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Antibacterial properties of copper-substituted cobalt ferrite nanoparticles synthesized by co-precipitation method

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ABSTRACT

Controlled growth and careful characterization of cobalt ferrite nanoparticles for antibacterial applications are challenging. Copper-substituted cobalt ferrite nanoparticles ($Cu_xCo_{1-x}Fe_2O_4$), where $x = 0.0$, 0.3, 0.5, 0.7 and 1.0, were synthesized using an economical and simple co-precipitation technique. The crystal structure and antibacterial properties of the samples as a function of Cu-substituted content were systematically studied. With increasing Cu concentration, the nanoparticle size decreased from ~30 to ~20 nm. The Fourier transform infra-red spectra exhibit two prominent fundamental absorption bands, at ~595 and 419 cm^{-1}. These bands correspond to intrinsic stretching vibrations of metals at tetrahedral and octahedral sites, respectively. The Raman scattering results reveal that increasing the Cu content enhances the local disorder at both tetrahedral and octahedral sub lattices. The results indicate that the substitution of Co with Cu in cobalt ferrite nanoparticles strongly influences the microstructure, crystal structure, and particle diameter, and also improves the antibacterial properties.

Introduction

The invention of new materials with improved properties and novel synthesis techniques is a challenge for material scientists seeking to fulfill recent technological demands. Nanostructure materials, because of their tremendous applications and interesting properties, have recently become a center of attention. Cobalt ferrite ($CoFe_2O_4$) nanoparticles are considered one of the most interesting metal-oxide materials because they have exceptional potential applications in many fields, such as ferrofluids technology (Sugimoto, 1999), high-density magnetic recording (Phua, Xu, Ma, & Ong, 2009), biomedical drug delivery (Pileni, 2001), biosensors (Zhen, He, Xu, & Shao, 2008), biocompatible magnetic nanoparticles for cancer treatment (Kim, Nikles, Johnson, & Brazel, 2008), and magnetic resonance imaging (Liu, Zou, Rondinone, & Zhang, 2000). The special properties required for biomedical applications of magnetic nanoparticles are precise control of particle size, dispersion, antibacterial properties, and biocompatibility.

According to the geometrical configuration of the oxygen nearest neighbors in spinel ferrites, the metal ions are located in two sub-lattices, namely the tetrahedral (A-site) and octahedral (B-site) arrangements (Waldron, 1955). Cobalt ferrite has an inverse spinel ferrite structure with collinear ferromagnetic properties that originate from the magnetic moment of anti-parallel spins between Fe^{3+} ions at tetrahedral A-sites and Co^{2+} at octahedral B-sites. The substitution of Co^{2+} in cobalt ferrite with other transition metals causes different properties, and it can be modified for specific applications. Several research groups have investigated the effect of doping with various cations to improve the physical properties of spinel ferrites (Gautam et al., 2011; Tanaka & Maenosono, 2008).

Mane, Birajdar, Patil, Shirsath, and Kadam (2011) reported that by varying the concentration of Co, Cu, and Zn in Co–Cu–Zn ferrite nanoparticles, the magnetic properties are enhanced and the lattice parameters are changed. Aghav et al. (2011) illustrated that substitution of Co^{2+} with Al^{3+} in $CoFe_2O_4$ nanoparticles leads to a decrease in the particle size, saturation magnetization, and magneton number. New materials exhibit improvement in the structural and magnetic properties. Chromium substituted cobalt ferrites $CoCr_xFe_{2-x}O_4$ ($0 \le x \le 1$) nanoparticles were synthesized by a sol–gel method in the research of Singhal, Jauhar, Singh, Chandra, and Bansal (2012). They found that by varying the Cr^{3+} concentration, the lattice parameters, particle size, density, band gap, and saturation magnetization were changed.

Among various chemical methods for synthesis of different types of metal oxides, the co-precipitation process has several advantages over other methods, including good homogeneity, low

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cost, high purity of product, and no need for organic solvents or heat treatment. Recently, the co-precipitation method has been developed for the preparation of magnetite nanoparticles using metallorganic precursors. Furthermore, no surfactant needs to be removed from the nanoparticles before they can be applied in the precision industry and biomedical fields. Therefore, the co-precipitation technique is a favorable alternative to other conventional methods for the preparation of ceramic oxide composites (De et al., 2000). In spite of the great amount of research on the biomedical properties of magnetic materials and transition metal-doped ferrite nanoparticles in particular (Pankhurst, Connolly, Jones, & Dobson, 2003), examining the antibacterial properties of these materials through their synthesis and characterization deserves further attention. This study is an attempt to enhance and optimize the antibacterial activity against Gram-negative *Escherichia coli* (*E. coli*) bacteria of cobalt ferrite nanoparticles by substitution of Co^{2+} with Cu^{2+}. To accomplish this, nanoparticles of copper-substituted cobalt ferrite with various Cu concentrations were synthesized via a co-precipitation method and characterized using field-emission scanning electron microscope (FESEM), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), and Fourier transform infrared (FT-IR) and Raman spectroscopy. In addition, their antibacterial properties were investigated by measuring the optical density (OD) and inhibition zone diameter (IZD).

Experimental

Copper-substituted cobalt ferrite nanoparticles with a chemical composition of $Cu_xCo_{1-x}Fe_2O_4$, where $x = 0.0$, 0.3, 0.5, 0.7, and 1.0, were prepared by a wet chemical co-precipitation method using stoichiometric amounts of cobaltous chloride ($CoCl_2{\cdot}6H_2O$), cupric chloride ($CuCl_2{\cdot}2H_2O$), and anhydrous ferric chloride ($FeCl_3$) dissolved in distilled water. Citric acid was used as a chelating agent. The neutralization was carried out with sodium hydroxide solution and the pH was maintained at 8. Finally, pure single-phase spinel structures were synthesized by annealing the precipitates at 800 °C for 10 h at a heating rate of 3 °C/min.

The structural properties of samples were investigated using Cu-Kα radiation (0.154 nm) at 40 kV and 100 mA with XRD equipment built by D8 Advance Diffractometer (Bruker, USA). The 2θ range was set to 20–70° with a resolution and step size of 0.011° and 0.02°, respectively. The Shimadzu TA-50WSI TGA/DTA instruments was used to examine the thermal decomposition behavior of the samples by means of thermogravimetry (TG) and differential thermal analysis (DTA) in air with a heating rate of 10 °C/min. A FESEM (JSM 6380LA, JEOL, Japan) with EDX attached was employed for observing nanoparticles, size calculation, and elemental analysis (a thin layer of gold was deposited on samples by sputter coater for better conductivity to avoid charging effect). The FT-IR spectra were recorded using a 5DX FT-IR (PerkinElmer, USA). Raman spectroscopy was performed using a Spectrum GX (NIR, FT-Raman, Spectrum, Germany) system with an Nd crystal laser source with a spot size of 1 μm.

The antibacterial activity of the prepared nanoparticles in the form of nanofluids was examined by calculating the growth curve of *E. coli* HB 101 protected in a Luria–Bertani (LB) broth medium (Zhang, Jiang, Ding, Povey, & York, 2007). The growth curves were obtained by determining the time growth of optical density (OD) for all samples. The measurements were performed at a wavelength of 600 nm using a UV/vis spectrophotometer (Lightwave S2000, WPA, UK) at a frequency of once an hour. For further analysis of the antibacterial properties of the samples, the following procedures were carried out. A colloidal suspension of the synthesized nanoparticles (2 mg/mL) was applied to agar plates in which *E. coli* bacteria were cultured. After 24 h of incubation, the inhibition zone diameter was measured in millimeters (mm).

Results and discussion

The morphology and chemical composition of cobalt ferrite and copper-substituted cobalt ferrite nanoparticles ($Cu_xCo_{1-x}Fe_2O_3$, with $x = 0.0$, 0.3, 0.5, 0.7, and 1.0) were examined via FESEM coupled with EDX, and the results are presented in Fig. 1. Samples with $x = 0.0$ and 0.3 exhibited irregular particles, where the agglomeration process caused large clusters to form. The average particle size was found to decrease from ~32 to ~20 nm with increasing copper-substituted concentration into $CoFe_2O_3$ nanoparticles. The decrease in the particle size can be ascribed to the formation of Cu–O–Fe on the surface of the doped nanoparticles, which in turn retards the growth of crystal grains and assists in the separation of particles. Therefore, confined particles appeared with smaller dimensions.

The presence of Cu in $CoFe_2O_3$ nanoparticles was confirmed with the help of the EDX technique (inset Fig. 1(e)). The EDX spectra indicate that the nanoparticles are composed of Co, Fe, O, Cu, Au, and C. Weak peaks for C and Au are attributed to the carbon tape used as a support and the Au thin coating for FESEM imaging purposes.

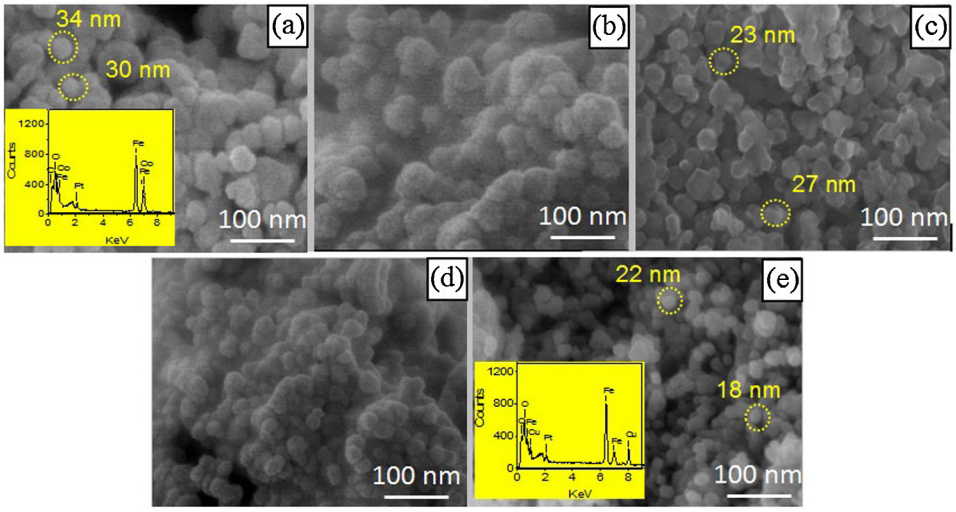

Fig. 1. Top-view FESEM images of $Cu_xCo_{1-x}Fe_2O_4$ with $x = 0.0$ (a), 0.3 (b), 0.5 (c), 0.7 (d), and 1.0 (e). Insets of (a) and (e) indicate EDX spectra of the corresponding samples.