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To cite this article: Xu Guo *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **300** 032083

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A Novel Magnetically Recoverable Photocatalyst for Removal of Organic Compounds from Contaminated Water

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Abstract. A novel magnetically recoverable core-shell $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ photocatalyst has been developed featuring fast magnetic separation, stability and high photocatalytic activity under simulated solar light. This novel core-shell photocatalyst exhibited high photocatalytic activity towards degradation of chlorsulfuron (ChS) under simulated solar light. The complete degradation of ChS over the $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ photocatalyst took only about 60min. As a result, the developed photocatalytic integrated microspheres can effectively degrade organic pollutants and can be easily recovered by a magnet, and reused at least five times without appreciable reduction in photocatalytic efficiency. Therefore, the $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ photocatalyst developed in this study is a promising alternative for degrading organic pollutants.

1. Introduction

Heterogeneous photocatalysis has been considered as a cost-effective alternative for the degradation of various hazardous organic contaminants from wastewater, since the pollutants can be oxidized quickly and non-selectively [1]. Typically, the aqueous suspensions of photocatalysts are employed for the wastewater treatment. However, separation and recovery of micro- and nano- scale photocatalysts is very difficult and high cost [2]. To solve these problems, many researchers have focused on catalysts immobilization on supporting materials such as glass, aluminosilicate, silicone sealant, activated carbon and cotton. However, a considerable decrease in photocatalytic efficiency and selectivity can be observed because of the catalysts immobilization diminished the active surface area-to volume ratios. Recently, magnetic core-shell photocatalysts have been of great interest which is composed of a magnetic core and a photocatalytic shell. It has been proved that the composite magnetic photocatalysts could be separated easily by magnetic field. Ag_3PO_4 semiconductor was reported in photocatalytic applications, which can utilize visible light to rapidly decompose organic contaminants in aqueous solution [1, 3]. The motivation of the present research is developing a novel magnetically recoverable core-shell $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ photocatalyst, featuring fast magnetic separation, and high photocatalytic activity under solar light. Chlorsulfuron (ChS) is a systemic sulfonylurea herbicide for the selective pre- and post-emergence control of broad-leaved and grass weeds in cereal crops. However, its high phytotoxicity and relatively high solubility make them dangerous to water environment. Urgent needs exist also for detoxification procedures of herbicide waste.

Therefore, in the present work, to evaluate the performance of the developed magnetically recoverable photocatalysts ($\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$) for decomposing organic contaminants in aqueous



solution under simulated solar light, photocatalytic degradation experiments of Chlorsulfuron (ChS) were carried out, and the recycle ability of the magnetic photocatalysts was also investigated.

2. Experimental

2.1. Sample preparation

The Fe_3O_4 nanoparticles were synthesized using a solvothermal method [4]. 2.70g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 4.10g of $\text{NaAc} \cdot 3\text{H}_2\text{O}$ (as a dispersed agent) were added to 80mL of ethylene glycol (EG), which acted as both solvent and reductant. The solution was then sealed in a 100mL Teflon-lined stainless steel autoclave and treated for 24h at 180°C , and then cooled to room temperature. The resulting black precipitate at the bottom of the autoclave was separated by magnetic force. After that, the precipitate was washed five times with ethanol, five times with distilled water, and then dispersed in 20mL distilled water for the next step synthesis. The synthesized Fe_3O_4 aqueous solution (10mL) mentioned above was added to 50mL 11.9g L^{-1} NaH_2PO_4 solution ($\text{pH}=4.12$), and then mechanical vibration in a water-bathing constant temperature vibrator at room temperature for 24h to form magnetic nanoparticles enriched with phosphate functional groups through electrostatic interaction. And then, AgNO_3 aqueous solution (0.015M) was added with drop by drop to the above solution under the continuous mechanical vibration, and then kept at room temperature for 5h. The as-prepared $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$ nanoparticles were separated by external magnetic field and washed five times with distilled water, and then dispersed in 20mL distilled water. The obtained $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$ aqueous solution (10mL) were further reacted with NaCl (0.1M), in which these $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$ were used as both template and silver ion source. During this in situ ions-exchange process, the $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$ surface could be replaced by Cl^- ions to form AgCl films, and then separated by external magnetic field and washed five times with distilled water, finally dried for 12h at 60°C . Thereby the $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4/ \text{AgCl}$ structure has been synthesized.

For comparison, pure Ag_3PO_4 was prepared by the ion-exchange method, i.e., AgNO_3 (0.015M) was solved in distilled water, and then NaH_2PO_4 aqueous solution (0.01M) was added with drop by drop to the above solution, and then kept at room temperature for 5h.

2.2. Analysis

Powder X-ray diffraction (XRD) was obtained on a X-ray diffractometer (RINT2200, Rigaku, Japan) using $\text{Cu K}\alpha$ ($\lambda=0.15406\text{nm}$) operated at 40kV and 40mA. Structure and morphology of samples were characterized by scanning electron microscope (SEM) (JSM-5600, JEOL, Japan) at an accelerating voltage of 20kV.

To investigate the production of free radicals species generated during the irradiation, a photoluminescence (PL) technique was applied. Terephthalic acid as a probe molecule easily reacts with $\bullet\text{OH}$ to form highly fluorescent product, 2-hydroxyterephthalic acid [5]. The intensity of the PL peak of 2-hydroxyterephthalic acid is in proportion to the amount of $\bullet\text{OH}$ radicals produced in water. The optimal concentration of terephthalic acid solution was about $5 \times 10^{-4} \text{ mol L}^{-1}$ in a diluted NaOH aqueous solution ($2 \times 10^{-3} \text{ mol L}^{-1}$) for the photocatalysis. PL spectra of the generated 2-hydroxyterephthalic acid were measured on a fluorescence spectrophotometer (F-4500, Hitachi, Japan) at 425nm excited by 315nm light of 2-hydroxyterephthalic acid.

3. Results and discussion

3.1. Characterization

Fig.1 presents typical SEM and XRD images of the samples prepared at various stages. Fig.1 (A) shows the SEM image of the Fe_3O_4 microspheres. It can be seen that the Fe_3O_4 microspheres have a relatively uniform diameter of about 400 nm by using a solvothermal method. Fig.1 (B) shows the SEM image of the $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$. From this image, we can see that after being coated with Ag_3PO_4 , the color of the microspheres is much brighter than that of Fe_3O_4 microspheres implying that a thin

film of Ag_3PO_4 was coated onto the surface of the Fe_3O_4 microspheres. Fig.1(C) shows the SEM image of $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$. It can be observed that the AgCl microspheres contact intimately with the $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4$ to form a AgCl shell. XRD was used to investigate the phase structures of the samples. Fig.1 (D) shows the XRD pattern of $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$. The successful coating and subsequent crystallization of Ag_3PO_4 and AgCl layer have been further confirmed.

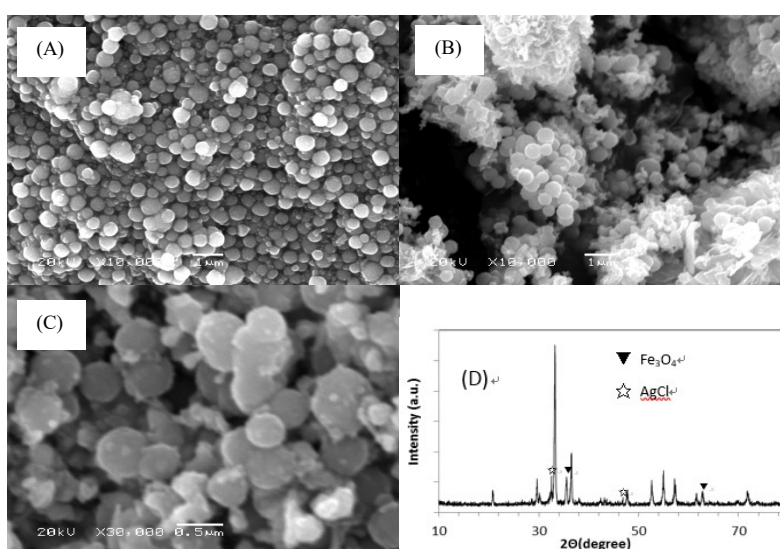


Figure 1. SEM and XRD patterns of the samples.
((A) Fe_3O_4 spheres, (B) $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4$, (C) $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ and (D) XRD of $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$)

3.2. Degradation experiment

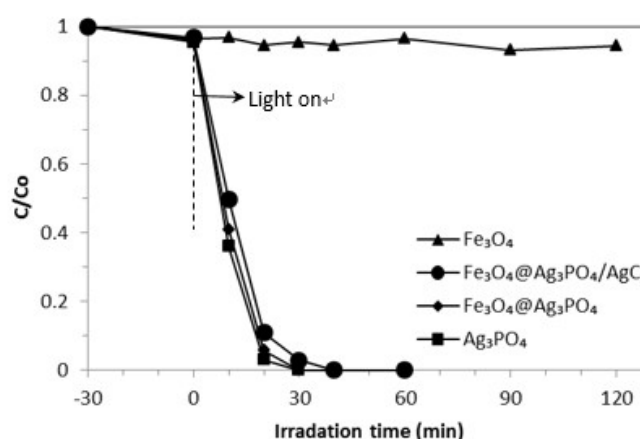


Figure2. Photocatalytic degradation of ChS over the Fe_3O_4 spheres, pure Ag_3PO_4 , $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4$ and $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$.

The photocatalytic performances of the $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4$ and $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ were explored for the degradation of ChS under a simulated solar irradiation at room temperature (Fig.2). After the irradiation, the degradation was rapid. Among them, the pure Ag_3PO_4 exhibited the highest photocatalytic activity. Specifically, the ChS can be completely degraded in 30min under a simulated

solar irradiation. Furthermore, the complete degradation of the ChS over the $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4$ photocatalyst took about 40min, while the $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ catalyst needed about 60min. However, in the case of the Fe_3O_4 microspheres, there was no apparent change in the concentration of ChS. As shown in Fig. 2, it can be clearly seen that all the Ag_3PO_4 -modified heterocatalysts exhibited high photocatalytic activities for the degradation of ChS. Golden coloured Ag_3PO_4 can absorb solar energy with a wavelength shorter than 530nm, which is higher than other photocatalysts [1]. And the absorption spectrum of Ag_3PO_4 revealed an indirect bandgap of 2.36eV as well as a direct transition of 2.43eV. The bandgap satisfies the energy criterion thermodynamically for the uphill reactions involved in organic decomposition. Therefore, the Ag_3PO_4 -modified photocatalysts exhibited higher photocatalytic activity under solar light.

In order to analyze the involved active species on $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ in the photocatalytic process, the formation of hydroxyl radicals ($\bullet\text{OH}$) was detected by the PL technique using terephthalic acid as a probe molecule. For comparison, WO_3/Pd was also examined under the same condition. An obvious peak was observed in the presence of $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ after 10min irradiation (Fig.3), which is caused by chemical reactions of terephthalic acid with $\bullet\text{OH}$ formed at the photocatalysts/water interface [2]. However, the formation of $\bullet\text{OH}$ in WO_3/Pd is seriously depressed, and only a weak peak was observed after 10min irradiation at about 425nm implying its weak photocatalytic activity under the solar light. It could be explained that the Ag_3PO_4 -modified photocatalysts has higher photocatalytic activities than others.

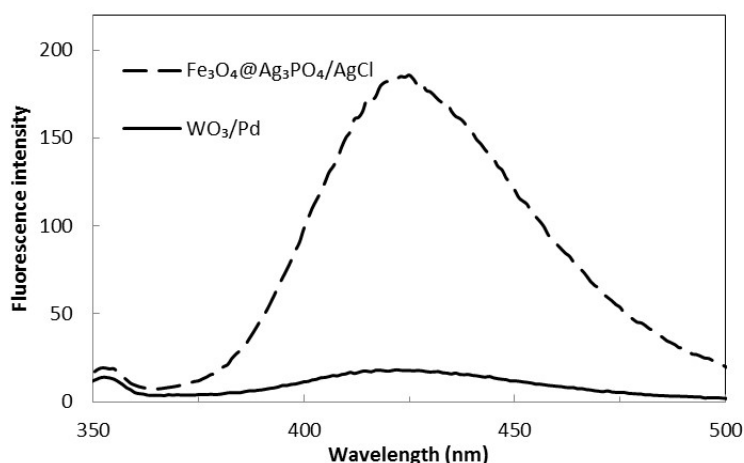


Figure 3. PL spectral changes observed during illumination of $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ and $\text{WO}_3\text{-Pd}$ after 10min.

3.3. Separation and reuse of core-shell photocatalysts

It is well known that Ag_3PO_4 is slightly soluble in aqueous solution, which greatly reduces its structural stability during the photocatalytic process [3]. It was observed that the bright brown photocatalysts turned to black after photocatalytic degradation experiments without coating AgCl shell. Due to the photocorrosion of the Ag_3PO_4 catalyst, the by-products, black metallic Ag particles, would generate in the reaction solution and attach themselves onto the surface of the photocatalysts, which would inevitably prevent light absorption, decrease its photocatalytic activity and make reuse of the photocatalysts difficult. Herein, a successful and easy procedure was used to resolve the above problems by the growth of AgCl nanoshells on the surfaces of $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4$ to turn into $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$. The insoluble AgCl nanoshells could effectively protect the Ag_3PO_4 photocatalysts from dissolution in aqueous solutions and enhance their stabilities during the photocatalytic process. Fig.4. shows the recycling effect of the $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4$ and $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ core-shell particles for photocatalytic degradation of ChS. It can be seen that

the degradation activity of $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4$ decreased sharply only after one degradation cycle. The efficiency decreased to about 40%, 18%, 8% and 5% for the 2nd, 3rd, 4th and 5th degradation cycles, respectively. In contrast, the degradation activity of $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ almost remained unchanged obviously after 5 degradation cycles. That is due to the different solubility behaviours of Ag_3PO_4 and the AgCl in the present system. The Ag_3PO_4 without AgCl film possesses a relatively high solubility of about 0.02 g L^{-1} in aqueous solution at room temperature. However, in the case of the $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ heterocatalysts, the AgCl nanolayers possess a lower solubility ($1.9 \times 10^{-3}\text{ g L}^{-1}$), which are in intimate contact with the of the Ag_3PO_4 , preventing the dissolution of the Ag_3PO_4 photocatalysts [3]. Thus, their structural stabilities during the photocatalytic process have been greatly enhanced for the reuse of the photocatalytic processes.

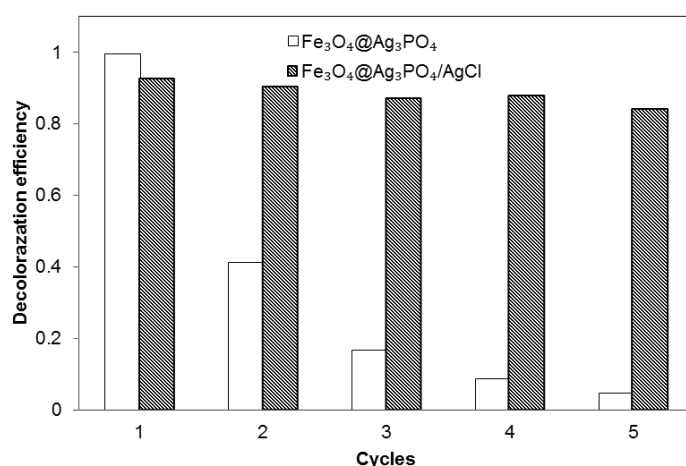


Figure 4. Comparison of recycling reuse between $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4$ and $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ for 60min irradiation after 5 cycles.

4. Conclusion

A novel magnetically recoverable core-shell $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ photocatalyst has been developed. ChS (50mL, 1 mg L^{-1}) can be completely degraded after about 60min under a simulated solar light irradiation. The role of the AgCl nanolayer in this heterophotocatalyst is to prevent the dissolution of the Ag_3PO_4 , which simply enhances their structural stability during the photocatalytic reaction. Such a novel composite photocatalyst can effectively degrade organic pollutants and can be easily recovered by a magnet, which was reused at least five times without any appreciable reduction in photocatalytic efficiency. This work provides a new method in integrating multifunctional composite photocatalytic nanosystems with both enhanced photocatalytic activity for organic pollutants degradation and magnetically separable recycling performance.

Acknowledgments

This work was financially supported by Project that Survey and Evaluation on Water and soil quality and engineering geology of Xiong'an New District (Tianjin Center of China Geological Survey) (No. DD20189122).

References

- [1] Z.G. Yi, J.H. Ye, N. Kikugawa, T. Kako, S.X. Ouyang, H. Stuart-Williams, H. Yang, J.Y. Cao, W.J. Luo, Z.S. Li, Y. Liu, R.L. Withers, An orthophosphate semiconductor with photooxidation properties under visible-light irradiation, *Nat. Mater.* 9 (2010) 559-564.
- [2] X. Yu, S. Liu, J. Yu, Superparamagnetic $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2@\text{TiO}_2$ composite microspheres with superior photocatalytic properties, *Appl. Catal. B: Environ.* 104 (2011) 12-20.

- [3] Y. Bi, S. Ouyang, J. Cao, J. Ye, Facile synthesis of rhombic dodecahedral AgX/Ag₃PO₄ (X = Cl, Br, I) heterocrystals with enhanced photocatalytic properties and stabilities, *Phys. Chem. Chem. Phys.* 13 (2011) 10071-10075.
- [4] B. Lv, Y. Xu, H. Tian, D. Wu, Y. Sun, Synthesis of Fe₃O₄/SiO₂/Ag nanoparticles and its application in surface-enhanced Raman scattering, *J. Solid State Chem.* 183 (2010) 2968-2973.
- [5] J. Yu, W. Wang, B. Cheng, B.-L. Su, Enhancement of Photocatalytic Activity of Mesoporous TiO₂ Powders by Hydrothermal Surface Fluorination Treatment, *J. Phys. Chem. C* 113 (2009) 6743-6750.