



## Short Communication

Performance of magnetically recoverable core–shell  $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$  for photocatalytic removal of methylene blue under simulated solar lightXu Guo <sup>a,b</sup>, Nan Chen <sup>a,\*</sup>, Chuanping Feng <sup>a,\*</sup>, Yingnan Yang <sup>b</sup>, Baogang Zhang <sup>a</sup>, Gen Wang <sup>a</sup>, Zhenya Zhang <sup>b</sup><sup>a</sup> School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing 100083, China<sup>b</sup> Doctoral Program in Life and Environmental Sciences, University of Tsukuba, Tsukuba 305-8572, Japan

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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 exhibiting rapid magnetic separation, stability and high photocatalytic activity under simulated solar light has been developed. Briefly,  $\text{Ag}_3\text{PO}_4$  is immobilized on  $\text{Fe}_3\text{O}_4$  nanoparticles and then an  $\text{AgCl}$  shell is formed by in situ ion exchange. The complete degradation of the methylene blue (MB) over the  $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$  photocatalyst only took about 60 min, much faster than  $\text{WO}_3\text{-Pd}$  photocatalyst.  $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$  nanocomposites can be easily recovered by a magnet, and reused at least five times without any appreciable reduction in photocatalytic efficiency.

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## 1. Introduction

Increased concern about the organic contaminants in water has arisen because of the danger they pose to life in contact with the polluted water. Some organic contaminants are recalcitrant (nonbiodegradable) and can persist for long periods of time [1,2]. Various methods are employed to degrade organic contaminants including chemical treatment such as chlorination [3], electrochemical treatment [4], physical treatment [5], photocatalysis [6], and ozonation and biologically activated carbon filtration [7]. Heterogeneous photocatalysis is considered a cost-effective method that degrades various hazardous organic contaminants in water because pollutants can be oxidized quickly and non-selectively [2,8–11]. To enhance the photocatalytic performance of photocatalysts, micro- and nano-scale particles with large surface areas have been developed. A large surface area provides an increased proportion of active sites, which could improve the photocatalytic performance. In addition, smaller particles could shorten the distance that electrons and holes migrate from the bulk material to active sites [12]. However, separation and recovery of micro- and nano-scale photocatalysts are very difficult and expensive [8,13]. To solve these problems, many researchers have immobilized catalysts on supporting materials such as glass [14], aluminosilicate [10], silicone sealant [15], and activated carbon and cotton [2,11]. However, a considerable decrease in photocatalytic efficiency and selectivity is generally

observed because catalyst immobilization decreases the active surface area-to volume [16].

Magnetic separation by applying external magnetic fields is an alternative method to separate and recover magnetic particles [17]. Recently, magnetic core–shell photocatalysts composed of a magnetic core and photocatalytic shell have attracted great interest [12,13,16,18–21]. Composite magnetic photocatalysts can be readily separated under an applied magnetic field. However, most of the core–shell photocatalysts reported to date are  $\text{TiO}_2$ -based materials [13,18–20].  $\text{TiO}_2$  possesses a wide bandgap ( $E_g = 3.2$  eV), so wavelengths shorter than 388 nm are necessary for photocatalytic excitation [9]. However, the solar spectrum is only around 4% UV, whereas 43% is visible [22]. Therefore development of magnetic photocatalysts that efficiently use solar energy for organic degradation is an attractive prospect.

$\text{Ag}_3\text{PO}_4$  is a semiconductor used in photocatalytic applications, which can use visible light to rapidly decompose organic contaminants in aqueous solution [8,22–24]. While most photocatalysts show a comparatively low quantum yield (about 20%),  $\text{Ag}_3\text{PO}_4$  can achieve a quantum yield of up to 90% at wavelengths longer than 420 nm [23]. Umezawa et al. [22] reported that the excellent photocatalytic performance of  $\text{Ag}_3\text{PO}_4$  can be attributed partly to the highly dispersive band structure of the conduction-band minimum resulting from  $\text{Ag } s - \text{Ag } s$  hybridization without localized  $d$  states. However,  $\text{Ag}_3\text{PO}_4$  is slightly soluble in aqueous solution, which decreases its structural stability. Epitaxial growth of an  $\text{AgCl}$  shell on the surface of  $\text{Ag}_3\text{PO}_4$  can be used to protect  $\text{Ag}_3\text{PO}_4$  from dissolving in aqueous solution [23]. However, the separation and reuse of  $\text{Ag}_3\text{PO}_4$ -modified photocatalysts are still difficult. The aim of the present research is to

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develop a novel magnetically recoverable core–shell photocatalyst with a magnetite ( $\text{Fe}_3\text{O}_4$ ) core and  $\text{Ag}_3\text{PO}_4/\text{AgCl}$  shell. The ability of the photocatalyst to photocatalytic degradation of methylene blue (MB) and its recyclability are investigated.

## 2. Experimental

### 2.1. Sample preparation

$\text{Fe}_3\text{O}_4$  nanoparticles were synthesized using a solvothermal method [25]. The synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles were then dispersed in distilled water (10 mL), and added to the  $\text{NaH}_2\text{PO}_4$  solution (50 mL,  $11.9 \text{ g L}^{-1}$ ,  $\text{pH} = 4.12$ ). The solution was vibrated mechanically in a water-bathing constant temperature vibrator for 24 h to form magnetic nanoparticles enriched with phosphate functional groups through electrostatic interaction. And then,  $\text{AgNO}_3$  aqueous solution (0.015 M) was added with drop by drop to the above solution under continuous mechanical vibration, and then the solution was maintained at room temperature for 5 h. The as-prepared  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$  nanoparticles were separated by an external magnetic field, washed five times with distilled water, and then dispersed in distilled water (20 mL). The obtained  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$  aqueous solution (10 mL) was reacted with  $\text{NaCl}$  (0.1 M) where  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$  acted as both template and silver ion source. During this in situ ion-exchange process, the  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$  surface could form an  $\text{AgCl}$  film. The resulting  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4/\text{AgCl}$  nanocomposite was separated by an external magnetic field, washed five times with distilled water, and then dried for 12 h at  $60^\circ \text{C}$ .

### 2.2. Degradation experiment

The photocatalytic activities of the samples were evaluated by degradation of MB under a simulated solar lamp (XC-100B, SERIC Ltd., Japan). The light intensity was measured with a photometer (Li-250A, Li-COR, USA), and was about  $0.7 \text{ mW cm}^{-2}$ . A photocatalyst (0.1 g) was added to an aqueous solution of MB ( $50 \text{ mL}$ ,  $2 \text{ mg L}^{-1}$ ) at room temperature in air. The suspension was magnetically stirred for 30 min in the dark to establish an adsorption–desorption equilibrium to eliminate the influence of adsorption. A lamp was switched on to initiate the reaction. During irradiation, samples were taken at different time intervals for 120 min or until complete degradation was observed. Samples were centrifuged and then the decolorization of MB was measured with a UV–vis spectrophotometer (UV-1600, Shimadzu Corporation, Japan).

To investigate the stability and recyclability of the as-prepared composite magnetic photocatalysts ( $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$  and  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4/\text{AgCl}$ ), recycling experiments were also performed. In the recycling experiments, after the photocatalysts were separated from the solution by an external magnetic field, the remaining solution was removed. Separated photocatalysts were washed five times with distilled water, and then used in the next degradation experiment.

### 2.3. Analysis

Powder X-ray diffraction (XRD) measurements were obtained on an X-ray diffractometer (RINT2200, Rigaku Corporation, Japan) using  $\text{Cu K}\alpha$  ( $\lambda = 0.15406 \text{ nm}$ ) operating at 40 kV and 40 mA. The structure and morphology of samples were characterized by scanning electron microscope (SEM, JSM-5600, JEOL Ltd., Japan) at an accelerating voltage of 20 kV and transmission electron microscope (TEM, F20, FEI, Japan) operating at 200 kV. UV–visible spectra of samples were recorded on a spectrophotometer (Cary 5000, Varian, Inc., USA). The zeta-potential of the particles in their aqueous suspensions was measured using Zetasize Nano-ZS (ZEN3600, Malvern Instruments). A photoluminescence (PL) technique was used to investigate the production of free radical species during irradiation. Terephthalic acid

as a probe molecule readily reacts with  $\cdot\text{OH}$  to form a highly fluorescent product, 2-hydroxyterephthalic acid [26]. The PL spectra of the generated 2-hydroxyterephthalic acid were measured on a fluorescence spectrophotometer (F-4500, Hitachi Ltd., Japan) at 425 nm excited by 315 nm light of 2-hydroxyterephthalic acid.

## 3. Results and discussion

### 3.1. Characterization

XRD was used to investigate the phase structures of the samples. Fig. 1. shows typical XRD patterns of the samples at various stages. Fig. 1A shows the XRD pattern of  $\text{Fe}_3\text{O}_4$  nanoparticles, which could be assigned to a spinel phase (Joint Committee on Powder Diffraction Standards, JCPDS, 19-0629). Fig. 1B shows the XRD pattern of  $\text{Ag}_3\text{PO}_4$  (JCPDS, 06-0505). The successful coating and subsequent crystallization of  $\text{Ag}_3\text{PO}_4$  and an  $\text{AgCl}$  layer were also confirmed (Fig. 1C and D).

Typical SEM and TEM images of the samples at various stages of preparation are presented in Fig. 2(A–C). Fig. 2A shows SEM and TEM images of the  $\text{Fe}_3\text{O}_4$  spheres. The  $\text{Fe}_3\text{O}_4$  spheres have a relatively uniform diameter of about 300 nm. Fig. 2B shows SEM and TEM images of the  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$ . The spheres are much brighter than the  $\text{Fe}_3\text{O}_4$  ones implying that a thin film of  $\text{Ag}_3\text{PO}_4$  was coated onto the surface of the  $\text{Fe}_3\text{O}_4$  spheres [8]. The obvious core–shell structure of  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$  is confirmed in a representative TEM image. The magnetic core is surrounded by an  $\text{Ag}_3\text{PO}_4$  shell. The  $\text{Ag}_3\text{PO}_4$  coating is uniform with an average thickness of about 50 nm. Fig. 2C shows typical SEM and TEM images of  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4/\text{AgCl}$  that were fabricated by reacting with  $\text{NaCl}$  aqueous solutions.  $\text{AgCl}$  is attached on the surface of the  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$ .

Fig. 2D shows the zeta-potential of the aqueous suspension of nanoparticles as a function of pH. The values of the zeta-potential in all suspensions decreased as the pH was increased. The aqueous suspension of the synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles shows an isoelectric point (IOP) at the neutral pH values. At  $\text{pH} < 6.8$ , it was observed that the  $\text{Fe}_3\text{O}_4$  nanoparticles exhibited positive zeta-potential values. This favored the adsorption of the negatively charged ions [27]. In this study, the synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles were dispersed in distilled water, and added to  $\text{NaH}_2\text{PO}_4$  solution ( $\text{pH} = 4.12$ ). Therefore,  $\text{Fe}_3\text{O}_4$  nanoparticles were enriched with phosphate groups through electrostatic interaction at  $\text{pH} 4.12$  (zeta-potential 36.8 mV). After coating  $\text{Ag}_3\text{PO}_4$ , a relatively high zeta-potential ( $-35.2 \text{ mV}$ ) can provide an electrostatic repulsive force between the nanoparticles to prevent agglomeration at the neutral pH values.

UV–vis absorption spectra of the studied catalysts are depicted in Fig. 3A. Pure  $\text{Ag}_3\text{PO}_4$  absorbs solar energy with a wavelength shorter than approximately 530 nm. In contrast to pure  $\text{Ag}_3\text{PO}_4$ , the absorption edge of  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$  and  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4/\text{AgCl}$  generates red shift,  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$  and  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4/\text{AgCl}$  also exhibit higher absorption in the visible region than the pure  $\text{Ag}_3\text{PO}_4$ .

### 3.2. Degradation experiment

The photocatalytic degradation of MB by  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$  and  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4/\text{AgCl}$  under simulated solar irradiation at room temperature was investigated (Fig. 3B). It was reported that  $\text{WO}_3\text{-Pd}$  photocatalyst exhibits high photo oxidative capability for organic dye decomposition under simulated solar light [9]. For comparison, the performance of a typical  $\text{WO}_3\text{-Pd}$  photocatalyst was also investigated. About 37% of MB was removed by  $\text{WO}_3\text{-Pd}$  after 120 min irradiation. In contrast, the decolorization of MB by  $\text{Ag}_3\text{PO}_4$ -modified photocatalysts was rapid. Pure  $\text{Ag}_3\text{PO}_4$  exhibited the highest photocatalytic activity of the catalysts, completely degrading MB within 30 min under simulated solar irradiation. Complete degradation of MB over the  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4$  photocatalyst took about 40 min, while the  $\text{Fe}_3\text{O}_4@ \text{Ag}_3\text{PO}_4/\text{AgCl}$  catalyst needed about 60 min. Golden-colored  $\text{Ag}_3\text{PO}_4$  can absorb solar energy with a

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