb visible light, the sensitization possibility for samples should be considered. Then, the photocatalytic activity of the samples was also evaluated by colorless phenol degradation to ensure the visible-light photocatalytic activity and exclude the dye sensitization under visible light. The degradation of phenol with Ag₃PO₄ triangular prism, N-doped TiO₂, and commercial TiO₂ (P25) under visible-light irradiation was presented in Figure 4(c). It is clear that the concentration of phenol decreases with the irradiation time. Moreover, the Ag₃PO₄ triangular prism sample shows slightly higher photocatalytic activity for colorless phenol degradation compared to N-doped TiO₂ and commercial TiO₂ (P25).

The enhanced photocatalytic activity of Ag₃PO₄ triangular prism could be ascribed to the optical absorption property and unique electronic structure of Ag₃PO₄ crystals. Since the optical absorption edge of Ag₃PO₄ triangular prism is around 525 nm, the sample of Ag₃PO₄ triangular prism could strongly absorb a large part of visible light (400–525 nm). In addition, the highest valence band edge potential of Ag₃PO₄ crystals is 2.67 V (versus normal hydrogen electrode), which has strong driving force for photocatalytic degradation of pollutants [27].

The photocatalytic stability of Ag₃PO₄ triangular prism was shown in Figure 5. It is observed that the photocatalytic activity of Ag₃PO₄ triangular prism is decreased slowly in five successive experimental runs. This result indicates that the photocatalytic activity of Ag₃PO₄ triangular prism is unstable, which needs to be improved in the later study.

4. Conclusions

A new morphology, Ag₃PO₄ triangular prism, was successfully synthesized in the mixture solvent of DMF and H₂O under ultrasonic condition within 4 h. This synthetic method does not need the assistance of any hard/soft template. Although the Ag₃PO₄ triangular prism shows lower adsorption affinity for MB molecules, the photocatalytic results indicate that Ag₃PO₄ triangular prism shows enhanced photocatalytic activity compared with N-doped TiO₂ and commercial TiO₂ (P25). In addition, the photocatalytic stability of Ag₃PO₄ triangular prism needs to be further improved by various methods in the later study.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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