The pH dependence of Ag₃PO₄ synthesis on visible light photocatalytic activities

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Abstract. The Ag₃PO₄ morphology modification may affect the photocatalytic activity due to changing the surface energy. It may be designed by coprecipitation under different pH solutions. The pH dependence of Ag₃PO₄ synthesis on photocatalytic reactivities was investigated. The Ag₃PO₄ catalysts were synthesized in water-ethanol mixture solution under variation of pH from 3 to 11. The products were characterized using XRD, DRS, SEM, and BET specific surface area. Photocatalytic activities were studied using the degradation of RhB under visible light irradiation. The results showed that the mixed morphologies of the sphere, cube, tetrahedron, and irregular were formed. The highest activity of Ag₃PO₄ was obtained from the synthesis at a pH of 11, which may be caused by a smaller particle size and a higher amount of tetrahedron.

1. Introduction

Recently, Ag₃PO₄ photocatalyst has been widely developed by researchers. Due to low bandgap energy, the Ag₃PO₄ can be utilized for water treatment technology under solar light irradiation. The photocatalytic ability of this catalyst depends on the morphology, size, and composite design. The morphology of Ag₃PO₄ can be controlled by different starting material, concentration, and additive addition. The morphology of the cube was successfully prepared under ammonia [1]. This morphology has higher activity compared to the irregular shape. Other researchers can design the rhombic dodecahedron that improves the catalytic activity [2], higher than that of the cube. It is because the rhombic dodecahedron has higher surface energy. The surface energy of (110) facet in rhombic dodecahedron is higher than that of (100) facet in the cube. The morphology of Ag₃PO₄ can be controlled using the different concentrations of KH₂PO₄ starting material [3]. In this case, the Ag₃PO₄ synthesized with 0.15 M of KH₂PO₄ showed the highest catalytic activity. The mixed morphology of sphere and tetrahedron with a smaller size, defect, and high crystallinity was produced by this method. The addition of additive in the preparation of Ag₃PO₄ enhanced catalytic activity. For instance, the tartaric acid additive can grow the hollow microspheres of Ag₃PO₄ that have high surface areas [4]. This product exhibits high efficient photocatalytic activity under visible light irradiation.

The tremendous development of Ag₃PO₄ is composite design. The composite of Ag₃PO₄/AgI [5], Ag₃PO₄/TiO₂ [6,7], AgBr/Ag₃PO₄ [8], Ag₃PO₄/BiPO₄ [9], Ag/Ag₃PO₄/WO₃ [10] and Ag₃PO₄@g-C₃N₄ core@shell [11] were successfully prepared. Ag₃PO₄/AgI can improve the catalytic reaction through a Z-scheme mechanism composed of AgI, Ag₃PO₄, and Ag. In this system, the metallic Ag nanoparticles acted as the bridge of charge transmission [5]. The heterojunction structures of Ag₃PO₄/TiO₂ can be
designed by wrapping the surface of Ag$_3$PO$_4$ with TiO$_2$ under the sol-gel method [6]. The high catalytic may be caused by the hole-transfer between the valence band (VB) of TiO$_2$ and Ag$_3$PO$_4$. Another heterostructure, Ag$_3$PO$_4$ nanoparticle/TiO$_2$ nanobelt was also successfully synthesized [7]. This heterostructure exhibited higher stability than the Ag$_3$PO$_4$ nanoparticles. The excellent properties of AgBr/Ag$_3$PO$_4$ composite were prepared using the facile coprecipitation method [8]. This material transformed into Ag/AgBr/Ag$_3$PO$_4$ system that improves the stability of photocatalytic reaction. The composite of Ag$_3$PO$_4$ quantum dots/BiPO$_4$, which has a p–n junction properties, can be prepared by coprecipitation [9]. The excellent photocatalytic activity of this photocatalyst is mainly caused by a strong visible-light absorption of Ag$_3$PO$_4$ quantum dot and high separation of photogenerated electron-hole pairs. The composite of Ag/Ag$_3$PO$_4$/WO$_3$ prepared by a union of deposition-precipitation and photo-reduction method enhanced photocatalytic performance [10]. The high catalytic activity was caused by the synergistic effect of Ag$_3$PO$_4$ and WO$_3$ and the bridge of Ag nanoparticles. The type of core-shell composite of Ag$_3$PO$_4$@g-C$_3$N$_4$ promoted high strong interaction and high contact of the interface that enhanced the photogenerated charge separation [11].

Up to now, researchers have still developed the method of improvement in this catalyst. The pH of the solution in coprecipitation might affect the morphology. It is very challenging because the pH treatment is an easy process of synthesis. A facile sonochemical method was used to synthesize Ag$_3$PO$_4$ particles at a pH of 3,7,11 [12]. The samples prepared at pH of 7 and 11 exhibited similar morphology and size with the average particle size of ~300 nm. In contrast, the sample prepared at a pH of 3 is composed of polyhedral micro-particles with a larger size of 5–8 μm. Inspired by this finding, it is very challenging to synthesize the Ag$_3$PO$_4$ at different pH using the coprecipitation method. The coprecipitation method is the low-cost method due to no energy utilized in the preparation. This paper presented the pH dependence of Ag$_3$PO$_4$ synthesis under the coprecipitation method. The pH solution significantly affects the properties of Ag$_3$PO$_4$. The highest catalytic activity was obtained at a pH of 11.

2. Materials and Methods

2.1. Material Preparation

The starting material of AgNO$_3$ with 3.36 g was dissolved in 25 mL of a water-ethanol mixture (1: 1). The pH variation was setting on the ethanol-water mix with the addition of 0.1 M HNO$_3$ to obtain the solution of pH 3 and 5 and using 0.1 M NaOH to adjust the pH of 9 and 11. The solution of phosphate ion was created using 1 g of H$_3$PO$_4$ dissolved in 25 mL of ethanol. The phosphate solution was slowly added to the solution of AgNO$_3$ in water-ethanol under stirring for 30 minutes. The precipitate was separated and washed with deionized water three. The precipitates were dried in an oven at 105°C for 7 hours.

2.2. Material Characterization

The Ag$_3$PO$_4$ structures were investigated using by X-ray Diffractometer (XRD) (Cu Ka, λ=1.5406 Å). The shape of the crystal was studied using the Scanning Electron Microscopy (SEM). The absorption and bandgap energy were determined using the Diffuse Reflectance Spectroscopy (DRS). Surface area samples were determined using the BET method.

2.3. Photocatalytic Activity

Photocatalytic activities were evaluated through the degradation of Rhodamine B (RhB) [3]. The RhB solutions with 10 mg/L and 100 mL of volume were introduced into a beaker glass and stirred. The blue light of the LED lamp was put at 10 cm above the surface of the RhB solution. The reaction was carried out in the dark for 30 minutes and continue with the reaction in the light. Every 10 minutes, 5 ml of the samples were centrifuged (1500 rpm, 60 minutes), and then the absorbance of RhB was measured by UV-Vis. The photocatalyst stability was evaluated under three cycles of the catalytic reaction.
3. Results and Discussion
The body-centered cubic structures (JCPDS No. 06-0505) were identified in all of Ag₃PO₄ synthesized under different pH solutions (figure 1), indicating that the variation of pH solution did not affect the structure of Ag₃PO₄. The impurities were not observed in the samples, suggesting that the samples were in a high purity crystalline.

![Figure 1](image1.png)

**Figure 1.** X-ray diffraction of Ag₃PO₄ synthesized under water-ethanol solution in the different pH solutions.

![Figure 2](image2.png)

**Figure 2.** DRS of Ag₃PO₄ synthesized under water-ethanol solution at different pH solutions.

Figure 2 showed the absorption of Ag₃PO₄ synthesized at different pH solutions. There is a difference absorption edge among the samples, the sample prepared at pH of 7 showed higher absorption in the visible region of wavelength. It indicates that the different pH solution affects the absorption and bandgap energy. The bandgap energies of the samples are shown in table 1.

| pH solution of synthesis | Bandgap energy (eV) | Rate constant (min⁻¹) |
|--------------------------|---------------------|-----------------------|
| 3                        | 2.29                | 0.0365                |
| 5                        | 2.30                | 0.0385                |
| 7                        | 2.27                | 0.0383                |
| 9                        | 2.29                | 0.1051                |
| 11                       | 2.31                | 0.1176                |

*Table 1. Bandgap energies and rate constants of Ag₃PO₄ synthesized in a variety of pH.*

Figure 3 showed the morphology of Ag₃PO₄ prepared at a pH of 3, 7, and 11. The morphologies of sphere, cubes, tetrahedron, and irregular were formed. The sample prepared at pH of 3 was dominated by irregular, whereas the cubes and the tetrahedron were not perfectly created. With increasing the pH solution, the tetrahedron concentration increases. The higher amounts of the tetrahedron with the smaller particle size are found at a pH of 11. Based on these results, the morphology of Ag₃PO₄ is significantly affected by pH solution of synthesis. The acid solution might not suppress the agglomeration and producing a large particle, whereas the basic solution might prevent the agglomeration and producing...
small particles. This phenomenon is very important for the photocatalytic reaction, which is influenced by particle size and morphology. However, both acid and basic solution has produced ununiform in particle size distribution.

![Figure 3. SEM images of Ag₃PO₄ photocatalyst synthesized at pH of 3 (a), 7 (b), and 11 (c).](image)

**Table 2.** Particle size and specific surface area (S.S.A) of Ag₃PO₄ synthesized under different pH solution

| pH solution of synthesis | Particle size (μm) | S.S.A (m²/g) |
|--------------------------|--------------------|--------------|
| 3                        | 2.5 – 5.0          | 6.18         |
| 7                        | 1.5 – 4.5          | 6.56         |
| 11                       | 1.0 – 3.5          | 7.00         |

![Figure 4. The photocatalytic activity of Ag₃PO₄ synthesized under the water-ethanol solution in different pH solutions.](image)

![Figure 5. Cycling runs in the photodegradation of RhB using the Ag₃PO₄ photocatalyst prepared at a pH of 3, 7, and 11.](image)

Figure 4 showed the photocatalytic activity of Ag₃PO₄ synthesized under the water-ethanol mixture in different pH solutions. After the blue light turns on, the concentration of RhB decreases significantly,
indicating that all of the samples have photocatalytic activity. The samples prepared at pH of 9 and 11 exhibit higher catalytic activity compared to a pH of 3, 5, and 7, suggesting that the higher pH solution can improve the photocatalytic ability. This higher activity may be caused by smaller particle size and higher tetrahedron content, as shown in Fig.3(c). The smaller particle size of Ag₃PO₄ can increase the surface area (table 2), which leads to improving catalytic activity.

Figure 5 showed the photocatalytic reaction up to 3 cycles. At cycle II, the photocatalytic activity of the sample prepared at pH of 11 showed a similar ability with the cycle I, indicating that this sample has high stability. However, at cyclic III, the catalytic activity decreases. It might be caused by little loss of the catalyst when collecting the sample after the photocatalytic reaction. The photocatalytic activities of the sample prepared at a pH of 3 and 7 decreases at cycle II, implying that these samples have low stability.

4. Conclusion
The photocatalysts of Ag₃PO₄ were successfully synthesized under the water-ethanol mixture solution with the variation of pH. The results showed that the mixed morphology of sphere, cube, tetrahedron, and irregular was formed. The highest activity and stability of Ag₃PO₄ were obtained under the preparation at a pH of 11, which may be caused by smaller particle size and higher tetrahedron content.

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