

Facile synthesis of porous Ag_3PO_4 particles and its application in MB wastewater degradation under visible light irradiation*

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Porous Ag_3PO_4 nanoparticles were synthesized via polystyrene (PS) templates assisted method in the aqueous solution. The crystal structure, composition, physical property and morphologic properties of the synthesized PNPs were characterized by XRD, FT-IR, N_2 adsorption-desorption and SEM. Under visible light, the porous Ag_3PO_4 nanoparticles exhibit enhanced adsorption performance and photo catalytic activity towards the degradation of MB stimulant dyeing wastewater, which is mainly ascribed to PNPs present the enhanced pore structures and increased active sites.

Keywords: Ag_3PO_4 ; Polystyrene; MB Degradation; Visible Light.

1. Introduction

In the past decades, photocatalysis has been considered as a cost-effective alternative for the purification of dye-containing wastewater[1, 2]. TiO_2 -based photocatalysts have been widely used for photo-catalytic degradation of dyes; however, TiO_2 with a relatively wide band gap of 3.2 eV limits its efficient utilization of sunlight[3]. Therefore, it is highly desirable to design new visible-light-induced photocatalysts from the viewpoint of using visible light.

Currently, Ag-based semiconductors, exhibiting strong visible light absorption and obvious visible light catalytic activity, have been gained great attention due to its good potential application in removal and degradation of pollutants in water[4]. Of the well-known Ag-based photocatalysts, silver orthophosphate (Ag_3PO_4) with high photooxidative capabilities for organic dye decomposition under visible light irradiation attracted considerable attention since it was reported by Yi et al.[5, 6]. Up to now, various methods have been

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proposed in order to further enhance and optimize the photocatalytic properties of Ag_3PO_4 under visible light radiation via modification to increase surface area.

Porous semiconductor-based photocatalysts are promising materials for destroying and transforming hazardous chemical wastes due to their excellent photocatalytic activity. These materials exhibit good photocatalytic activity but remain far from efficient for practical applications. Therefore, preparations for Ag_3PO_4 porous particles with low cost and excellent photocatalytic activity will not only further enlarge the scope of applications, but also bring economic benefits.

In this study, we attempted via PS templates assisted method to prepare porous Ag_3PO_4 nanoparticles, and investigated the feasibility of using the prepared porous Ag_3PO_4 nanoparticles as catalysts for the degradation of MB solution under visible light irradiation.

2. Experimental

2.1. Materials

All chemical reagents were analytical grade without further purification. Deionized (DI) water was used in the whole experiment.

2.2. Preparation of porous Ag_3PO_4 nanoparticles

Polystyrene microspheres were synthesized by a conventional chemical approach (emulsion polymerization) which has been reported in our previous work[7]. PS/ Ag_3PO_4 composite nanoparticles were synthesized by a simple deposition–precipitation process as following: Firstly, 1.0 mL prepared PS emulsion and 0.5 g PVP were suspended in 50 mL distilled water, followed by the addition of 0.2 g AgNO_3 and required amount of Na_2HPO_4 solution (0.03 M) was added drop by drop to this suspension under stirring. The mixture solution was stirred for 4 h under dark condition and centrifuged at 5000 rpm. The obtained products were washed several times with distilled water and absolute ethyl alcohol and dried at 60°C for 12 h.

At last, porous Ag_3PO_4 nanoparticles were obtained by calcining PS/ Ag_3PO_4 composite nanoparticles at 550 °C for 4 h to remove polymer cores.

2.3. Characterization of the as-prepared photocatalysts

N_2 adsorption–desorption measurements at 77K (Micromeritics Tristar ASAP 3000) using Brunauer–Emmett–Teller (BET) method. Phase determination of the as-obtained products was carried out by an X-ray diffractometer (XRD, PANalytical B.V., X'Pert Pro MPD). Microstructural characterizations of the

samples were carried out by field emission scanning electron microscopy (FE-SEM, Japan Hitachi Ltd, S4800). Fourier transform infrared (FT-IR) spectra measurements were performed on a FTS-3000 Fourier transform infrared spectrophotometer with KBr as the reference sample.

2.4. Photocatalytic activity measurements

Photocatalytic activity of the as-obtained photocatalysts was assessed by the photocatalytic degradation of the MB aqueous solution under visible light irradiation. A series of cylindrical quartz photoreactors with a volume of 80 mL were used, inside which a 500 W Xe arc lamp with a 420 nm optical filter was positioned as the visible-light source, its vessel was surrounded by a circulating water jacket to prevent warming of the reaction solution. 50 mg photocatalyst was ultrasonically dispersed in 50 mL of MB aqueous solution (20 mg L^{-1}) for 10 min and then stirred in the dark for 60 min to reach the adsorption–desorption equilibrium. The decolorization ratio of MB was evaluated by measuring the absorbance of the reaction liquid at 10 min interval. About 3 mL of solution was collected, then filtered through $0.45 \mu\text{m}$ millipore filter to remove the solid particles.

3. Results and Discussion

3.1. The results of characterizations analysis

The specific surface area of as-prepared PS/Ag₃PO₄ and porous Ag₃PO₄ samples were measured and the results were $0.416 \text{ m}^2\text{g}^{-1}$ and $5.21 \text{ m}^2\text{g}^{-1}$. Apparently porous Ag₃PO₄ is characterized by larger specific surface areas than PS/Ag₃PO₄ sample and the BET specific surface area. Figure 1a and Figure 1b show the nitrogen adsorption–desorption isotherms and the corresponding pore size distribution curves of porous Ag₃PO₄. The nitrogen adsorption–desorption isotherms of sample is type IV according to the IUPAC classification, indicating the presence of mesoporous (2~50 nm), and this finding is consistent with pore size distributions [8]. Indeed porous Ag₃PO₄ sample exhibit less wide pore size distribution from 2 to 10 nm. The partial mesoporous structure of the nanoparticles results in the increase of the surface area, which is helpful for the improvement of the diffusion of organic pollutant molecules because these porous structures contain efficient transport pathways to reactants and products.

The XRD patterns of PS, PS/Ag₃PO₄ and porous Ag₃PO₄ are shown in Figure 1c. Amorphous PS showed a very broad diffraction peak at 19° . As for porous Ag₃PO₄, all of the diffraction peaks can be clearly assigned to the cubic phase of Ag₃PO₄ (JCPDS card no. 06-0505). This phase was characterized by the appearance of Bragg diffraction peaks at $2\theta = 20.88^\circ, 29.70^\circ, 33.29^\circ, 36.59^\circ$,

47.79°, 52.70°, 55.02°, 57.28°, 61.64° and 71.90°, which were indexed to the (110), (200), (210), (211), (310), (222), (320), (321), (400) and (421) planes of Ag_3PO_4 , respectively[9]. It can be seen that PS/ Ag_3PO_4 composite exhibit similar XRD patterns to porous Ag_3PO_4 . That is to say, no diffraction peaks of PS were found in XRD patterns of the composites.

Figure 1d shows the typical FT-IR spectrums of PS, PS/ Ag_3PO_4 and porous Ag_3PO_4 . The peaks observed at 3059 and 3024 cm^{-1} were due to the stretching vibration of the aromatic C–H, while the absorption peaks at 2922 and 2848 cm^{-1} were due to the stretching vibration of the aliphatic C–H. Besides, the appearance of the band at 1600 cm^{-1} was attributed to the stretching vibration of the skeleton of benzene ring, and the peak observed at 1452 cm^{-1} was due to the bending vibration of the methylene. The absorption peaks at 756 and 697 cm^{-1} were due to the stretching vibration of the five adjacent C–H on the benzene ring. Obviously, the peaks observed at 539 cm^{-1} and 3, 418 cm^{-1} were contributed by the distortion vibration of C=C of styrene and the stretching vibration of the O–H, respectively[7]. FT-IR peaks of porous Ag_3PO_4 at 1010 and 550 cm^{-1} , which are corresponding to the stretching vibrations of PO_4^{3-} [10]. In the case of PS/ Ag_3PO_4 composites, both the typical absorption peaks of PS and Ag_3PO_4 were observed. The characteristic peaks' intensity of composites is weaker than one component.

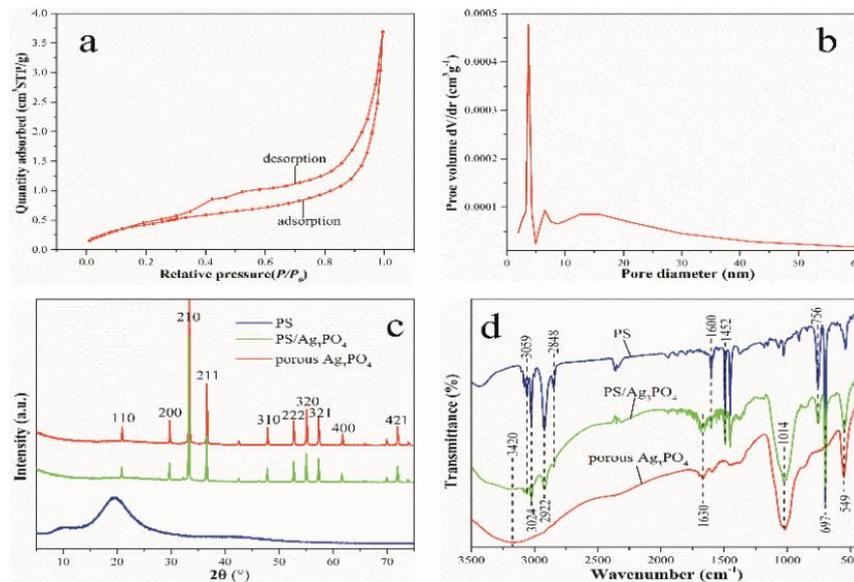


Fig. 1. Nitrogen adsorption–desorption isotherms(a) and corresponding pore size distribution curves (b) of porous Ag_3PO_4 . XRD pattern (c) and FT-IR spectra (d) of the as-prepared samples

The microstructure of PS/Ag₃PO₄ and porous Ag₃PO₄ was observed by SEM. Figure 2a. shows the irregular morphology of Ag₃PO₄ and the smooth surface of the PS nanosphere. The surfaces of some PS nanosphere are well covered by Ag₃PO₄ nanoparticles. Through calcinations, PS nanospheres were removed and the abundant pore structures are formed (Figure 2b). It is beneficial to improve surface area of Ag₃PO₄ and expose more active sites, which further enhance photocatalytic performance.

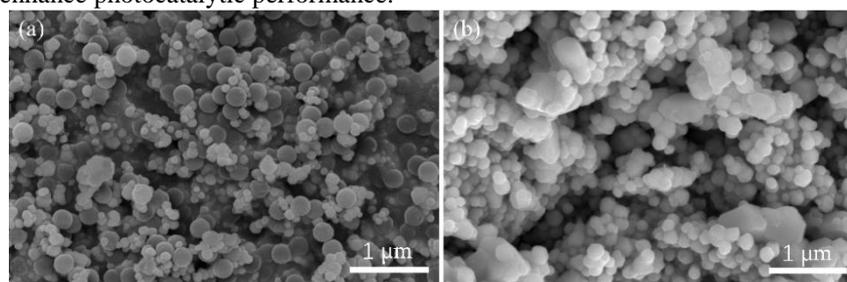


Fig. 2. SEM image of PS/Ag₃PO₄ (a) and porous Ag₃PO₄ (b).

3.2. Photocatalytic activity of as-prepared photocatalysts

It is well known that the adsorption performance of a photocatalyst towards the target pollutant molecules is one of the decisive factors to affect the photocatalytic activity. To investigate the adsorption properties of the obtained photocatalysts, their adsorption behaviors over MB in darkness were measured and presented in Figure 3a. Experimental results prove that the porous Ag₃PO₄ exhibit the strongest adsorption performance. Moreover, the larger specific surface area of the porous Ag₃PO₄ compare with PS/Ag₃PO₄ particles also facilitate the adsorption of the MB molecules.

The concentration changes of MB during the photodegradation process under visible-light irradiation are shown in Figure 3b. A negligible photodegradation of MB is observed in the absence of any photocatalyst. When PS/Ag₃PO₄ and porous Ag₃PO₄ are employed as photocatalysts, 89.6% and 96.9% of MB are decomposed after 60 min, respectively, suggesting that porous Ag₃PO₄ is a more efficient visible-light-driven photocatalyst.

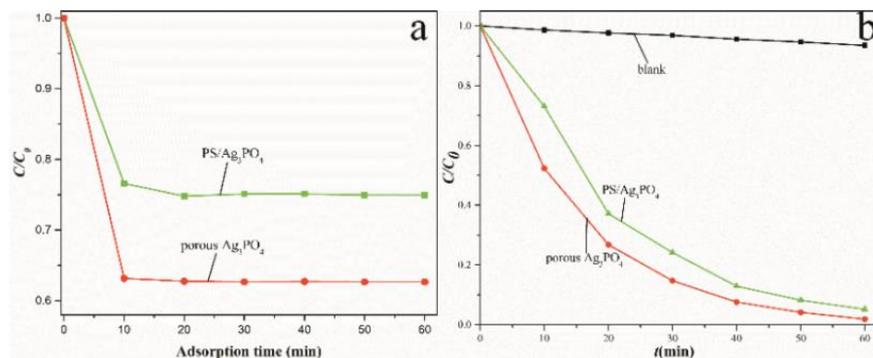


Fig. 3. Adsorption properties (a) and photocatalytic activities (b) of obtained samples for MB degradation.

4. Conclusions

Porous Ag₃PO₄ nanoparticles with high surface area were synthesized via polystyrene (PS) templates assisted method in the aqueous solution. Under visible light, the porous Ag₃PO₄ nanoparticles exhibit enhanced adsorption performance and photocatalytic activity towards the degradation of MB simulant dyeing wastewater. On the basis of the results of this study, the porous Ag₃PO₄ nanoparticles are expected to be a promising visible-light photocatalyst for environment purification field.

References

1. C. Chen, W. Ma, J. Zhao, *Chemical Society Reviews*, 39 (2010) 4206-4219.
2. M. Mehrjouei, S. Müller, D. Möller, *Chemical Engineering Journal*, 263 (2015) 209-219.
3. A. Ajmal, I. Majeed, R.N. Malik, H. Idriss, M.A. Nadeem, *RSC Advances*, 4 (2014) 37003-37026.
4. J. Li, W. Fang, C. Yu, W. Zhou, L. Zhu, Y. Xie, *Applied Surface Science*, (2015).
5. X. Chen, Y. Dai, X. Wang, *Journal of Alloys and Compounds*, 649 (2015) 910-932.
6. Z. Yi, J. Ye, N. Kikugawa, T. Kako, S. Ouyang, H. Stuart-Williams, H. Yang, J. Cao, W. Luo, Z. Li, Y. Liu, R.L. Withers, *Nat Mater*, 9 (2010) 559-564.
7. H. Wang, Q. Xu, X. Zheng, W. Han, J. Zheng, B. Jiang, Q. Xue, M. Wu, *J Nanopart Res*, 16 (2014).
8. K.S. Sing, *Pure and applied chemistry*, 57 (1985) 603-619.
9. Y. Song, Y. Lei, H. Xu, C. Wang, J. Yan, H. Zhao, Y. Xu, J. Xia, S. Yin, H. Li, *Dalton Transactions*, 44 (2015) 3057-3066.

10. Q. Liang, W. Ma, Y. Shi, Z. Li, X. Yang, *CrystEngComm*, 14 (2012) 2966-2973.