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 60 min. 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. \( \text{Ag}_3\text{PO}_4 \) 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$_3$O$_4$ nanoparticles were synthesized using a solvothermal method [4]. 2.70g of FeCl$_3$•6H$_2$O and 4.10g of NaAc•3H$_2$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$_3$O$_4$ aqueous solution (10mL) mentioned above was added to 50mL 11.9g L$^{-1}$ NaH$_2$PO$_4$ solution (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 Fe$_3$O$_4$@Ag$_3$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 Fe$_3$O$_4$@Ag$_3$PO$_4$ aqueous solution (10mL) were further reacted with NaCl (0.1M), in which these Fe$_3$O$_4$@Ag$_3$PO$_4$ were used as both template and silver ion source. During this in situ ions-exchange process, the Fe$_3$O$_4$@Ag$_3$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 Fe$_3$O$_4$@Ag$_3$PO$_4$/AgCl structure has been synthesized.

For comparison, pure Ag$_3$PO$_4$ was prepared by the ion-exchange method, i.e., AgNO$_3$ (0.015M) was solved in distilled water, and then NaH$_2$PO$_4$ 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 Cu Kα ($λ=0.15406$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 •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 •OH radicals produced in water. The optimal concentration of terephthalic acid solution was about $5×10^{-4}$ mol L$^{-1}$ in a diluted NaOH aqueous solution ($2×10^{-3}$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$_3$O$_4$ microspheres. It can be seen that the Fe$_3$O$_4$ microspheres have a relatively uniform diameter of about 400 nm by using a solvothermal method. Fig.1 (B) shows the SEM image of the Fe$_3$O$_4$@Ag$_3$PO$_4$. From this image, we can see that after being coated with Ag$_3$PO$_4$, the color of the microspheres is much brighter than that of Fe$_3$O$_4$ microspheres implying that a thin
film of Ag$_3$PO$_4$ was coated onto the surface of the Fe$_3$O$_4$ microspheres. Fig.1(C) shows the SEM image of Fe$_3$O$_4$@Ag$_3$PO$_4$/AgCl. It can be observed that the AgCl microspheres contact intimately with the Fe$_3$O$_4$@Ag$_3$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 Fe$_3$O$_4$@Ag$_3$PO$_4$/AgCl. The successful coating and subsequent crystallization of Ag$_3$PO$_4$ and AgCl layer have been further confirmed.

Figure 1. SEM and XRD patterns of the samples.

((A) Fe$_3$O$_4$ spheres, (B) Fe$_3$O$_4$@Ag$_3$PO$_4$, (C) Fe$_3$O$_4$@Ag$_3$PO$_4$/AgCl and (D) XRD of Fe$_3$O$_4$@Ag$_3$PO$_4$/AgCl)

3.2. Degradation experiment

The photocatalytic performances of the Fe$_3$O$_4$@Ag$_3$PO$_4$ and Fe$_3$O$_4$@Ag$_3$PO$_4$/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$_3$PO$_4$ 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 Fe₃O₄@Ag₃PO₄ photocatalyst took about 40min, while the Fe₃O₄@Ag₃PO₄/AgCl catalyst needed about 60min. However, in the case of the Fe₃O₄ microspheres, there was no apparent change in the concentration of ChS. As shown in Fig. 2, it can be clearly seen that all the Ag₃PO₄-modified heterocatalysts exhibited high photocatalytic activities for the degradation of ChS. Golden coloured Ag₃PO₄ can absorb solar energy with a wavelength shorter than 530nm, which is higher than other photocatalysts [1]. And the absorption spectrum of Ag₃PO₄ 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 Ag₃PO₄-modified photocatalysts exhibited higher photocatalytic activity under solar light.

In order to analyze the involved active species on Fe₃O₄@Ag₃PO₄/AgCl in the photocatalytic process, the formation of hydroxyl radicals (•OH) was detected by the PL technique using terephthalic acid as a probe molecule. For comparison, WO₃/Pd was also examined under the same condition. An obvious peak was observed in the presence of Fe₃O₄@Ag₃PO₄/AgCl after 10min irradiation (Fig.3), which is caused by chemical reactions of terephthalic acid with •OH formed at the photocatalysts/water interface [2]. However, the formation of •OH in WO₃/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 Ag₃PO₄-modified photocatalysts has higher photocatalytic activities than others.

Figure 3. PL spectral changes observed during illumination of Fe₃O₄@Ag₃PO₄/AgCl and WO₃-Pd after 10min.

3.3. Separation and reuse of core-shell photocatalysts

It is well known that that Ag₃PO₄ 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 Ag₃PO₄ 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 Fe₃O₄@Ag₃PO₄ to turn into Fe₃O₄@Ag₃PO₄/AgCl. The insoluble AgCl nanoshells could effectively protect the Ag₃PO₄ photocatalysts from dissolution in aqueous solutions and enhance their stabilities during the photocatalytic process. Fig.4. shows the recycling effect of the Fe₃O₄@Ag₃PO₄ and Fe₃O₄@Ag₃PO₄/AgCl core-shell particles for photocatalytic degradation of ChS. It can be seen that
the degradation activity of Fe$_3$O$_4$@Ag$_3$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 Fe$_3$O$_4$@Ag$_3$PO$_4$/AgCl almost remained unchanged obviously after 5 degradation cycles. That is due to the different solubility behaviours of Ag$_3$PO$_4$ and the AgCl in the present system. The Ag$_3$PO$_4$ without AgCl film possesses a relatively high solubility of about 0.02g L$^{-1}$ in aqueous solution at room temperature. However, in the case of the Fe$_3$O$_4$@Ag$_3$PO$_4$/AgCl heterocatalysts, the AgCl nanolayers possess a lower solubility (1.9×10$^{-3}$g L$^{-1}$), which are in intimate contact with the of the Ag$_3$PO$_4$, preventing the dissolution of the Ag$_3$PO$_4$ photocatalysts [3]. Thus, their structural stabilities during the photocatalytic process have been greatly enhanced for the reuse of the photocatalytic processes.

![Comparison of recycling reuse between Fe3O4@Ag3PO4 and Fe3O4@Ag3PO4/AgCl for 60min irradiation after 5 cycles.](image)

**Figure 4.** Comparison of recycling reuse between Fe3O4@Ag3PO4 and Fe3O4@Ag3PO4/AgCl for 60min irradiation after 5 cycles.

4. Conclusion

A novel magnetically recoverable core-shell Fe$_3$O$_4$@Ag$_3$PO$_4$/AgCl photocatalyst has been developed. ChS (50mL, 1mg 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$_3$PO$_4$, 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.

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