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Enhanced photocatalytic degradation of tetracycline hydrochloride by novel porous hollow cube $ZnFe_2O_4$

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ABSTRACT

As a broad-spectrum antibacterial agent, tetracycline hydrochloride (TCHC) was widely used in medical treatment and animal husbandry. However, the TCHC in various systems such as the soil, rivers and foods, had caused great harm to the environment and human health. Among the many methods for treated tetracycline hydrochloride in wastewater, the photocatalytic treatment had great advantages. In this study, we used Prussian blue as a precursor to synthesized porous hollow spinel cube $ZnFe_2O_4$ for photocatalysis. The experimental results showed that the degradation rates of the prepared porous hollow cube $ZnFe_2O_4$ (l-$ZnFe_2O_4$) significantly better than the commercially available $ZnFe_2O_4$ (g-$ZnFe_2O_4$) and the $ZnFe_2O_4$ prepared by the coprecipitation method (p-$ZnFe_2O_4$). In addition, we made a further introduction on the degradation mechanism of TCHC. The porous hollow cube $ZnFe_2O_4$ could be expected to provide a green and effective for material degradation of tetracycline hydrochloride in water.

1. Introduction

As a broad-spectrum antimicrobial agent, tetracycline hydrochloride (TCHC) was widely used in the medicine and livestock husbandry, and with the discharge of the above waste water, it was widely distributed in the water environment [1–3]. TCHC in water was accumulated in plants and animals over a long period time, eventually reaching the human body by the food chain, which could cause serious harms to the human body. At present, there were some treatments for antibiotics in water, such as biological methods [4], physical methods [5] and chemical methods [6,7]. However, these methods possessed some fatal weaknesses in the degradation process, such as low efficiency, large energy consumption and giving rise to secondary pollution. The photocatalysis technology had the thorough degradation ratios, little secondary pollution, and almost all the antibiotics in the water could be degraded in the sewage treatment. Moreover, directly using sunlight in the room temperature, was a promising green technology for treatment of antibiotic in wastewater [8–10].

Since 1972, Fujishima [11] and Honda first discovered that TiO_2 electrodes electrolyzed water to generate H_2 and O_2 under light irradiation. And in 1976, Carey et al. [12] first used TiO_2 materials for photocatalytic degradation of highly toxic and low concentrations of PCBs (Polychlorinated biphenyls) materials. Since then, photocatalytic materials were focused by many researchers. As an important metal oxide, spinel zinc ferrite ($ZnFe_2O_4$) had been widely used in magnetic [13–15], lithium battery electrode material [16–18], gas sensing material [19] and so on. Especially for photocatalytic materials, $ZnFe_2O_4$ and its composites were widely used in the study of photocatalytic degradation of pollutants due to their good properties of narrow band gaps, good visible light response, good thermal stability and low toxicity [20–23]. For example, Xu et al. [36] reported that $ZnFe_2O_4$ was responsive to visible light, and the composite material of $ZnFe_2O_4$ and Ag/AgBr can effectively increase the visible light response range of Ag/AgBr, and increased the photocatalytic efficiency under visible light. In addition, Xu et al. [37] using Zn-Fe mixed metal-organic framework as precursor prepared the flake ZnO/$ZnFe_2O_4$, it was obvious degradation effect on rhodamine B (RhB) and methylene blue (MB) under UV–vis light. More importantly, Zn^{2+} and Fe^{3+} elements were located at the available octahedral and tetrahedral sites of the close-packed oxygen atoms, respectively, which could enhance the separation efficiency of the photo-generated charges, and then would improve the photocatalytic degradation [24].

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At present, various methods have been studied for the fabrication of $ZnFe_2O_4$ such as co-precipitation [33], hydrothermal [38] and sol-gel methods [39] et al. Metal-organic frameworks (MOFs) were a class of crystalline compounds that are self-assembled by metal ions and multidentate organic ligands. Due to its controllable pore size, modifiable pore surface, ultra-low density and ultra-high specific surface area, it was always as a promising new material for fabricating hollow structures [26,27]. Synthesis of $ZnFe_2O_4$ using MOFs as precursor is attracting attention of many researchers [20,28,37,40]. In addition, the hollow structure could modulate the index of refraction and enhance light scattering, which were beneficial for the degradation of organic pollutants [20]. Moreover, there were some large number of active sites for adsorption and reaction in the surface. More importantly, a large quantity of nanoparticles was accumulated in the shell, so water, oxygen and reactants could permeate through the shell through porous channels for better oxidation [25]. For example, Habibi et al. [41] studied the photocatalytic effect of different $ZnFe_2O_4$, the results showed that the porous $ZnFe_2O_4$, has better photocatalytic performance than $ZnFe_2O_4$. To our best knowledge, however, there are little reports about photocatalytic degradation of tetracycline hydrochloride by the porous hollow cube $ZnFe_2O_4$.

In our work, we successfully synthesized a novel porous hollow cube $ZnFe_2O_4$ by calcination using MOF (Prussian Blue (PB)) as precursor. In addition, degradation of TCHC in aqueous were studied using the porous hollow cube $ZnFe_2O_4$. The results showed that the porous hollow cube $ZnFe_2O_4$ showed superior performance for effective degradation of TCHC in aqueous. At the same time, we also provided a reference mean in wastewater treatment and degradation of antibiotics.

2. Experimental sections

2.1. The experimental materials

Polyvinylpyrrolidone (PVP, K30, MW ~ 40,000) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). $K_4Fe(CN)_63H_2O$ (≧99.5%) was purchased from Aladdin (Shanghai, China). Zinc acetate (≧98%) was purchased from Sinopharm Chemical ReagentCo., Ltd (Shanghai, China). Tetracycline hydrochloride (TCHC) (≧96%) was purchased from Aladdin (Shanghai, China). Eehanol (≧99.7%) was purchased from Fuyu Fine Chemical Co., Ltd (Tianjing, China).

2.2. Synthesis of the porous hollow cube $ZnFe_2O_4$

The porous hollow cube $ZnFe_2O_4$ material was prepared by using PB as the MOF precursor [28]. First, 20 g of PVP was dissolved into 250 ml of 0.1 M HCl solution under magnetic stirring 30 min to obtain a clear solution. Second, 0.6 g of $K_4Fe(CN)_63H_2O$ was added into the solution under magnetic stirring 30 min to obtain a bright yellow solution. The solution was sealed into an airtight container, and incubated at 80 °C for 24 h to get the blue insolubles. Third, the blue insolubles (PB) was centrifuged at 11,000 r/min and washed three times with distilled water and ethanol. The obtained precipitants were dried at 70 °C for 12 h in vacuum. The cubic PB was successfully synthesized. Fourth, 0.2 g of homemade PB was weighed accurately and dissolved into 40 ml of ethanol under magnetic stirring for 10 min. Fifth, 0.14 g of anhydrous zinc acetate was added into the solution under magnetic stirring for 10 min. Sixth, the solution was heated at 70 °C to evaporate the ethanol. The blue solid was collected and ground for 5 min in agate. At last, it was heated at 700 °C at a heating rate of 2 °C/min for 6 h. The porous hollow spinel cube $ZnFe_2O_4$ was prepared. The above steps were mainly divided into two major steps as shown in Fig. S1.

2.3. Characterization of the porous hollow cube $ZnFe_2O_4$

X-ray diffraction (XRD) data for crystalline structure of $ZnFe_2O_4$ powder were obtained in the 2θ range from 10°–80° by the D8 ADVANCE X-ray diffraction (BRUKER-AXS, Germany). The surface properties and composition are conducted by the ESCALAB 250XI multi-functional imaging X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, America). The test conditions are as follows: monochromatic Al Ka ($h\nu$ = 1486.6 eV), power 150 W, 500 μm beam spot and the binding energy is calibrated with C 1s 284.8 eV. The morphology and particle size of the $ZnFe_2O_4$ were analyzed by the ΣIGMA + X-Max20 field emission scanning electron microscope (FESEM) (Carl Zeiss, Germany) with an accelerating voltage of 5 kV. The UV–vis absorption spectrum was measured using U4100 UV Spectrometer (Hitachi, Japan), and the wavelength range was from 200 nm to 800 nm. The TEM images, HRTEM images and SAED images of the samples were obtained by the Tecnai G2 F20 field emission transmission electron microscope (FEI, America) with an acceleration voltage of 200 kV. Adsorption-desorption curve of nitrogen in the sample was analyzed by the ASAP2020 (M) automatic surface area micro-gap analyzer (Micromeritics Instrument, America).

2.4. Photocatalytic performance evaluation

The photocatalytic activity of the porous hollow cube $ZnFe_2O_4$ for the degradation of TCHC in aqueous was evaluated using a 300 W Xe lamp equipped with 350 nm–780 nm reflection filter and 420 nm cutoff filter (irradiation wavelength of 420 nm–780 nm) as the light source at ambient temperature. First, 500 mg/L of the catalyst was added into 100 mL solution of 40 mg/L of TCHC, and magnetic stirred 30 min to achieve sufficient adsorption/desorption equilibrium in dark. The liquid level of solution and the cut-off filter distance was 10 cm. Then, the sample was collected at given time intervals under light irradiation and throughout the reaction under constant magnetic stirring. The removed sample was centrifuged at 12,000 r/min for 5 min, and the supernatant was aspirated with a syringe and the concentration of TCHC was measured at a wavelength of 356 nm using the Alpha 1860 A UV–vis spectrophotometer (Puyuan, China). Degradation rate of TCHC can be calculated by the following formula:

$$\text{Degradation Rate (DR) \%} = C_t/C_O(\%) \quad (1)$$

where C_O was the absorbance of the sample before the dark reaction and C_t was the absorbance of the sample after degradation.

3. Results and discussion

3.1. The formation mechanism of the material

The fabrication process of the porous hollow cube $ZnFe_2O_4$ involved two steps. The First step was shape-controlled synthesis of PB precursor. In this step, Fe^{2+} was oxidized to Fe^{3+} by HCl, and then formed PB. During nucleation and growth processes of PB, polyvinylpyrrolidone (PVP) was employed as an effective capping gent could drive the Fe^{2+} and $[Fe(CN)_6]^{3-}$ to self-assemble with a cubic shape [29]. In the second step, The Zn^{2+} was evenly dispersed in the PB surface, during calcination treatment in air and 2 °C/min, the $ZnFe_2O_4$ are formed on the surface of cubic. Simultaneously, the organic of MOF (PB) precursor including PVP and cyanide ligand could be slowly decomposed [30], and the small voids were generated when the gas diffused outward passing through $ZnFe_2O_4$ oxide layer in the process. The porous hollow cube $ZnFe_2O_4$ was synthesized when PB precursor completely consumed. The formation mechanism of the porous hollow cube $ZnFe_2O_4$ could be illustrated by Fig. 1.

3.2. Structural analysis

Fig. 2 showed the XRD patterns of the porous hollow cube $ZnFe_2O_4$. Diffraction peaks of the sample at 2θ were 18.20, 30.10, 35.00, 42.80,