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Controlled synthesis of monodisperse $CoFe_2O_4$ nanoparticles by the phase transfer method and their catalytic activity on methylene blue discoloration with H_2O_2

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ABSTRACT

Monodisperse spinel $CoFe_2O_4$ nanoparticles have been synthesized through the solvothermal-assisted phase transfer method using aqueous soluble metal salts as starting materials and sodium oleate (SO) as the phase-transfer agent. The as-synthesized nanoparticles were characterized by X-ray diffraction, transmission electron microscopy, infrared spectroscopy, vibrating sample magnetometry, ultraviolet and visible spectrophotometry and Mössbauer spectrum. The results revealed that the as-obtained nanoparticles have a cubic spinel structure and an average diameter of 2–6 nm. It was found that SO played an important role during the transfer of the hydrophilic inorganic precursor from aqueous phase to the organic phase. On the basis of the experimental results, a possible mechanism for the formation of the nanoparticles was proposed. Surface functionalization of the as-prepared nanoparticles was conducted to render the hydrophobic nanoparticles water-soluble, which makes the nanoparticles suitable for catalytic applications. The nanoparticles showed catalytic activity in the oxidation of methylene blue with H_2O_2 as an oxidizing agent.

1. Introduction

In recent years, magnetic nanoparticles especially ferrites are attracting more and more attention due to their multifaceted applications such as high-frequency magnetic materials [1], biomedical materials [2,3], gas sensors [4] and catalyst [5,6] in view of their unique electronic and physical structures. As one typical ferrite with inverse-spinel structure, cobalt ferrite ($CoFe_2O_4$) has been extensively studied because of its high coercivity, moderate saturation magnetization, remarkable chemical stability and mechanical hardness [7,8]. The size and shape controllable synthesis of nanocrystals is a particularly active research field due to structure-dependent properties, among which monodisperse nanocrystals achieved more attention not only owing to the above mentioned reasons but also because they can be used as building blocks to construct supercrystals and superlattices [9,10]. Recent studies on monodisperse ferrite nanoparticles revealed that not only can they show high magnetocrystalline anisotropy but also they can be used to construct superlattices with magnetotransport properties [11], which urgently need the development of a simple and cost-effective synthesis route for monodisperse $CoFe_2O_4$ nanoparticles.

Many groups have developed a range of methods for synthesizing monodisperse $CoFe_2O_4$ nanoparticles such as alkalide reduction [12], reverse micelles [13,14] and coprecipitation [15]. However, the obtained products often suffer from particle agglomeration and a broad size distribution. One of the more successful routes involves thermal decomposition of mixed organic Co^{2+} and Fe^{3+} compounds, such as metal acetylacetonates, metal carbonyls, etc., in high boiling point solvents [16]. In combination with the use of surfactants, such as oleic acid and oleylamine, this procedure can also be used to control the morphology of $CoFe_2O_4$ nanoparticles [17,18]. However, most of these reported strategies for preparing monodisperse $CoFe_2O_4$ nanoparticles usually suffer from high cost of the precursors or organic solvent and their inherent toxicity. Recently, the application of phase transfer in synthesizing nanoparticles has become a promising technique to challenge this key scientific problem [19]. Compared with other general approaches, this protocol allowed nanoparticles to be synthesized in an organic medium using aqueous soluble metal salts as starting materials, which are relatively inexpensive and easily obtained. To date, the phase transfer approach has been exploited for the synthesis of a series of metal, metal oxide, alloy, semiconductor and semiconductor–metal hybrid nanoparticles [20–22]. The objective of this work is to develop a route to synthesize monodisperse cobalt ferrite nanoparticles in organic phase under solvothermal conditions with low cost. Herein, a modified two-phase system using water-soluble metal salts as starting materials and SO as phase transfer agent

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was resorted to facilitate the solvothermal treatment and size-controllable monodisperse cobalt ferrite nanoparticles were obtained. This facile and inexpensive two-phase solvothermal method may be extended to the fabrication of other MFe_2O_4 (M=Co, Ni, Mn, etc.) nanomaterials and multiple metal oxide. However, the as-prepared monodisperse nanoparticles are only well dispersed in organic solvents and unsuitable for their potential uses, such as in biological [23,24] and catalytic fields [25]. Therefore, a simple ligand exchange experiment was carried out, which renders these particles with hydrophilic surface and allows us to execute subsequent properties exploitation.

Water pollution by dyes is a serious environmental problem and a range of resolutions have been designed to degrade them, of which the Fenton oxidation process has been one of the most active and attractive systems because those generated highly potent chemical species $^{\bullet}OH$ can oxidate dyes [26–29]. In this work, catalysis of the obtained $CoFe_2O_4$ nanoparticles for the degradation of aqueous MB dye with existence of H_2O_2 was also investigated.

2. Experimental section

2.1. Synthesis of $CoFe_2O_4$ nanoparticles

All chemicals were of analytical grade and used without further purification. In a typical synthesis procedure, 0.15 mmol of $FeCl_3{\cdot}6H_2O$ and 0.075 mmol of $Co(NO_3)_3{\cdot}9H_2O$ were dissolved in 10 ml of deionized water to form a transparent solution followed by the addition of deionized water (5 ml) containing 0.6 mmol of SO. After 15 ml of toluene was added, stirring was continued for 10 min. Then the metal ions were successfully transferred from water to toluene, as evidenced by the complete color bleaching of the aqueous phase. The mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave at room temperature and 0.5 ml of tert-butylamine was rapidly added to the above two-phase system. The autoclave was sealed and kept at 180 °C for 24 h and then cooled naturally. The products were collected by centrifugation and washed with deionized water and absolute ethanol several times and dried in air at 60 °C for 12 h. In our experiment procedure, the reaction temperature and the amount of SO were adjusted to monitor the size distribution of the as-prepared nanoparticles. The as-prepared monodisperse nanoparticles were only well dispersed in organic solvents.

2.2. Surface functionalization of the as-prepared nanoparticles

To endow those as-prepared hydrophobic nanoparticles water solubility, ligands exchange reaction was conducted based on the method described by Vo et al. [30]. In a typical procedure, acetic acid aqueous solution (30%) was mixed with cyclohexane containing $CoFe_2O_4$ nanoparticles with final volume ratio of 5:1. After 8 h of stirring at room temperature, oleates capping on the nanoparticles were replaced by acetate and the nanoparticles were transferred into aqueous phase from cyclohexane. Then, the nanoparticles were separated via centrifugation and redispersed into water solution.

2.3. Catalysis test

The catalytic property of $CoFe_2O_4$ nanoparticles for the discoloration of MB dye aqueous solution was investigated and monitored by observing the change of the absorbance intensity at the wavelength of 665 nm, the maximum absorbance wavelength (λ_{max}) of the MB dye. In a typical procedure, a certain amount of $CoFe_2O_4$ nanoparticles was homogeneously dispersed into the MB dye aqueous solution (20 mg/L) and stirred for another 25 min in the dark to get adsorption equilibrium. Then aqueous H_2O_2 solution was rapidly injected in the mixture. The blue color of the mixture gradually vanished, indicating $CoFe_2O_4$ nanoparticles catalyzed the oxidization of the MB dye.

2.4. Characterization of $CoFe_2O_4$ nanoparticles

The phase of the prepared samples was monitored by X-ray diffraction (XRD) using an D/tex-Rigaku Ultima IV diffractometer with Cu-Kα source. A JEM-2100 transmission electron microscope operating at 200 kV accelerating voltage was used for transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images. FT-IR was obtained by using a Nicolet Nexus 670 FT-IR spectrometer with a resolution of 0.09 cm^{-1}. The samples for FT-IR measurement were prepared by grinding the dried powder of $CoFe_2O_4$ nanoparticles with KBr together, and then compressed into thin pellets. Magnetic measurements for the samples were carried out at room temperature using a vibrating sample magnetometer (LakeShore VSM 736). The Mössbauer spectrum was measured using a Mössbauer spectrometer in a consultant acceleration mode with a 25 mCi $^{57}Co(Pd)$ source, and the spectrum was calibrated by a 25 μm α-Fe foil at room temperature. The Mössbauer parameters were fitted by a standard least-squares fitting program. Unico UV-2802S ultraviolet and visible (UV–vis) spectrophotometer was employed for the analysis of MB dye discoloration.

3. Results and discussion

The XRD patterns of $CoFe_2O_4$ nanoparticles synthesized at 180 °C with different amounts of SO are shown in Fig. 1. The peaks of Fig. 1a–c can be well assigned to cubic $CoFe_2O_4$ crystals (JCPDS card no. 22-1086), which indicates that these samples are pure $CoFe_2O_4$ crystals without any impurity. However, when the amount of SO decreased to 0.03 mmol, some Fe_2O_3 (PDF no. 33-0664) and Co_3O_4 (PDF no. 42-1467) peaks as marked by the red line in Fig. 1d appear, indicating that SO played an important role in the purity control of the prepared cobalt ferrite nanoparticles. As displayed by previous reports, the Co^{2+} and Fe^{3+} ions in aqueous solution were firstly complexed with SO to be Co^{2+}-oleate complex and Fe^{3+}-oleate complex according to the following

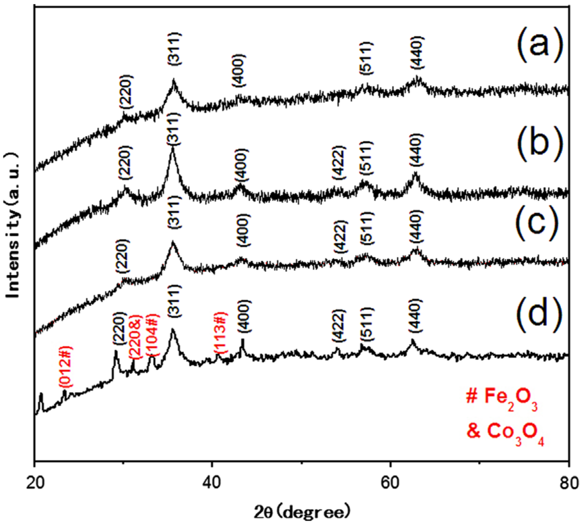

Fig. 1. XRD patterns of $CoFe_2O_4$ nanoparticles prepared at 180 °C with (a) 0.6 mmol SO, (b) 0.3 mmol SO, (c) 0.15 mmol SO and (d) 0.03 mmol SO.