A facile method for the synthesis of Ag$_3$PO$_4$ visible light photocatalyst has been developed to improve the photocatalytic activity and stability. The as-prepared samples are investigated by X-ray powder diffraction, scanning electron microscopy, infrared spectroscopy, photoluminescence (PL) spectroscopy, and UV-Vis diffuse reflectance spectroscopy techniques. The results reveal that the prepared Ag$_3$PO$_4$ has cube structure with a band gap of 2.26 eV. The as-prepared samples show higher photocatalytic activity for methylene blue (MB) degradation than that of N-TiO$_2$ under visible light irradiation.

1. Introduction

Semiconductor based photocatalysts have received great attention due to their applications in environmental pollution mediation and solar energy conversion [1–6]. However, the major challenge in the practical applications is their poor efficiency in visible light range or insufficient charge separation ability. To resolve this problem, significant efforts have been devoted to the exploration and fabrication of novel photocatalytic materials for improving photocatalytic properties [7, 8]. To address this issue, diverse techniques in recent years have been focused on the exploration and fabrication of novel semiconductor catalysts to improve photocatalytic properties [9–11]. Recently, Bi and coworkers have reported the new use of a Ag$_3$PO$_4$ semiconductor in photocatalytic applications, which exhibits extremely high photooxidative capabilities for O$_2$ evolution from water as well as organic dyes decomposition under visible light irradiation [12, 13]. Otherwise, this novel photocatalyst can achieve quantum efficiency up to 90% at wavelengths longer than 420 nm, significantly higher than previously reported values. Interestingly, they have further studied the facet effect on photocatalytic performances based on single-crystalline Ag$_3$PO$_4$ rhombic dodecahedrons exposed with {110} planes and cubes bound by {100} planes [14]. Unfortunately, Ag$_3$PO$_4$ nanoparticles suffer from stability issues in practical applications because they can photochemically decompose if no sacrificial reagent is involved. Furthermore, the consumption of a large amount of noble metal, silver, strongly limits its practical environmental applications. So it remains a great challenge to develop feasible methods for the synthesis of well-defined hierarchical Ag$_3$PO$_4$ nanoparticles.

Herein, we successfully fabricated spherical Ag$_3$PO$_4$ sub-micron particles by a simple hydrothermal method. The as-prepared samples were characterized and used for photocatalytic degradation of MB under visible light irradiation.
2. Experimental

In a typical experiment, using CH₃COOAg and K₂HPO₄ as starting materials, (A) 0.50 g of CH₃COOAg (0.003 mol) is dissolved in 20 mL of deionized water and stirred for 10 minutes, and the solution pH adjusts to 9 with ammonia. (B) 0.1742 g of K₂HPO₄ (0.001 mol) is dissolved in 15 mL of deionized water and stirred for 10 minutes. Then solution (B) is added dropwise to solution (A) with stirring. After the resulting solution is magnetically stirred for 30 minutes, the suspension is transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 120°C for 24 h. After being cooled naturally to room temperature, the products are collected by centrifugation, washed with deionized water and absolute ethanol several times, and dried under vacuum at 60°C for 24 h. The as-synthesized samples are denoted as Ag₃PO₄·120.

As a comparison, a precipitation method is used to prepare to Ag₃PO₄·0.50 g of CH₃COOAg (0.003 mol) is dissolved in the beaker with 20 mL of deionized water and magnetically stirred for 10 minutes, then 0.1742 g of K₂HPO₄ (0.001 mol) and 0.5182 g C₂H₅H₂Na₂O₇·2H₂O (0.002 mol) are added to the solution. The solution pH adjusts to 5 with HNO₃ (0.01 M). The suspension is stirred for 6 h at room temperature. The products are collected by centrifugation, washed with deionized water and absolute ethanol several times, and dried under vacuum at 60°C for 24 h. The as-synthesized samples are denoted as Ag₃PO₄·P.

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Bruker D8-Advance, Germany) using Cu Ka radiation. The surface morphology was examined by a scanning electron microscopy (SEM, Quanta 250, FEI Company). UV-Vis diffuse reflectance spectra (DRS) were recorded with a UV-Vis spectrophotometer by using BaSO₄ as the reference (UV-2500, Shimadzu). The Fourier transform infrared (FTIR) spectrum was recorded with a GX spectrophotometer (Nicolet 100, Perkin-Elmer) with the KBr wafer technique. The photoluminescence (PL) spectrum was conducted on a Hitachi F-2500 fluorescence spectroscope.

The photocatalytic reaction was conducted in a 200 mL cylindrical glass vessel fixed in the XPA-II photochemical reactor. A 500 W Xe lamp was used as the simulated solar light source (UV-visible light), and a house-made filter was mounted on the lamp to eliminate infrared irradiation. The visible-light was obtained by using the cut-off filter. The cut-off filter was made up of 1 M sodium nitrite solution which can absorb the light with wavelength under 400 nm [15, 16]. This solution was injected into the interlayer of the quartz cool trap and was placed behind the water filter to completely remove the UV portion of the radiation and to supply a visible-light source. MB with the concentration of 20 mg/L was used as contamination. In order to obtain an optimally dispersed system and reach complete adsorption/desorption equilibration, 20 mg photocatalyst powder dispersed in 200 mL reaction solutions by supersonic for 15 min and then the suspension was magnetically stirred in dark for 1 h. During the photocatalytic reaction, air was blown into the reaction medium at a flow rate of 200 mL/min. At regular intervals, 8 mL of the suspension was filtered and then centrifuged. The concentration of the remaining MB was measured by its absorbance (A) at 664 nm with a Hitachi UV-2550 spectrophotometer. The degradation ratio of MB can be calculated by X = (A₀ - A)/A₀ × 100%.

3. Results and Discussion

3.1. SEM and XRD Analyses of the As-Synthesized Samples. The XRD patterns of the as-prepared samples synthesized by different methods are shown in Figure 1. It is clear to see that all of the diffraction peaks of Ag₃PO₄·120 corresponded to the cubic phase of Ag₃PO₄ (JCPDS number 06-0505) [14], as well as the characteristic diffraction peaks (110), (200), (210), (211), (310), (222), (320), (321), (400), and (420) (Figure 1(a)). The crystal type of Ag₃PO₄·P is the same as that of Ag₃PO₄·120. It is noted that the as-prepared samples are all of the cubic phase of Ag₃PO₄.

Figure 2 shows the typical SEM images of Ag₃PO₄·P products synthesized by different reacting temperatures of hydrothermal method. It can be truly seen that the single-crystalline Ag₃PO₄ submicromes with spherical and smooth surfaces have been fabricated in large quantities, and their main diameters range from 500 to 800 nm (Figure 2(a)). With the increase of the reaction temperature, the morphology of crystalline Ag₃PO₄ was unchanged obviously (Figures 2(a)–2(c)). However, the diameters of single-crystalline Ag₃PO₄ are more and more large. Ag₃PO₄·P is irregular oval ball and the main diameters range from 5 μm (Figure 2(d)).

3.2. DRS and IR Analyses of the As-Prepared Samples. Figure 3 shows the UV-Vis absorption spectra of Ag₃PO₄·120, Ag₃PO₄·P, and N-TiO₂. The UV-Vis spectrum of the Ag₃PO₄·120 indicates that it absorbs sunlight with a wavelength less than 548 nm, corresponding to 2.26 eV of band gap energy. This result does not agree with the light-absorption property of Ag₃PO₄ powders reported by another group [17]. This maybe was attributed to the surface plasmon resonance effect.
of the coexistence of silver [18, 19]. However, the absorption band edge of Ag₃PO₄-P is the same as Ag₃PO₄-120; N-TiO₂ appears at 424 nm based on its UV-Vis spectrum, respectively.

This feature of UV-Vis light absorption properties of the as-prepared samples suggests that the Ag₃PO₄-120 photocatalyst could be used for visible light photocatalytic reactions.

The IR patterns of the Ag₃PO₄-120, Ag₃PO₄-P are shown in Figure 4. The IR peaks of the samples prepared by hydrothermal and precipitation methods have all appeared in 551 cm⁻¹ and 1015 cm⁻¹, which is attributable to the P–O antisymmetric stretching mode of PO₄³⁻. The IR peak at 846 cm⁻¹ may be C–O vibration, which is the impurities of precursor. The peaks appearing at 1399 cm⁻¹ and 1655 cm⁻¹ are due to torsional vibration H₃O⁺. The weak signal of C–H bond is observed at 3230 cm⁻¹ [20, 21].

3.3. Photocatalytic Activities of the As-Synthesized Samples. Figure 5 shows the effect of reacting temperature of hydrothermal on the rate of MB degradation under visible light irradiation. The photodegradation efficiency of Ag₃PO₄-120 is 92% after 4 min illumination, but that of Ag₃PO₄-180 is only 35%. After 10 min irradiation, the photodegradation efficiency of Ag₃PO₄-120 can nearly reach 95%; Ag₃PO₄-100 and Ag₃PO₄-160 both reach about 90%. Ag₃PO₄-120 has higher photocatalytic efficiency than other different reacting temperatures of samples. For comparison, the photocatalytic performances of Ag₃PO₄-P and commercial N-doped TiO₂
catalysts have also been studied and compared in Figure 6. As shown in Figure 6, it can be clearly seen that except for N-doped TiO$_2$ catalysts, all these Ag$_3$PO$_4$ samples exhibit excellent photocatalytic activities for the MB degradation. Ag$_3$PO$_4$-120 especially exhibits the highest photocatalytic activity, which can nearly completely degrade MB dye in only 4 min. The absorption variation of MB dye over Ag$_3$PO$_4$-120 at different irradiation times is shown in Figure 7. The Ag$_3$PO$_4$-120 sample needs about 6 min that the MB dye is nearly colorless. At present, we consider that Ag$_3$PO$_4$-120 can effectively improve light harvesting as a result of its high surface area. On the other hand, such novel spherical structures could promote the separation of photoexcited carriers and minimize the probability of electron-hole recombination [22]. However, the photocatalytic mechanism over Ag$_3$PO$_4$-120 structure cannot be completely understood and a more detailed study is still needed.

As reusability of photocatalyst is a key issue for practical application, Figure 8 shows that the reusability of Ag$_3$PO$_4$-120 for degradation of MB under visible light irradiation. As no obvious decrease of degradation is observed after three runs, the Ag$_3$PO$_4$ nanoparticles can be concluded to be stable during the photocatalytic reaction.

Notably, the photocatalytic activity of Ag$_3$PO$_4$-120 is higher than that of Ag$_3$PO$_4$-P and N-TiO$_2$, which can be explained from the PL analysis. The PL spectra are widely used to investigate the migration, transfer, and recombination processes of the photogenerated electron-hole pairs in a semiconductor, since PL emission arises from the recombination of free carriers. Figure 9 shows the PL spectra of Ag$_3$PO$_4$-120, Ag$_3$PO$_4$-P, and N-TiO$_2$ excited by 254 nm. As shown in Figure 9, it is clear to see that there is a significant decrease in the PL intensity of Ag$_3$PO$_4$-120 compared to that of Ag$_3$PO$_4$-P and N-TiO$_2$. A weaker intensity of the peak represents a
lower recombination probability of photogenerated charge carriers. The lower of the observed PL intensity can be associated with the electron transfer process from excited CB to VB in Ag$_3$PO$_4$ lattice, through which the process of electron transfer takes place. Hence, the samples prepared by this method prevent the charge carrier recombination probabilities and improve the separation of charge carriers. The decrease in intensity can also be attributed to the generation of new defect or vacancy sites like oxide ion vacancy [22]. Therefore, Ag$_3$PO$_4$-120 could effectively inhibit the recombination of photogenerated charge carriers, which helps the separation of photogenerated electron-hole pairs. It can be established that Ag$_3$PO$_4$-120 is very promising for the photocatalysis with satisfying efficiency.

4. Conclusion

In summary, we have demonstrated a facile and efficient hydrothermal method for fabricating Ag$_3$PO$_4$ submicron particles at low temperature. Moreover, its photocatalytic performance studies indicated that this novel Ag$_3$PO$_4$ structures exhibited much higher activities than that of Ag$_3$PO$_4$-P and N-doped TiO$_2$ for the organic contaminant degradation under visible light irradiation. This study clearly reveals that the rational fabrication of semiconductor nanostructure may be an effective technique for the development of highly efficient visible light sensitive photocatalysts.

Conflict of Interests

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

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References

[9] D. Ingram and S. Linic, "Water splitting on composite plasmonic-metal/semiconductor photoelectrodes: evidence for selective plasmon-induced formation of charge carriers near the


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