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Nanocrystalline zinc ferrite photocatalysts formed using the colloid mill and hydrothermal technique

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ABSTRACT

Nanocrystalline zinc ferrite ($ZnFe_2O_4$) photocatalysts with different crystallite sizes prepared using the colloid mill and hydrothermal technique are reported. This synthetic approach involves a very rapid mixing of Fe^{3+} cations with reducing agent and reduction process in a colloid mill reactor, followed by a slow oxidation of iron nuclei and structural transformation in a separate hydrothermal process. Material characterization has been presented by powder X-ray diffraction (XRD), chemical element analysis, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and UV–vis diffuse reflectance spectra. The results indicate that $ZnFe_2O_4$ nanocrystals with the uniform crystallite sizes have been obtained using *in situ* forming iron nuclei as the source of Fe. A possible formation mechanism of $ZnFe_2O_4$ nanocrystals was proposed. Furthermore, through photocatalytic investigation, these $ZnFe_2O_4$ nanocrystals displayed better abilities to photodecompose acid orange II azodye molecule under UV irradiation due to quantum confinement effect and high surface area structure, as compared to bulk $ZnFe_2O_4$ sample prepared by the conventional solid-state method. Since as-synthesized $ZnFe_2O_4$ nanocrystals have excellent chemical and thermal stabilities and exhibit good photocatalytic activities, it can be expected that they may have potential application in the field of industrial photo-degradation of organic azodye pollutants.

1. Introduction

In recent years, interest in transition metal ferrites of the type MFe_2O_4 nanocrystals has greatly increased due to their extensive use in high-density data storage, ferrofluid technology, magnetocaloric refrigeration, magnetic resonance imaging and heterogeneous catalysis [1–3]. For example, zinc ferrite ($ZnFe_2O_4$), known as semiconductor material, has a normal spinel structure with tetrahedral sites occupied by Zn^{2+} ions and octahedral sites by Fe^{3+} ions [4]. Its chemical and thermal stability has made $ZnFe_2O_4$ important materials, such as magnetic materials [5], catalysts [6–9], and absorbent materials [10,11], in the past decade. Particularly, increasing interests for nanoscale $ZnFe_2O_4$ have been extensively studied by worldwide researchers because of their unique size-dependent physical and chemical properties as compared to bulk counterpart materials [5].

It is well known that nanosized particles are of particular interest for catalytic applications due to their high surface to volume ratio. Several preparation techniques for $ZnFe_2O_4$ nanoparticles with uniform size have been developed including coprecipitation [11], sonochemical emulsification and evaporation [12], sol–gel technique [13], hydrothermal synthesis [14,15], mechanical milling [16,17], combustion method [18], reverse micelle technique [19], and organic precursor decomposition techniques [20–22]. However, in most of the above cases, they require handling of large amounts of organic salt, solvent or surfactant, which usually make expensive costs as well as environment pollution, and therefore are not suitable for large-scale industrial applications. On the other hand, it is generally accepted that the formation of homogeneous nanoparticles is strongly dependent on the local distribution of reactants or precursors, which is important for the nucleation and growth of nanoparticles. Therefore, it has always been a challenge or a hot issue to develop affordable and convenient synthesis route for nanoparticles with uniform crystallite size. Recently, we developed a facile pathway for the preparation of magnetic $CoFe_2O_4$ nanocrystals by a simple reduction–oxidation route [23]. This approach offers unique advantages for the uniform synthesis of special complex metal oxide nanoparticles due to the easily achievable high-speed nucleation of metallic precursors in the colloid mill reactor.

Semiconductor photocatalysts have been applied widely to degrade the organic pollutants for the remediation of hazardous wastes and contaminated groundwater, and the control of toxic air contaminants [24]. Much attention has been paid to the

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photocatalytic degradation of dyes with semiconductor compounds especially like TiO_2 under UV-light. In this contribution, we carefully investigate the uniform synthesis, microstructure and UV-light induced photo-degradation performance of nanocrystalline $ZnFe_2O_4$ with a narrow range of crystallite size. $ZnFe_2O_4$ nanocrystals were prepared via a modified reduction–oxidation route on the basis of the idea that slow oxidation of iron nuclei formed during the reduction in the colloid mill reactor has a remarkable inhibition effect on the growth of $ZnFe_2O_4$ under the hydrothermal conditions. To the best of our knowledge, there is no report on *in situ* forming iron nuclei precursor as the source of Fe for $ZnFe_2O_4$ nanocrystals. This applied approach, which needs neither the decomposition of complicated organic–metal complex precursors nor a large amount of specialized surfactants as template, is of significant importance in industrial applications as a consequence of low costs, benignancy to environment and synthetic convenience. Furthermore, the photocatalytic results show that resultant nanostructured $ZnFe_2O_4$ displayed better abilities to photodecompose acid orange II azodye molecule under UV irradiation due to quantum confinement effect and high surface area structure, as compared to bulk $ZnFe_2O_4$ sample prepared by the conventional solid-state method. It can be expected that as-synthesized zinc ferrite nanocrystals may have potential application in the field of industrial photo-degradation of organic azodye pollutants due to their excellent structural properties, such as thermal stability and strong resistance to acid and alkali.

2. Experimental

2.1. Synthesis of $ZnFe_2O_4$ nanocrystals

In a typical synthesis, three separate solutions were prepared prior to the synthesis. Solution A: analytical-grade $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in 50 mL of deionized water. Different concentrations of Fe^{3+} ions (0.088, 0.26 and 0.44 M) were used. Solution B: sodium borohydride was dissolved in 25 mL of deionized water to form a solution with the $[NaBH_4]/[Fe^{3+}]$ molar ratio of 2.0. Solution C: analytical-grade $Zn(NO_3)_2{\cdot}6H_2O$ were dissolved in 25 mL of deionized water to give a solution ($[Zn^{2+}] = 1/2[Fe^{3+}]$). Solutions A and B were simultaneously added rapidly to a colloid mill with rotor speed set at around 6000 rpm and mixed for 2 min, and then the resulting slurry was mixed with solution C. The mixture slurry was sealed in a Teflon-lined autoclave and heated at 120 °C for 12 h, respectively. The suspension was washed with deionized water several times and then ethanol, separately, and the obtained solid was dried at 80 °C for 12 h.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were collected using a Shimadzu XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, graphite-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). The samples, as unoriented powders, were step-scanned in steps of 0.04° (2θ) using a count time of 10 s/step.

Elemental analysis for metal ions in samples was performed using a Shimadzu ICPS-75000 inductively coupled plasma emission spectrometer (ICP-ES). Samples were dried at 100 °C for 24 h prior to analysis, and solutions were prepared by dissolving the samples in dilute hydrochloric acid (1:1) for 24 h at room temperature.

Room temperature Fourier transform infrared (FT-IR) spectra were recorded in the range 4000–400 cm^{-1} with 2 cm^{-1} resolution on a Bruker Vector-22 Fourier transform spectrometer using the KBr pellet technique (1 mg of sample in 100 mg of KBr).

X-ray photoelectron spectra (XPS) was recorded on a Thermo VG ESCALAB250 X-ray photoelectron spectrometer at a pressure of about 2×10^{-9} Pa using Al Kα X-ray as the excitation source. The binding energy (BE) calibration of the spectra has been referred to carbon 1s peak, located at BE = 284.8 eV.

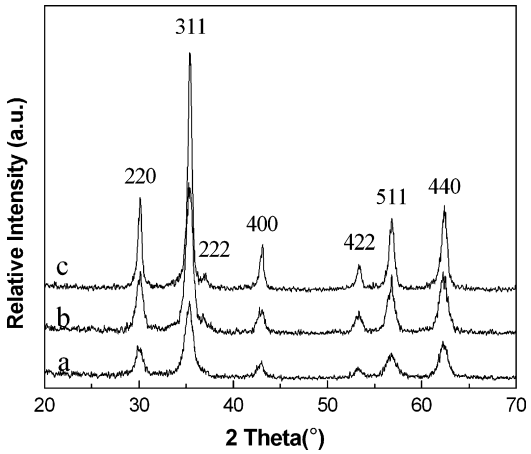

Fig. 1. XRD patterns for $ZnFe_2O_4$ synthesized by using different initial Fe^{3+} concentrations (a) 0.088 M, (b) 0.26 M and (c) 0.44 M.

Scanning electron microscopy (SEM) microanalyses of the samples were made using a Hitachi S4700 apparatus with the applied voltage of 20 kV, combined with energy dispersive X-ray spectroscopy (EDS) for the determination of metal composition.

Transmission electron microscopy (TEM) images were taken using a Hitachi H-800 transmission electron microscopy operated at 100 kV. For TEM analysis, a droplet of the ultrasonically dispersed samples in ethanol was placed onto an amorphous carbon-coated copper grid and then dried at air. High resolution transmission electron microscopy (HRTEM) was carried on a JEM-3010 high resolution transmission electron microscopy at an accelerating voltage of 200 kV.

The specific surface area determination was performed by BET method using a Quantachrome Autosorb-1C-VP Analyzer.

Solid state UV–vis diffuse reflectance spectra (DRS) were recorded at room temperature and in air by means of a Shimadzu UV-2501PC spectrometer equipped with an integrating sphere attachment using $BaSO_4$ as background.

2.3. Photo-degradation experiments

The photo-degradation experiments for acid orange II (AO-II) dye molecule over $ZnFe_2O_4$ ferrites were performed in a quartz reactor at ambient temperature. The UV source was two 36 W of H-type lamps (Beijing electric light sources research institute) with a maximum emission at approximately 254 nm. Typically, an aqueous AO-II solution (20 mg/L, 100 mL) containing 0.05 g of catalyst was vigorously stirred for 0.5 h in the dark to reach absorption–desorption equilibrium before the irradiation. Then, the mixture solution was irradiated by UV-light for a period of time. The extent of dye decomposition was determined by measuring the absorbance value at approximately 484 nm using a Shimadzu UV-2501PC spectrometer.

3. Results and discussion

3.1. Synthesis of $ZnFe_2O_4$ ferrite nanocrystals

Fig. 1 displays the powder XRD patterns for three $ZnFe_2O_4$ samples obtained by using different initial concentrations of Fe^{3+} ions. The high background of the profiles arises due to fluorescence from the Fe atoms [25]. All diffraction peaks can be indexed in a simple cubic lattice and the position along with relative intensity of