



Magnetic core–shell carbon microspheres (CMSs)@ZnFe₂O₄/Ag₃PO₄ composite with enhanced photocatalytic activity and stability under visible light irradiation



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ABSTRACT

Novel magnetic core–shell visible light responsive carbon microspheres (CMSs)@ZnFe₂O₄/Ag₃PO₄ composite photocatalyst with different mass ratios have been successfully synthesized through the solvothermal and *in situ* precipitation methods for the first time. The characteristics of the as-prepared materials were systematically determined by the XRD, XPS, SEM, FESEM-EDS, UV–vis DRS, VSM, and PL *etc.*; the results indicated that all of the composites showed good crystallinity and strong absorbance both in the UV and visible light regions. Moreover, a heterojunction structure was formed between the ZnFe₂O₄ and Ag₃PO₄. The photocatalytic performance of the composite was evaluated for 2,4-dichlorophenol (2,4-DCP) degradation, and enhanced photocatalytic activity and stability were achieved. When the mass ratio of CMSs, ZnFe₂O₄, and Ag₃PO₄ in the composite was 2:1:3, the apparent photodegradation rate constant of 2,4-DCP was 0.0184 min⁻¹, which was 7.36 times that of ZnFe₂O₄, 2.45 times that of Ag₃PO₄, and 4 times that of CMSs@ZnFe₂O₄ (mass ratio = 2:1). And after four times recycling, the photodegradation efficiency of 2,4-DCP over the CMSs@ZnFe₂O₄/Ag₃PO₄ (mass ratio = 2:1:3) can even reach approximately 89%. The investigation of the photocatalytic mechanism suggested that both the effective separation of the photoinduced electron–hole pairs and the active free radicals formed in the special core–shell interface contributed to the superior photocatalytic performance of the composite.

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1. Introduction

Over the past few decades, design and synthesis of highly efficient visible-light-driven photocatalysts have attracted considerable attention because of their potential applications in solar energy conversion and water pollutant treatment [1–3]. Silver orthophosphate (Ag₃PO₄), discovered by Yi and co-workers in 2010, is regarded as a significant breakthrough in the field of visible-light-driven photocatalysts [4]. More specifically, Ag₃PO₄ shows an extremely high quantum efficiency of approximately 90% at wavelengths of 420 nm in water oxidation with AgNO₃ as a scavenger [4]. However, as Ag₃PO₄ is light sensitive and slightly soluble in aqueous solution, it will be photocorroded and decomposed to Ag⁰ during the photocatalytic reaction process without any sacrificial electron acceptors. This process not only destroys the structure of

Ag₃PO₄ but also reduces its light absorption efficiency, inevitably influencing its photocatalytic activity and stability [4].

More recently, many efforts have been devoted to further optimize and improve the photocatalytic activity and stability of Ag₃PO₄. The methods include innovations in structure and morphology (*N*-dimensional nanostructures or facet-controlled structure) [5–13], cation/anion doping [14], metal deposition [15–18], immobilization with the support materials (such as graphene [19–23], CNTs [24,25], bentonite [26], polyacrylonitrile nanofiber [27,28], attapulgite [29], hydroxyapatite [30], layered double hydroxides [31], or flaky layered double hydroxides [32]), and fabrication of a special heterojunction/core–shell structure with other appropriate semiconductors, for example, Ag₃PO₄/WO₃ [33], Ag₃PO₄/CeO₂ [34], Ag₃PO₄/SrTiO₃ [35], Ag₃PO₄/Cr–SrTiO₃ [36], Ag₃PO₄/In(OH)₃ [37], BiOCl/Ag₃PO₄ [38], Ag₃PO₄/BiVO₄ [39], Ag₃PO₄/Bi₂MoO₆ [40], BiPO₄/Ag₃PO₄ [41], Ag₃PO₄/N–Sr₂Nb₂O₇ [42], AgX/Ag₃PO₄ (X = Cl, Br, I) [43–45], Ag@(Ag₂S/Ag₃PO₄) [46], g-C₃N₄-Ag₃PO₄ [47–49], MoS₂/Ag₃PO₄ [50], Ag₃PO₄/ZnO [51], Ag₃PO₄/SnO₂ [52], Ag₃PO₄/TiO₂ [53,54], AgO/Ag₃PO₄ [55],

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$\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4$ [56], $\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4$ [57], or $\text{CdS}@ \text{Ag}_3\text{PO}_4$ [58]. Excitingly, all of the modified Ag_3PO_4 catalysts show varying degree of enhanced photocatalytic performance compared to pure Ag_3PO_4 . It is noteworthy that the core-shell structure materials have been extensively studied for their controllable structure, which can be adjusted by changing the operation parameters [58,59]. In the photocatalytic process, the special interface structure can provide a potential driving force for the transfer and separation of photoinduced charge carriers (electrons and holes) and can enrich the reactants on the catalyst surfaces [58,60], favoring the photocatalysis.

ZnFe_2O_4 , a visible light responsive semiconductor catalyst with a narrower band gap of approximately 1.9 eV, has been widely applied in the conversion of solar energy, photocatalysis, and photochemical hydrogen production from water [61]. Moreover, ZnFe_2O_4 -based materials can be magnetically separated in a suspension system by virtue of the magnetic storage property of ZnFe_2O_4 . However, until now, there has been no report on the combination of Ag_3PO_4 and ZnFe_2O_4 . Therefore, the aim of this research is to develop a novel magnetic core-shell carbon microsphere (CMSs) $@ \text{ZnFe}_2\text{O}_4/\text{Ag}_3\text{PO}_4$ composite through the orderly deposition of ZnFe_2O_4 and Ag_3PO_4 onto the surface of carbon microspheres (CMSs). The characteristics of the as-prepared materials were detected through powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), field-emission scanning electron microscope (FESEM), energy dispersive X-ray spectroscopy (EDS), laser particle size analyzer, ultraviolet-visible diffuse reflectance spectra (UV-vis DRS), vibrating sample magnetometry (VSM), and photoluminescence (PL). Moreover, 2,4-dichlorophenol (2,4-DCP) was used to evaluate the photocatalytic activity and stability of the composite under visible light irradiation. Finally, the photocatalytic mechanism of the composite was also proposed.

2. Experimental

2.1. Materials

All reagents were of analytical purity and were used without further purification. AgNO_3 , $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, *tert*-butanol, disodium ethylenediaminetetraacetate, benzoquinone, $\text{C}_6\text{H}_{12}\text{O}_6$, KMnO_4 , NaNO_2 , H_2O_2 (30%), glucose, ethanol, ethylene glycol (EG), and 2,4-DCP were obtained from Sinopharm Chemical Reagent Co. Ltd., (Shanghai). HCl (37%) were obtained from Zhuzhou Xingkong Chemical and Glass Co. Ltd., (Zhuzhou).

2.2. Synthesis of CMSs $@ \text{ZnFe}_2\text{O}_4$

ZnFe_2O_4 was first prepared through a solvothermal method. Namely, 0.05 mol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.1 mol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved into 120 mL of EG and mechanically agitated for 1 h, and then 60 mL of EG with 0.075 mol $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ was added into the above mixture, which was stirred for 30 min. Afterwards, the mixture was transferred into a 200-mL sealed Teflon-lined stainless steel autoclave for 12 h at 180 °C under autogenous pressure. When the autoclave was cooled naturally to room temperature, the precipitate was isolated by a magnet and washed several times with absolute ethanol and distilled water, then dried in a vacuum oven and sieved to 80 mesh to achieve a uniform sample. The core-shell structure of CMSs $@ \text{ZnFe}_2\text{O}_4$ (mass ratio = 2:1) was obtained from the above as-prepared ZnFe_2O_4 and glucose, which were dispersed into ultrapure water and reacted in the Teflon-lined stainless steel autoclave for 4 h at 180 °C.

2.3. Synthesis of CMSs $@ \text{ZnFe}_2\text{O}_4/\text{Ag}_3\text{PO}_4$

The CMSs $@ \text{ZnFe}_2\text{O}_4/\text{Ag}_3\text{PO}_4$ composites with different mass ratios were synthesized by an *in situ* precipitation method. A typical procedure for the synthesis of CMSs $@ \text{ZnFe}_2\text{O}_4/\text{Ag}_3\text{PO}_4$ with a mass ratio of 2:1:3 was as follows. First, 0.21 g of CMSs $@ \text{ZnFe}_2\text{O}_4$ was dispersed into 100 mL of an ethanol solution ($V_{\text{ethanol}}:V_{\text{water}} = 4:1$) and treated with ultrasound for 10 min. Then, 50 mL of an AgNO_3 solution (1.5 mmol) was added to the mixture and vigorously stirred for 12 h to make Ag^+ combine adequately with the surface of CMSs $@ \text{ZnFe}_2\text{O}_4$. Afterwards, 50 mL of a $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ solution (0.5 mmol) was added dropwise into the above mixture and maintained with stirring for another 1 h. The precipitates were collected and washed repeatedly with absolute ethanol and ultrapure water, vacuum-dried overnight at 60 °C, and then crushed and sieved to 80 mesh. For comparison, pure Ag_3PO_4 and ZnFe_2O_4 were also prepared by the same method.

2.4. Characterization

Phase identification via X-ray diffraction (XRD) was conducted on an X-ray diffractometer (Rigaku D/max 2500 PC) using $\text{Cu K}\alpha$ radiation (40 kV, 100 mA) at a scanning rate of 4.0°/min with the 2θ range of 10–90°. X-ray photoelectron spectroscopy (XPS) was performed on the XPS-ESCALAB 250 spectrometer with an achromatic Al $\text{K}\alpha$ X-ray source and an analytical chamber with a base pressure of 2×10^{-9} Pa. The X-ray gun was operated at 150 W (15 kV, 10 mA). The morphology and microstructure of the samples were observed using scanning electron microscope (SEM, JEOL, JFC-1600), and field-emission scanning electron microscope (FESEM, Hitachi, SU8010) with energy-dispersive X-ray spectroscopy (EDS) analysis. The size distribution of the as-prepared materials was determined using a laser diffraction particle size analyzer (WJL-602). The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of the samples were measured using a UV-vis spectrophotometer (Shimadzu, UV-2550). The magnetic properties were measured at room temperature by a vibrating sample magnetometry (VSM, HH-15). The photoluminescence (PL) spectroscopy was obtained using a fluorescence spectrophotometer (Hitachi, F-4600).

2.5. Photocatalytic activity experiment

In this study, 2,4-DCP was used to evaluate the photocatalytic activity of the as-prepared photocatalysts. The photocatalytic reaction experiments were conducted in the photoreaction apparatus (BL-GHX-V, Bilang Biological Science and Technology Co. Ltd., Xi'an) using a 300 W Xe lamp with an ultraviolet cutoff filter (providing visible light ≥ 400 nm) as the light source. In each experiment, 25 mg of photocatalyst was added into a 50 mL 2,4-DCP solution as the initial concentration is 20 mg/L. Prior to illumination, the solution was magnetically stirred in the dark for 30 min to reach an adsorption-desorption equilibrium between the 2,4-DCP and the photocatalysts. Then, the solution was exposed to Xe lamp irradiation. As the reaction elapsed, the sample was taken out and filtered through 0.45 μm membrane filters immediately. The concentration of the residual 2,4-DCP in the reacted solution was measured by high performance liquid chromatography (HPLC, Hitachi L-2000). Each sample was measured through the parallel test for three times, and the average values are reported.

2.6. Photocatalytic stability experiment

The repeated experiments for 2,4-DCP degradation were conducted to evaluate the photocatalytic stability of the as-prepared catalysts. The detailed experimental processes were similar to the

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