Photodegradation of organic pollutants in wastewater with different morphologies of silver phosphate nanocatalysts

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Abstract. Photocatalyst can use the sunlight to photodegrade the environmental pollutants. In this article, AgNO3 and Na2HPO4 were used as raw materials to prepare different morphology Ag3PO4 nanocatalyst with different methods. They are solid phase method, conversion precipitation method and direct precipitation method. Four kinds of photocatalysts are donated as Ag3PO4-GX, Ag3PO4-SR, Ag3PO4-ZJ and Ag3PO4-ZH, respectively. The obtained materials were characterized by XRD, UV-VIS DRS, SEM and BET. XRD analyse results showed that the Ag3PO4 prepared by four methods have good crystallinity form sharp diffraction peak. UV-VIS DRS results showed that the band gap of four samples are 1.66 eV (Ag3PO4-GX), 1.91 eV (Ag3PO4-ZJ), 2.13 eV (Ag3PO4-ZH) and 3.37 eV (Ag3PO4-SR), respectively. SEM results showed that the samples prepared by direct precipitation method and hydrothermal method make Ag3PO4 particles more uniform and the samples have better morphology, more porous and uniform distribution of particles. The surface area of the samples prepared by the four methods is in the range of 20-35 m2/g. The photocatalytic capacity of four Ag3PO4 was investigates by methyl orange, methyl blue and ofloxacin. The photodegradation experiment showed that the Ag3PO4 photocatalyst prepared by direct precipitation method exhibited best degradation efficiency under the visible light irradiation. The mechanism of the remarkable photocatalysis was also explored by determining the role of active radicals. The results showed that h+ was the main active oxidation species in the presence of aerobic degradation of levofoxacin, while ·OH active species had little effect on the degradation of pollutants.

1. Introduction

With the improvement of people's living standards, environmental pollution has also occurred around us, and the organic pollutants produced have a great impact on the environment. Although there has a great deal of research on the environmental pollution treatment, there are still some problems such as slow degradation of environmental pollutants and difficulty in deep sewage treatment with traditional flocculation technology. Among numerous environmental pollution problems, water pollution is one of the most urgent problems to be solved [1]. Therefore, the effective treatment of organic pollutants in water pollution would directly affect the development of human society. In recent years, semiconductor photocatalytic technology that converts solar energy into hydrogen energy has provided a new way to control water pollution and energy scarcity at the same time. On the one hand, photocatalysts use solar oxidation to degrade organic pollutants. On the other hand, photocatalyst directly decomposes water to produce clean and pollution-free hydrogen under the action of solar energy, converts solar energy into chemical energy, and optimizes energy structure, which is of great
significance for solving environmental problems. Efficient use of solar energy is an ideal and scalable strategy to deal with the growing global energy demand and the crisis of serious environmental problems [2].

At present, Titanium dioxide has a wide application prospect in the field of photocatalysis [3], but due to its low quantum efficiency and narrow range of light reaction, it has defective in terms of expansion to production [4]. As a photocatalyst with strong photocatalytic ability under visible light, silver phosphate can absorb light with a wavelength of less than 530 nm in solar energy, high light raw electronic - hole on the separation efficiency, high photocatalytic activity, visible light response etc. The structure, morphology and surface properties of materials, the impact on the performance of silver phosphate and reactivity, the material characteristics of different preparation methods were different; the activity is also different, so the research on the different preparation methods of silver phosphate has been the broad masses of workers.

Kumar [5] synthesised layered cube Ag₃PO₄ microcrystals by adding Na₃HPO₄ solution to ([Ag(NH₃)₂]NO₃) solution which formed by mixing ammonia to silver nitrate solution. Yi [6] adopted density functional theory to study the physical and chemical properties of Ag₃PO₄ photocatalyst. The results showed that the material is an indirect band semiconductor. In this case, Ag₃PO₄ has a strong photooxidation ability in visible light due to the addition of phosphorus in adjusting the band gap structure and redox ability. Dinh [7] prepared highly active Ag₃PO₄ nanoparticles with a size of 8-16 nm by means of oleylamine in AgNO₃ toluene solution and H₃PO₄ ethanol solution. Hua [8] prepared Ag₃PO₄ product with porous microtubules with the adding of PEG200. The removing effect of rhodamine B via microtubules Ag₃PO₄ was better than that of tetrapod Ag₃PO₄. It has been reported that Ag₃PO₄ can be obtained by solid phase method, but the particles of Ag₃PO₄ do not obtain regular morphology and large size [9,10]. Therefore, it is very important to explore and prepare silver phosphate with regular morphologies and excellent photocatalytic properties. Here in, we prepared four Ag₃PO₄ catalysts with different morphologies by different synthetic methods, and compared the degradation performance of four catalysts to different organic substances.

2. Experimental study

2.1. Synthesis of nanocatalysts

Ag₃PO₄ nanoparticles were prepared with AgNO₃ and Na₃HPO₄ by four different methods. There are solid phase method, hydrothermal method [11], conversion precipitation method and direct precipitation method [12]. Four kinds of photocatalysts are donated as Ag₃PO₄-GX, Ag₃PO₄-SR, Ag₃PO₄-ZJ and Ag₃PO₄-ZH, respectively.

2.2. Characterization

X-ray diffraction (XRD-7000s, Japan), with high-intensity Cu Kα radiation (λ=0.02 nm) under the condition of tube voltage 40 KV and tube current 40 mA at 2-theta angles of 20–80° with a scan rate of 5°/min. Scanning electron microscopy (SEM-VEGA3, Czech) were carried out to analysis the surface morphologies of the samples. The BET (JW-BK-122W) surface areas were obtained using several values (Multi-point) of nitrogen adsorption under the condition of relative pressure (P/P₀) range of 0.05-0.3. The samples were degassed at 200°C for 3 h before the surface area measurement.

2.3. Photocatalytic experiments

The photocatalytic performance of the samples was researched by the degradation of methylene blue (MB) dye, methyl orange (MO) and ofloxacin as model pollutants. The photocatalytic activity of the four different photocatalysts is evaluated by using 10 mg/L MO, 10 mg/L MB and 20 mg/L Ofloxacine (pH=2.5) as the photoreaction probe under visible light irradiate (150 W tungsten lamp). The photocatalytic reactions were conducted using 0.010 g of these samples suspended in 50 mL target degradation solution, and then the ultrasonic treatment was used to disperse solution for 30 min.
3. Results and discussion

3.1. Catalyst characterization

The composition and crystallinity of the particles were analyzed by XRD. Figure 1 shows the XRD profiles of four Ag\textsubscript{3}PO\textsubscript{4} samples. The diffraction peaks of Ag\textsubscript{3}PO\textsubscript{4}-GX, Ag\textsubscript{3}PO\textsubscript{4}-ZJ and Ag\textsubscript{3}PO\textsubscript{4}-ZH appeared at 2\(\theta\)=20.884°, 29.695°, 33.292°, 36.587°, 42.485°, 47.791°, 52.695°, 55.021°, 57.283°, 61.642°, 71.897°, which could be assigned to the (110), (200), (210), (211), (220), (310), (220), (321), (400), (421) crystal planes of cubic Ag\textsubscript{3}PO\textsubscript{4} (JCPDS 06-0505). In each XRD spectrum, all the samples show good crystallinity form sharp diffraction peak. However, in the samples Ag\textsubscript{3}PO\textsubscript{4}-SR, the impurity peaks appeared at 38.116, 44.277, 64.426, 77.472 corresponding to (111), (200), (220), (311) plane reflections of hexagonal Ag (JCPDS 04-0783).

![Figure 1](image.png)

**Figure 1.** The XRD spectra of Ag\textsubscript{3}PO\textsubscript{4} samples.

UV-vis absorption of four Ag\textsubscript{3}PO\textsubscript{4} samples is demonstrated in figure 2. The band gap energy was calculated using Tauc’s relation \((\alpha h\nu)^2=A(h\nu-E_g)\) [13]. The band gap of four samples are 1.66 eV (Ag\textsubscript{3}PO\textsubscript{4}-GX), 1.91 eV (Ag\textsubscript{3}PO\textsubscript{4}-ZJ), 2.13 eV (Ag\textsubscript{3}PO\textsubscript{4}-ZH) and 3.37 eV (Ag\textsubscript{3}PO\textsubscript{4}-SR), respectively. In order to inspected The morphologies of the four samples were obtained by SEM observation [14]. As showed in the figure 3(a), the particle size and shapes of Ag\textsubscript{3}PO\textsubscript{4}-GX was not the same and the size distribution is between 1-10 μm, which prepared by solid state method. Ag\textsubscript{3}PO\textsubscript{4}-ZJ samples prepared by direct precipitation method are much more uniform cube shaped particle with the diameter about 8 μm (figure 3(b)). Ag\textsubscript{3}PO\textsubscript{4}-ZH samples prepared by transformation precipitation particles are cubic and spherical mixture, and the size distribution is between 2-5 μm (figure 3(c)). Ag\textsubscript{3}PO\textsubscript{4}-SR samples are a pile of spherical particles with the diameter about 2 μm (figure 3(d)). In comparison with the particle morphology prepared by different methods, it can be seen that the preparation process...
of Ag₃PO₄ have great influence on the morphology. The samples synthesis by direct precipitation process and hydrothermal method make Ag₃PO₄ particles more uniform. The samples have better morphology, more porous and uniform distribution of particles,it would have better photocatalytic activity.

Figure 3. The SEM images of Ag₃PO₄ photocatalyst prepared by different methods.

Figure 4. Nitrogen adsorption desorption isothermal curves of different Ag₃PO₄ samples. Figure 5. The pore size distribution curves of different Ag₃PO₄ samples.

The specific surface area of photocatalyst is a major parameter to measure the characteristics of the material, and its size has a great impact on photocatalytic properties. Figure 4 is isothermal adsorption desorption curves of four catalysts, it can be seen from the analysis that the adsorption- desorption hysteresis loop of all samples can be classified as type IV [15]. The pore size distribution of all samples are showed in figure 5, and it was determined with the BJH method [16]. Table 1 listed the BET, pore volume, and average pore size of the samples which were calculated from N₂ isotherms. It was showed that the specific surface areas are 23.653, 23.825, 35.127, and 32.636 m²/g for Ag₃PO₄-GX, Ag₃PO₄-ZJ, Ag₃PO₄-ZH and Ag₃PO₄-SR, respectively. It could be seen the sample produced by Ag₃PO₄-ZJ has large specific surface areas than other methods, but the difference between them is not huge.
Table 1. The specific surface area and pore size of different Ag₃PO₄.

| Catalyst     | BET(m²/g) | Pore volume(cm³/g) | Average pore size(nm) |
|--------------|-----------|--------------------|-----------------------|
| Ag₃PO₄-GX   | 23.653    | 0.020              | 3.837                 |
| Ag₃PO₄-ZJ   | 23.825    | 0.019              | 3.008                 |
| Ag₃PO₄-ZH   | 35.127    | 0.033              | 3.187                 |
| Ag₃PO₄-SR   | 32.636    | 0.028              | 3.274                 |

3.2. Photocatalytic activity
It could be study from figure 6(a) that Ag₃PO₄-ZJ has prominent photocatalytic activity and the degradation rate of MO was 99.8%. The blank test that it did not have photocatalyst. The result showed it has low degradation rate under visible light. Ag₃PO₄-SR and P25 have same poor photocatalytic activity, the degradation rate of MO is only 40%.

![Figure 6. Degradation of Organic compounds over different Ag₃PO₄ under visible light (a) MO, (b) MB, (c) Ofloxacin.](image)

The degradation process of MB has also obtained under visible light to observe the photocatalytic activity over four samples. The blank test indicates that it has low degradation undervisible light irradiation without photocatalysts. Figure 6(b) reveals the degradation efficiency against illumination time over different Ag₃PO₄ materials. The Ag₃PO₄-ZJ, Ag₃PO₄-ZH, Ag₃PO₄-GX and Ag₃PO₄-SR can remove 79.4%, 72.4%, 69.4% and 52.4% of MB in 2 h respectively under visible light. It’s observed easily that the Ag₃PO₄ photocatalyst has excellent performances than commodity P25.

Ofloxacin is an antibiotic useful for the treatment of a number of bacterial infections [16,17]. We studied the degradation of Ofloxacin catalytic performance over different Ag₃PO₄ catalysts which based on the absorption peaks of Ofloxacin solution at 286 nm, and the results are shown in figure 6(c). It could be observed from figure 6(c) that Ag₃PO₄-ZJ shows the best catalytic efficiency for the degradation of ofloxacin reaching to 30.1%.

3.3. Mechanism of photocatalytic activity
When the surface of the semiconductor catalyst is irradiated by the light source whose energy is higher than its absorption value, the photo-generated electron (e⁻) on the semiconductor valence band migrates to the conduction band, while the photo-generated hole (h⁺) on the semiconductor valence band could directly oxidize the organic molecule or form Hydroxyl radical (·OH) with OH⁻ in the solution. Photo-induced active radical trapping experiments were executed to measure the reactive species during the photo-degradation ofloxacin process (figure 7). The isopropanol (IPA) and ammonium oxalate (AO) are served as the hydroxyl radical (·OH) and hole (h⁺) scavenger, respectively [18]. The dosage of scavenger (concentration) was 0.01 times of ofloxacin. The degradation rate of ofloxacin was greatly reduced when the h⁺ capture agent (AO) added into solution. Compared with no capture agent, the degradation rate of several samples decreased by about 65%. When the hydroxyl radical scavenger (IPA) was added, the degradation rate of ofloxacin decreased...
slightly. It indicates that the holes (h⁺) could participate in the oxidation process for organic compound and h⁺ is the main active oxide species in the presence of ofloxacin, and the effect of the ·OH active species for the degradation of pollutants is relatively small.

Figure 7. The histograms of different trapping agents on photocatalytic reaction.

4. Conclusions
According to the above experiment, the most important conclusions could be obtained and summarized as follows:

- Four different morphology of Ag₃PO₄ photocatalysts were synthesized by four simple methods respectively. They are solid phase method, hydrothermal method, conversion precipitation method and direct precipitation method.
- Ag₃PO₄-ZJ showed a higher efficient photocatalytic activity than the other ones towards the degradation of MO, MB and ofloxacin under visible light irradiation.
- In the photocatalytic mechanism study, Through the Photo-induced active radical trapping experiments, we could get the conclusion that the photo-degradation of ofloxacin is dominant by the h⁺ oxidation process.

From the above research, we could know that the silver phosphate produced by the direct conversion method has excellent photocatalytic performance, which can provide a new idea for us to solve the water pollution, and we also understand that the h⁺ oxidation process has the dominant role in the photocatalytic degradation of pollutants. It can help us solve the problem of water pollution through photocatalytic oxidation by understanding the mechanism of photocatalytic degradation.

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