Preparation of tetrahedral Ag₃PO₄ and mechanism of photocatalytic degradation of RB-42

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Abstract: In this study, silver nitrate and sodium phosphate were used as raw materials to prepare highly active Ag₃PO₄ photocatalyst with visible light response. The structure, morphology and composition of the obtained samples were analysed by XRD, SEM and XPS. Moreover, the photocatalytic property was also investigated by means of degradation activity of reactive black-42(RB-42) in water. The effect of solution on photocatalytic degradation of RB-42 was investigated through the analysis of photocatalytic degradation kinetics. The results were showed that the nano Ag₃PO₄ is tetrahedral crystal. exhibit excellent efficient photocatalytic activity for the degradation of RB-42. when the addition of concentration of RB-42 was 10 mg·L⁻¹, pH was 5.8 and the amount of catalyst was 50mg·L⁻¹, the obtained sample removal efficiency was 80.7% under visible light irradiation. In addition, free radical capture experiments showed that •OH⁻ was the main active substance in the reaction system.

1. Introduction
A large number of synthetic organic dyes are being usually used in textiles, paints pharmaceuticals and other industries in recent years. The non-conventional process and disposal of these hazardous dye pollutants has discharged to increased levels in water contamination, and it has become a hot water environmental issue [1-5]. Accompanying with growth N3000 types, azo dyes constitute the largest groups of synthetic organic dyes. The presence of one or more azo groups (–N=N–)is a prominent feature of these dye molecules. They act as a bridge between their two organic parts and connect the aromatic ring to another organic entity [6-10]. These azo dyes could convert into different toxic aromatic amine compounds under various technique, such as oxidation/hydrolysis/other various chemical reactions, which will be one of the largest sources of ecological system contamination[11-13]. Therefore, the researchers to setting up the more efficient methods of risk to eliminate compounds from the water environment. It is obvious that advanced Oxidation Processes (AOPs) are the most preferred methods because of their rapidity and non selective degradation activity[14-19]. An effective as well as environmental compatibility photo-degradation by redox and easily reusable. Silver phosphate (Ag₃PO₄) specifically in tetrahedral shape is one of the popular catalysts under visible light irradiation. In this paper, tetrahedral Ag₃PO₄ was synthesized by precipitation method, and its composition,
morphism and properties were characterized. Combined with the degradation efficiency of RB-42 (Fig.1), the performance of Ag₃PO₄ was further assessed.

2. Experiment

2.1 Materials
AgNO₃, NH₃·H₂O, NaH₂PO₄ and ethanol were from alibaba chemicals. RB-42, sulfamethoxazole, isopropanol (IPA), benzoquinone (BQ) and Triethanolamine (TEOA) were procured from Sigma. Further, they were analytical reagent and explored without further purification in the other work, millipore water was used present experiments.

2.2 Synthesis of Ag₃PO₄
For synthesis of tetrahedral silver phosphate, initially 86mg of AgNO₃ solution was dissolved in 4 mL of ethanol simultaneous stirring. The above solution 14mL of 0.1M Na₃PO₄ ethanol solution was added and mixed rapidly. The whole preparation was took out out in a water bath maintained at 60°C. The obtained yellow product was washed three times with ethanol and dried slowly with vacuum to obtain tetrahedral Ag₃PO₄.

2.3 Characterization techniques
For X-ray diffraction (XRD) analysis was used as a BRUKER D8 (λ=1.5406 A₀) advance X-ray diffractometer with Cu Kα source. A FEI-Quanta FEG 200F Scanning electron microscope (SEM) was utilized to determined the morphology of the as-prepared samples. For X-ray Photoelectron Spectroscopy (XPS) data was employed Kratos Axis Ultra 165 spectrometer with a monochromated Al Kα X-ray source (hα=1486.6 eV).

2.4 Photocatalytic degradation of RB-42
For degradation of RB-42 a laboratory scale photoreactor equipped with a Xe lamp (250 W) (filter λ ≤ 420 nm) as a visible light source. The target pollutant was prepared into the required concentration solution and added into the self-made photocatalytic reactor. The dosage of photocatalyst was 50mg·L⁻¹. In the experiment of photocatalytic degradation of RB-42, the concentration of RB-42 was 10mg·L⁻¹, magneton was added into the reactor, the photocatalytic reaction bottle was put into the photocatalytic reactor, and the reaction temperature was adjusted to 25°C. Turn on the magnetic stirrer, put in the air, through a certain period of dark adsorption, make it reach the adsorption dissolution equilibrium, then sample and measure the absorbance, turn on the simulated solar light source, sample the target solution every 10 minutes and measure its residual concentration, and the removal rate was calculated by formula 2.1, the kinetic data was fitted with pseudo-first order kinetics shown as 2.2²⁰,²¹

\[
RM \% = \frac{C_0 - C_t}{C_0} 
\]  

(1)
\[ \ln \left( \frac{C_0}{C_t} \right) = k_t \]  

(2)

while ‘\( C_0 \)' is RB-42 initial concentration, ‘\( C_t \)' is the concentration at time ‘\( t \)' in which ‘\( k \)' is rate constant; where \( \ln \left( \frac{C_0}{C_t} \right) = k_t \), ‘\( C_0 \)' is RB-42 initial concentration, ‘\( C_t \)' is the concentration at time ‘\( t \)' , ‘\( k \)' is rate constant.

3. Results and discussion

3.1 XRD analysis

To understand the composition of the prepared photocatalysts, XRD analysis was applied and the results were showed in Fig.2. The Ag₃PO₄ indicated the diffraction peaks at 20 in 21.0°, 29.6°, 33.6°, 36.7°, 42.4°, 47.5°, 52.8°, 55.3°, 57.6°, 61.3°, 65.6°, 69.5°, 71.5°, 73.6° and 77.6° corresponding to (110), (200), (210), (211), (220), (310), (222), (320), (321), (400), (411), (420), (421), (332) and (422) body-centered cubic planes of Ag₃PO₄ (JCPDSNo. 84-0510)surely [22].

![Fig. 2 XRD pattern of Ag₃PO₄](image)

3.2 Morphology analysis

To entirely understand micro-structure and morphology of Ag₃PO₄ nanocomposite, the prepared catalyst were analysed by SEM (Fig.3). Typical SEM images of Ag₃PO₄ clearly showed the tetrahedron morphology with (111) facet exposed with a diameter about 0.5 μm (Fig.3a and 3b).

![Fig.3 SEM images of Ag₃PO₄](image)

3.3 XPS analysis

To determine the chemical state and surface composition of Ag₃PO₄ nanoparticles, the XPS analysis was carried out for the as prepared Ag₃PO₄ to investigate the elemental composition of the composite (Fig.4). In the survey spectrum of Ag₃PO₄ all the elements are presented corresponding to the composite, which confirmed the uniform distribution of the prepared composite (Fig.4a). The Ag high resolution XPS spectrum suggested two distinct peaks at 367.3 eV and 373.3 eV corresponding to Ag 3d₅/₂ and Ag 3d₃/₂ of Ag⁰ (Fig.4b) [23]. The P 2p XPS spectra ascribed a peak at 132.4 eV corresponding
to $P^{3+}$ in $\text{PO}_4^{3-}$ (Fig. 4c) \cite{24}. The two distinct peaks at 530.5 and 531.5 eV could be showed to O 1s, which corresponded to O of the $\text{Ag}_3\text{PO}_4$(Fig. 4d).

Fig. 4 XPS patterns of (a) survey, (b) Ag 3d, (c) P 2p, (d) O 1s

### 3.4 Photocatalytic activity and degradation

The kinetics of degradation RB-42 by using the prepare catalyst are showed in Fig. 5, which represents the leftover RB-42 relative concentrations in the solution as a function of irradiation time. The results indicated clearly that catalyst without UV and UV without catalyst were also exhibited very low photodegradation efficiency in degrading RB-42 during 60 min. But the prepared catalysts about 80.3% degradation efficiency was achieved by $\text{Ag}_3\text{PO}_4$ ($k=0.01278 \text{ min}^{-1}$) after 60 min of visible light irradiation. The high catalytic activity of $\text{Ag}_3\text{PO}_4$ photocatalyst is likely due to the high separation rate of photo-induced electron hole pairs and the high migration rate of electrons on the conduction band (CB). What’s more, the superior separation efficiency of photo-induced carriers in higher valance band (VB) potential facilitates and photo-oxidation capacity of the degradation the organic compounds. A series of reactions related to hydrogen production and pollutant degradation on the semiconductor surface can be mainly expressed as follows:

Fig. 5 Degradation kinetics of RB-42 by the prepared catalysts under visible light
3.5 Photocatalytic degradation mechanism
In order to understand the main mechanism of rb-42 photocatalytic degradation of organic pollutants and further determine the main active species in the degradation process of Ag$_3$PO$_4$, various chemicals were used as radical trapping agents, BQ, IPA and TEOA used for trapping O$_2$•−, •OH and h$^+$ respectively during photocatalysis, while no trapping agent was added simultaneously as blank control group. It can be seen that hydroxyl radical plays a decisive role in the process of photocatalytic oxidation. After the addition of IPA, the photocatalytic degradation rate is greatly reduced, only 20.1%, The degradation efficiency of BQ and TEOA was 41.5% and 83.1%, respectively. Compared with the control group, the photocatalytic degradation rate of 95.8% was reduced by 75.7%, 54.3% and 12.7% respectively (Fig.6). It was proved that •OH$^-$ played a leading role in the process of photocatalytic degradation of RB-42, and then O$_2$•− and h$^+$ were also important in the photocatalytic system. In order to further prove the role of free radical in the degradation of RB-42, the degradation rate was fitted according to the first-order kinetic equation. After BQ was added, the degradation rate of RB-42 decreased from 0.023min$^{-1}$ to 0.006min$^{-1}$, and the contribution rate of •OH$^-$ in the oxidation degradation process was calculated to be about 73.9%; Similarly, the contribution rates of O$_2$•− and h$^+$ were 42.8% and 12.5% respectively. Obviously •OH$^-$ was the main active substance in the reaction system. They were suggested that the main active species for degradation was •OH$^-$ > O$_2$•− > h$^+$.

![Fig.6 Effect of different quenchers on the photocatalytic oxidation of RB-42](image)

4. Conclusion
The highly stable and efficient separable tetrahedral catalyst of Ag$_3$PO$_4$ was synthesized and utilized for detoxification of RB-42. The efficient photocatalytic activity could be attributed to the superior visible light adsorption capability and reduced charge recombination effects of Ag$_3$PO$_4$. Though the photocatalytic degradation of RB-42 within 60min was not completed, the phytotoxicity results showed the detoxification of RB-42 was achieved successfully. These results suggested that the main reactive species responsible for degradation was •OH$^-$ > O$_2$•− > h$^+$. Hence, Ag$_3$PO$_4$ could be efficiently detoxify the organic compounds. It will provide theoretical support for water treatment.

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