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$Co_{0.5}Zn_{0.5}Fe_2O_4/Ag_3PO_4$: A magnetic, highly efficient visible-light photocatalyst and the Z-scheme mechanism for removal of anionic dye and tetracycline hydrochloride

Cuiping Lin, Xin Xie, Chen Li, Qishe Yan*

College of Chemistry and Molecular Engineering, Zhengzhou University, No.100 Science Avenue, High-Tech Zone, Zhengzhou, Henan 450001, China

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ABSTRACT

The magnetic $Co_{0.5}Zn_{0.5}Fe_2O_4$ incorporated Ag_3PO_4 photocatalysts were fabricated by facile sol-gel and hydrothermal route. The resulting $Co_{0.5}Zn_{0.5}Fe_2O_4/Ag_3PO_4$ composites were characterized by XRD,[1] SEM,[2] UV–vis DRS,[3] FT-IR[4] and VSM.[5] The results indicated that the magnetically separable composites with good dispersity showed a strong absorption in the uv–vis region and the saturation magnetization was 85.25 emu g^{-1}. Anionic dye methyl orange (MO) and tetracycline hydrochloride (TCH) were used to evaluate the activity of the photocatalysts. The result revealed that the magnetic composites exhibited enhanced photocatalytic activity and stability under the visible light irradiation. The ·OH and $\cdot O_2^-$ radicals were found to be the major active species during the photodegradation of TCH, while$\cdot O_2^-$ played the important role in photodegrading MO. And a Z-scheme mechanism for the enhanced photocatalytic process was proposed.

1. Introduction

Tetracyclines hydrochloride (TCsH), including tetracycline hydrochloride (TCH), oxytetracycline hydrochloride, doxycycline hydrochloride, and chlortetracycline hydrochloride, are widely used in veterinary medicine since they are cheaper, more stable, and easier for oral absorption [1]. However, antibiotics used for human treatment may enter the environment through excreta or the release of surplus drugs into the sewage system, and the sewage from sewage treatment plants will eventually be released into the local aquatic environment [2]. Previous studies have reported that these residues were harmful to both humans and animals, such as food pollution, environmental pollution, biodiversity crisis and bacterial resistances [3–5]. Hence, the removal of TCsH from both wastewater and natural water raised increasing concerns for environmental protection. Various technologies were available to the water purification, but they still had difficulties to remove the TCsH from the water body completely by the traditional water treatments like biological/physicochemical methods, due to their antibacterial, the hydrophilic property, and the stable naphthacene ring structure [6,7]. To date, photocatalytic oxidization has been proved that it has enormous potential to remove unfriendly antibiotic pollutant from water through oxidation imparted [8,9]. However, the as-synthesized samples, mostly in form of powders, decide that a considerable number of photocatalytic reactions were carried out in the state of suspension, and have the difficulty in separation and recycle of the photocatalyst powders after reaction, which has been considered as a severe limitation for the practical application of these photocatalytic processes for water treatment. Therefore, the development of a kind of recyclable photocatalyst has become the focus of current research [7,10].

Spinel ferrite materials were considered to apply in the study of photocatalytic application due to their excellent characteristics, for instance enrich electrical properties, superior magnetic properties, narrow band gap, catalytic applications, low cost and good photochemical stability [7,11–13]. The spinel ferrite structure MFe_2O_4, where M refers to the metal cation, can be described as a cubic close-packed arrangement of oxygen atoms, with metal cations and Fe ions at two different crystallographic sites tetrahedral and octahedral, respectively [11]. In recent years, it has been reported that spinel was used in wastewater treatment, such as Fe_3O_4 [14–16], $ZnFe_2O_4$ [13,17],

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* Corresponding author.
E-mail address: yanqishezzu@163.com (Q. Yan).

[1] X-ray diffraction.

[2] Scanning electron microscope.

[3] UV–vis diffuse reflectance spectrum.

[4] Fourier transfer infrared spectroscopy.

[5] Vibrating sample magnetometer.

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$CoFe_2O_4$ [12,18], $MnFe_2O_4$ [12,19], $SnFe_2O_4$ [7,20], Ni Fe_2O_4 [12] and $CuFe_2O_4$ [12,19,21]. Cobalt zinc ferrite, a new type of ferrite material is gradually being widely concerned with the general formula as $Zn_xCo_{1-x}Fe_2O_4$ [22–24]. $Zn_xCo_{1-x}Fe_2O_4$-based hetero-system has been studied in the field of photocatalytic technology as $Zn_{0.7}Co_{0.3}Fe_2O_4$/rGO [25], $Co_{0.5}Zn_{0.5}Fe_2O_4/NiFe_2O_4$ [26] and $Co_{0.5}Zn_{0.5}Fe_2O_4$/g-C_3N_4 [27], for removing organic pollutants from wastewater.

Ag_3PO_4 as a photocatalytic material is widely known owing to its excellent visible light response and high photocatalytic performance [28,29]. In this paper, $Co_{0.5}Zn_{0.5}Fe_2O_4/Ag_3PO_4$ heterojunction structures (CZF/A) were constructed for obtaining a kind of convenient recovery and efficient visible-light driven photocatalysts that were prepared by a facile sol-gel and hydrothermal method. MO and TCH were used as the target contaminants to evaluate the photocatalytic activities of CZF/A under visible light condition.

2. Experimental

2.1. Materials

The chemicals used in this study were all analytical grade (A.R.). Cobalt (II) nitrate ($Co(NO_3)_2·6H_2O$) and iron (III) nitrate nonahydrate ($Fe(NO_3)_3·9H_2O$) were obtained from Tianjin Fengchuan Chemical Reagent Science And Technology Co., Ltd., zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$) was bought from Shanghai Macklin Biochemical Co., Ltd., silver nitrate ($AgNO_3$) was purchased from Sinopharm Chemical Reagent Co., Ltd., polyethylene glycol 4000 (PEG), TCH, methyl orange (MO) and disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4·12H_2O$) were achieved from Tianjin Kermel Chemical Reagents development center, polyvinylpyrrolidone (PVP) was obtained from Shanghai Aladdin industrial corporation, citric acid monohydrate was bought from Tianjin Deen reagent Co., Ltd. The reagents were used without further purification. And the water used in the experiment was deionized water.

2.2. Preparation of CZF/A nanocomposites

2.2.1. Preparation of $Co_{0.5}Zn_{0.5}Fe_2O_4$

The $Co_{0.5}Zn_{0.5}Fe_2O_4$ particle was obtained by a sol-gel method as follows. 25 mmol $Co(NO_3)_2·6H_2O$, 25 mmol $Zn(NO_3)_2·6H_2O$ and 100 mmol $Fe(NO_3)_3·9H_2O$ were first dissolved in 20 mL deionized water, stirred continuous for 30 min to make them mixed evenly. Then, 80 mL citric acid monohydrate (0.3 M) was added into the mixture solution with a vigorously magnetically stirred. After 3 h of water bath reaction at 80 ℃, placed the wet gel obtained from the above reaction into the oven and heated at 100 ℃ for 14 h. The dry gel was finally transferred to muffle furnace after grinding, and calcined at 750 ℃ for 2 h.

2.2.2. Preparation of CZF/A composites

The $Co_{0.5}Zn_{0.5}Fe_2O_4/Ag_3PO_4$ (CZF/A) composites with different Ag_3PO_4 contents were prepared through a hydrothermal route. 1.0 g PEG was first dissolved in 100 mL deionized water, and 150 mg $Co_{0.5}Zn_{0.5}Fe_2O_4$ was put in the solution with ultrasonic vibration dispersed for 30 min. 10 mL solution contained 146 mg silver nitrate was added to the above mixed solution, continued to further ultrasound for 30 min. Then, 20 mL disodium hydrogen phosphate dodecahydrate was added dropwise into the suspension, in which the amount of Na_2HPO_4 was excessive to ensure the formation of precipitation with silver ions. After continuous sonicated for 1 h at room temperature, the above mixture was transferred to the Teflon-lined stainless steel high pressure reaction kettle, heated at 120 °C for 16 h. The final products were centrifuged and then washed with deionized water and absolute ethyl alcohol before being dried at 80 °C in air overnight. For the convenience of narration, the compounds were named as PEG-CA, PVP-CA and 0-CA, respectively (there PEG, PVP and number 0–2 are the prefixes mean the addition of surfactant or not, C means $Co_{0.5}Zn_{0.5}Fe_2O_4$, and A means Ag_3PO_4).

In the meantime, adjusted the mass ratio (m-Ag_3PO_4/m-CZF, 80%, 60% and 40%), no surfactant and the other conditions remained unchanged, obtained the 0-CA, 1-CA and 2-CA. For the purpose of comparison, the pure Ag_3PO_4, PEG-Ag_3PO_4, PVP-Ag_3PO_4 and $ZnFe_2O_4$ were prepared with the adjustment procedure based on the above mentioned.

2.3. Characterization methods

The as-prepared samples were characterized on a X-ray diffraction using a Cu Kα radiation (λ = 0.15406 Å) at a scanning rate of 10°/min in the 2θ range of 5–90° at room temperature (XRD, X′ Pert-PRO, PANalytical, Holland). Scanning electron microscopy (SEM) images were observed on TM-1000 microscope. The UV–vis diffuse reflectance spectroscopy (UV–vis DRS, Cary 5000, Agilent, USA) results were measured in the range of 200–800 nm equipped with an integrating sphere attachment. Fourier transfer infrared spectroscopy (FT-IR, Nicolet iS50, Thermo, USA) using KBr pellets. Vibrating sample magnetometer (VSM, MPMS-XL-7, Quantum Design, USA) was used to measure the magnetic properties of samples.

2.4. Photocatalytic activity tests

In this part of the experiment, MO and THC were used to evaluate the photocatalytic activity of the as-prepared samples under the visible light irradiation. A 300 W Xe lamp was used as the visible light source ($\lambda > 420$ nm) with a cutoff filter, and a cooling reflux device was used to keep the system at room temperature (28 ± 2 °C). 50 mg of photocatalyst was suspended in the target solutions (20 mg L^{-1}, 50 mL). Prior to illumination, the suspension was magnetically stirred in the dark for 30 min to reach adsorption-desorption equilibrium between the target pollutants and the photocatalysts. During the irradiation, the samples were withdrawn at given time intervals, the concentration of the target solutions were measured by UV–visible spectrophotometer (Shimadzu UV-2450).

3. Results and discussion

3.1. Characterization of the CZF/A composites

The X-ray diffraction patterns of the as-prepared CZF/A composites were presented in Fig. 1(A). As could be seen, the peaks at around 20.8°, 29.7°, 33.3°, 36.6°, 42.5°, 47.8°, 52.7°, 55.0° and 57.3° (marked "◆") were contributed to the (110), (200), (210), (211), (220), (310), (222), (320) and (321) crystal planes of Ag_3PO_4 (JPCDS Card no.06-0505). It could be also observed that the CZF/A composites combined the patterns of the respective component. Moreover, no other crystalline peaks were observed from the composites patterns, it should be noted that the typical diffraction peaks of $Co_{0.5}Zn_{0.5}Fe_2O_4$ and Ag_3PO_4 appeared in the patterns of the CZF/A composites.

The Fig. 1(B) showed the XRD patterns of the recycled 0-CA composite photocatalyst. As the results showed, the diffraction peaks of the 0-CA sample has hardly changed from the original sample after once cycle. And after four cycles, The diffraction peaks intensity of silver phosphate in the 0-CA sample was relatively weak. On the contrary, the diffraction peaks intensity of the $Co_{0.5}Zn_{0.5}Fe_2O_4$ does not change much.

The morphological properties of the obtained samples were showed in Fig. 2. The pure $Co_{0.5}Zn_{0.5}Fe_2O_4$ showed a roughly block morphology in the range of 12 μm with aggregates of nanoparticles (Fig. 2(a)). As depicted in Fig. 2(c)-(g) the Ag_3PO_4 NPs were distributed separately on $Co_{0.5}Zn_{0.5}Fe_2O_4$ surface as nanoislands, the agglomeration of $Co_{0.5}Zn_{0.5}Fe_2O_4$ particles were reduced. Especially with the participation of surfactants (Fig. 2f and g), the dispersed $Co_{0.5}Zn_{0.5}Fe_2O_4$ samples showed a small lamellar and fluffy cotton-like morphology growing