Synthesis and photocatalytic activity of Ag₃PO₄/TiOF₂ composites with enhanced stability

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Ag₃PO₄/TiOF₂ composite photocatalysts were synthesized by a facile chemical precipitation approach using as-prepared TiOF₂ cubes as precursor. The as-synthesized Ag₃PO₄/TiOF₂ composites were characterized by X-ray diffraction pattern (XRD), field emission scanning electron microscopy (SEM), and UV-vis absorption spectra. The photocatalytic activity and stability of as-synthesized samples were evaluated by photo-degradation of organic methylene blue (MB) under visible light irradiation. Results showed that pure Ag₃PO₄ exhibited poor photocatalytic stability. However, when Ag₃PO₄ and TiOF₂ were compounded, the stability of composite photocatalysts was highly enhanced. Furthermore, the reason for enhanced photocatalytic stability of Ag₃PO₄/TiOF₂ composites was discussed.

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1. Introduction

Nowadays, environmental pollution is affecting human survival and development. Photocatalysis is considered as an efficient, stable, and environmentally friendly method for controlling environmental pollutants [1]. In the past, TiO₂ has been widely used as a photocatalyst in the photo-degradation of organic pollutants. However, TiO₂ cannot make use of visible light which accounts for 45% of solar spectrum because of a large band gap (3.2 eV). Therefore, the discovery of new efficient visible-light-driven photocatalysts attracts much attention.

In the year of 2010, a breakthrough on visible-light-driven photocatalysts was made by J. Ye’s research team, who reported the use of Ag₃PO₄ as an active visible-light-driven photocatalyst for oxidation of water and photo-decomposition of organic compounds [2–4]. Their research demonstrated that Ag₃PO₄ photocatalyst exhibited high quantum efficiency under visible light irradiation. However, it must be noted that the biggest shortcoming of Ag₃PO₄ photocatalyst is its instability during photocatalytic reaction, which is the main hindrance for the practical application of Ag₃PO₄ as a recyclable and highly efficient photocatalyst. Therefore, it is a highly crucial task to improve the photocatalytic stability of Ag₃PO₄. Recent reports indicated that the insoluble AgX (X = Cl, Br, I) nanoshells on the surface of Ag₃PO₄ could improve its photocatalytic activity and stability [5]. In addition, various coupled systems such as Ag₃PO₄/TiO₂ [6,7], Ag₃PO₄/Ag [8], Ag₃PO₄/SnO₂ [9], Fe₃O₄/Ag₃PO₄ [10], and Ag₃PO₄/reduced graphite oxide sheets [11] composites have been developed to improve the photocatalytic activity and stability of Ag₃PO₄. It is urgent to develop novel composite systems with enhanced photocatalytic stability of Ag₃PO₄. Recently, H. Li’s research group found a new visible-light-driven TiOF₂ photocatalyst [12]. They found that TiOF₂ cubes exhibited high activity and strong durability in photocatalytic degradation of Rhodamine B (RhB) and 4-chlorophenol (4-CP) under visible light irradiation.

Compounding of Ag₃PO₄ and TiOF₂ might enhance the photocatalytic stability of Ag₃PO₄ by improving the separation of electron-hole pairs resulting from the coupling effects of Ag₃PO₄ and TiOF₂. To the best of our knowledge, there is no research on the synthesis of Ag₃PO₄/TiOF₂ composite photocatalysts. In this work, we synthesized the Ag₃PO₄/TiOF₂ composite photocatalysts for the first time and investigated the photocatalytic stability.

2. Experimental

2.1. Synthesis

Firstly, TiOF₂ cubes were synthesized by a hydrothermal method [13], which were used as precursor for preparing composite photocatalyst. Secondly, Ag₃PO₄/TiOF₂ composites were synthesized by a chemical precipitation approach. In a typical process, a quantity of 0.032 g of the as-synthesized TiOF₂ powders were dispersed into 50 mL of deionized water and sonicated for 30 min. Immediately after sonication, 1.0121 g of AgNO₃ solution (0.15 mol/L) was then added drop wise into the above
TiOF₂ composites were checked. After one cycle, the photocatalyst microscopy (SEM, Hitachi S-4800). Diffuse re D/max-2400 diffractometer (Rigaku, Japan) using Cu-Ka radiation. 

2.2. Characterization

X-ray diffraction (XRD) experiments were carried out with a D/max-2400 diffractometer (Rigaku, Japan) using Cu-Ka radiation. The morphologies of samples were examined by scanning electron microscopy (SEM, Hitachi S-4800). Diffuse reflectance ultraviolet–visible (UV–vis) absorption spectra of as-prepared samples were measured using a Perkin Elmer 950 spectrometer, while BaSO₄ was used as a reference.

2.3. Photocatalytic degradation

In a typical photocatalytic degradation process, 20 mg of photocatalyst was suspended in the MB solution (10 mg/L, 90 mL). Before irradiation, the suspensions were stirred in the dark for 1 h to ensure the establishment of adsorption–desorption equilibrium. A 500 W Xe lamp with a cutoff filter of 420 nm was employed for the visible–light irradiation source and positioned 17 cm away from the reactor. The concentration of MB solution at some points was analyzed by measuring the light absorption of clear MB solution at 664 nm using a spectrophotometer. The percentage of degradation was calculated by C/C₀. Here, C is the concentration of remaining MB solution at each irradiated time interval (20 min), while C₀ is the initial concentration. To test the stability and reusability of samples, the cycling runs in photocatalytic degradation of MB in the presence of pure TiOF₂, pure Ag₃PO₄, and Ag₃PO₄/TiOF₂ composites were checked. 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.

3. Results and discussion

The XRD patterns of as-prepared pure TiOF₂, pure Ag₃PO₄, and Ag₃PO₄/TiOF₂ composites at various molar ratios were shown in Fig. 1. All the diffraction peaks of as-prepared pure TiOF₂ sample could be indexed to the TiOF₂ phase (JCPDS no. 01-0490), and the pure Ag₃PO₄ sample can be indexed to the cubic Ag₃PO₄ phase (JCPDS no. 06-0505). Moreover, it is found that the composite samples displayed two phases of cubic Ag₃PO₄ phase and TiOF₂ phase, confirming the formation of Ag₃PO₄/TiOF₂ composites. Furthermore, the intensity of diffraction peaks (such as (1 0 0) and (2 1 0) planes) attributed to TiOF₂ phase increased gradually with the increase in the ratio of TiOF₂ in the composite.

The SEM images of pure Ag₃PO₄ and Ag₃PO₄/TiOF₂ composites were displayed in Fig. 2. It is observed that the particle size of as-prepared pure Ag₃PO₄ is in the range of 300–500 nm (Fig. 2a). In the Ag₃PO₄/TiOF₂ composite samples, the spherical Ag₃PO₄ particles are dispersed on the surfaces of TiOF₂ cubes, and the edge length of TiOF₂ cube is about 3–5 μm. In addition, it is noted that the number of TiOF₂ cubes increases with the increase in the ratio of TiOF₂ in the composite.

The photocatalytic activity was investigated after the sample suspension reached adsorption–desorption equilibrium in the dark. From Fig. 3, it is found that the self-degradation of MB is not obvious, indicating the MB molecules are stable under visible light irradiation and can be used as a pollution model to test the photocatalytic activity of samples. The percentage of photocatalytic degradation of MB for as-prepared samples after irradiation for 2 h follows the order pure Ag₃PO₄ > Ag₃PO₄/TiOF₂ (5:1) > Ag₃PO₄/TiOF₂ (1:1) > Ag₃PO₄/TiOF₂ (1:5) > pure TiOF₂. As shown in Fig. 3, it means that pure Ag₃PO₄ exhibits higher photocatalytic activity than Ag₃PO₄/TiOF₂ composites. Moreover, it is noted that the percentage of photocatalytic degradation decreases gradually for pure Ag₃PO₄, which means poor photocatalytic stability of pure Ag₃PO₄. The percentage of photocatalytic degradation after eight cycling runs for pure Ag₃PO₄ is almost close to zero. In contrast, the percentage of photocatalytic degradation after 8 cycling runs for Ag₃PO₄/TiOF₂ (5:1) composite is about 76%, which is nearly identical to that after the first cycling run. It means that the photocatalytic activity of Ag₃PO₄/TiOF₂ composites remains unchanged during cycling runs of photocatalytic reactions. In short, the photocatalytic stability of Ag₃PO₄/TiOF₂ composite photocatalyst was highly enhanced compared with that of pure Ag₃PO₄.

The UV–vis absorption spectra of pure TiOF₂, pure Ag₃PO₄, and Ag₃PO₄/TiOF₂ composites at various molar ratios before and after cycling runs of photocatalytic reaction were shown in Fig. S1 in the Supplementary data. It is observed that the plasmon resonance band at 450 nm attributed to the Ag nanoparticles [14] was clearly observed in the sample of pure Ag₃PO₄. However, the plasmon resonance band was not observed in the samples of pure TiOF₂ and Ag₃PO₄/TiOF₂ composites. This result clearly indicated that the partial reduction of Ag₃PO₄ into metallic Ag particles in the sample of Ag₃PO₄ had taken place during the photocatalytic degradation process. In contrast, there is no Ag particles appeared in the samples of Ag₃PO₄/TiOF₂ composites after photocatalytic reactions, suggesting the photocatalytic stability of Ag₃PO₄/TiOF₂ composite photocatalysts was highly enhanced compared with that of pure Ag₃PO₄.

The promoting photocatalytic stability of Ag₃PO₄/TiOF₂ composite can be explained as follows: Ag₃PO₄ and TiOF₂ have different conduction bands (Eᵥ), valence bands (Eᵥ) and Fermi levels (Eᵥ) (the detail analysis of level energies was shown in the Supplementary data). When the mixed Ag₃PO₄/TiOF₂ composite is formed, the Fermi energies of these two phases have to be the same in the boundary between the Ag₃PO₄ and TiOF₂ phases, which is similar to that in the BiVO₄/TiO₂ system [15]. This leads to both of the Eᵥ and Eᵥ of Ag₃PO₄ lie above that of TiOF₂, as shown in Fig. 4. Under visible light irradiation, a larger number of electrons are excited to the Eᵥ from the Eᵥ of Ag₃PO₄ and then transferred to the Eᵥ of TiOF₂, while the
holes left on the valence bands of Ag$_3$PO$_4$. Thus, the enriched electrons on the surface of TiOF$_2$ could facilitate their participation in a multiple-electron reduction reaction of oxygen (O$_2$ + 2H$^+$ + 2e$^-$ → H$_2$O$_2$), which effectively protects Ag$_3$PO$_4$ semiconductors to avoid its self-corrosion by a single-electron reduction reaction (Ag$^+$ + e$^-$ → Ag). Therefore, the Ag$_3$PO$_4$/TiOF$_2$ composite photocatalyst exhibits enhanced photocatalytic stability compared with that of pure Ag$_3$PO$_4$. It is thought that TiOF$_2$ was used as an electron acceptor and protected Ag$_3$PO$_4$ particles to avoid the self-corrosion of Ag$_3$PO$_4$. On the other hand, the left holes on the valence bands of Ag$_3$PO$_4$ could migrate to the surface of photocatalysts and participate in the photooxidative reaction, and then decompose the MB molecules.

4. Conclusions

Ag$_3$PO$_4$/TiOF$_2$ composite photocatalysts were successfully synthesized by a chemical precipitation method. XRD patterns showed that the composed samples had two phases of cubic Ag$_3$PO$_4$ and TiOF$_2$ phase. SEM images indicated that the nano-sized Ag$_3$PO$_4$ particles were deposited on the surfaces of TiOF$_2$ cubes. Moreover, photocatalytic result indicated that the photocatalytic stability of Ag$_3$PO$_4$/TiOF$_2$ composites was highly enhanced compared with that of pure Ag$_3$PO$_4$. It is considered that the enriched electrons participate in
a multiple-electron reduction reaction in the Ag₃PO₄/TiOF₂ composite, and thus effectively protects Ag₃PO₄ to avoid its self-corrosion by a single-electron reduction reaction.

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**Appendix A. Supporting information**

Supplementary data associated with this article can be found in the online version at [http://dx.doi.org/10.1016/j.matlet.2014.12.063](http://dx.doi.org/10.1016/j.matlet.2014.12.063).

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