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Size-controlled high magnetization $CoFe_2O_4$ nanospheres and nanocubes using rapid one-pot sonochemical technique

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Abstract

Highly crystalline single phase spherical and monodisperse cobalt ferrite ($CoFe_2O_4$) nanoparticles (NPs) with uniform shape and size distribution have been synthesized by one pot-rapid sonochemical method. The effect of different solvents, such as aqueous, alcoholic, and a mix of water/ethanol in 1:1 volume ratio on the shape, size, and crystalline structure of $CoFe_2O_4$ NPs were studied using X-ray diffraction, transmission electron microscopy, energy dispersive spectroscopy and Fourier transform infrared spectroscopy. The size of $CoFe_2O_4$ nanoparticle was controlled in the range from 20 to 110 nm based on the solvent medium used in the synthesis process. Furthermore, the evolution from spherical to cubic morphology of cobalt ferrite NPs is achieved by simply changing the solvent medium from aqueous to alcoholic medium. The magnetic properties of all the synthesized $CoFe_2O_4$ NPs were studied by vibrating sample magnetometer (VSM) at room temperature. The magnetization value was found to be particle size dependent, and high magnetization (Ms) of 92.5 emu/g was obtained for the $CoFe_2O_4$ NPs sample synthesized in a mixed solution of water and ethanol. A possible reaction mechanism for the formation of cobalt ferrite NPs by the sonochemical technique was discussed. The facile method adopted in our study appears to be a promising route for synthesis of highly crystalline nanoparticles within short times and without the need for using any calcination process.

Keywords: C. Magnetic properties; Cobalt ferrite ($CoFe_2O_4$); Monodisperse; Sonochemical method

1. Introduction

Cobalt ferrite ($CoFe_2O_4$) nanoparticle is considered as one of the most promising magnetic oxide materials, because of its high coercivity (Hc), moderate saturation magnetization (Ms), large magnetostrictive coefficient, remarkable mechanical hardness and high chemical stability [1]. All of these properties make it as a potential material for different electronic applications, such as recording media and noncontact torque sensors [2,3]. Furthermore, recent studies reported on the utilization of $CoFe_2O_4$ nanoparticles in different applications, such as catalyst, hyperthermia treatment, magnetic resonance imaging, and biosensor [4–6]. Most of these applications require particles with highly crystalline structure, uniform size and shape distribution, because the electrical, optical and magnetic properties depend strongly on the dimensions of the nanoparticles [7].

Many groups have worked to synthesize cobalt ferrite nanoparticles using different methods such as, hydrothermal, polyol, sol–gel, and coprecipitation [1,4,8,9]. Though all these methods provide good benefits in synthesis of $CoFe_2O_4$ NPs with different structures, but in most cases the $CoFe_2O_4$ NPs obtained were severely aggregated with nonuniform shape and

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size distributions. Furthermore, the nanoparticles in most cases need a subsequent annealing process to be well crystalline. Moreover, some of these methods need the usage of large amounts of surfactant, require deoxygenated protection, and take long synthesis times. However, the sonochemical method is considered as one of the most promising techniques for synthesis of NPs, where the sonochemistry arises from acoustic cavitation phenomenon, that is, the formation, growth, and collapse of bubbles in liquid medium [10]. Furthermore, the extremely high temperature of about 5000 K, high pressure (~20 MPa), and very high cooling rate (~1010 K/s) are supposed to come from the collapse of the bubbles, and thus can obtain extreme reaction conditions which lead to many unique properties of the synthesized particles in sonochemistry [11]. Moreover, the advantages of the sonochemical approach over conventional methods in the synthesis of metal oxide NPs, including more uniform size distributions, a higher surface area, faster reaction time, and improved phase purity, have been recognized by many research groups [12].

In our previous work, we developed a sonochemical method to synthesize highly crystalline magnetite (Fe_3O_4) NPs with uniform shape and size distribution in only aqueous medium [13]. Herein, we successfully synthesized highly crystalline, high magnetization monodisperse $CoFe_2O_4$ NPs with uniform sphere shape in one-step surfactantless sonochemical process without any deoxygenated protection. Furthermore, the synthesis time used in our experiment is only 70 min, and that too is worked out without the need for any subsequent annealing. In addition, since the solvent plays an important role in the reaction not only to control the nucleation and crystal growth but also in the formation of ferrite [14,15], the effect of different solvents of aqueous, alcohol, mixed of water/ethanol, and aqueous/PVP is therefore examined on the morphology and the magnetic properties of the cobalt ferrite NPs by various structural and magnetic characterization techniques.

2. Experimental

2.1. Materials

Iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), Cobalt sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$), polyvinyl pyrolidone (PVP), Sodium hydroxide (NaOH), and ethyl alcohol (C_2H_5OH) (99%) were purchased from Samchun Pure Chemical Co., Ltd. All the obtained chemicals were of analytical reagent grade and were used as received without any further purification, and the synthesis process was carried out under an ambient temperature.

2.2. Synthesis of monodisperse cobalt ferrite ($CoFe_2O_4$) nanoparticles

We synthesized cobalt ferrite nanoparticles ($CoFe_2O_4$ NPs) exactly in the same manner as described in our previous work [13] but with a small modification by using different solvent media. In a typical synthesis, 8 mM $FeSO_4 \cdot 7H_2O$ and 4 mM $CoSO_4 \cdot 7H_2O$ was dissolved in suitable amount of distilled water (aqueous medium) for 10 min using magnetic stirrer, and then sonicated using an ultrasonic processor for 70 min. 3 M NaOH was injected in the reaction after 15 min of starting ultrasonication. The ultrasonic processor (Vibra Cell-VCF 1500, Sonics and Materials) with a maximum power of 1500W was used in this experiment. The sonoreactor was equipped with a titanium horn having 5 cm^2 of irradiating surface area, and a piezoelectric transducer supplied by a 20 kHz generator immersed below the surface of the sonicated liquid. Finally, the obtained mixture was washed and sonicated (using cleaner SH-3400) for five times in water and ethanol while collecting the precipitate using a magnet. It was subsequently dried in a vacuum oven to obtain $CoFe_2O_4$ NPs (herein after referred to as S1). The same procedure was adopted twice again to obtain $CoFe_2O_4$ NPs by changing the solvent medium to ethanol (in this case, the sample is referred to as S2), and to a mixed solution of water/ethanol in 1:1 volume ratio (here, it is referred to as S3) in place of distilled water. Further, in order to understand the role of a stabilizing agent in the synthesis of $CoFe_2O_4$ NPs, we also added 1 g of polyvinyl pyrolidone (PVP) to the aqueous medium as an additive, and this sample is herein after referred to as S4.

2.3. Characterization

The crystal structures of the synthesized $CoFe_2O_4$ NPs were analyzed by X-ray powder diffraction technique (XRD, Rigaku D/max-2500 at a voltage of 40 kV, a current of 300 mA and a scanning rate of 2 °/min with a step size of 0.01°). The size and morphology of the nanoparticles were characterized using transmission electron microscopy (TEM, The Tecnai G2 F20 operated at 200 kV). The chemical composition was analyzed by the energy dispersive X-ray spectrometer (EDS) embedded on the TEM. Fourier transform infrared (FTIR) spectroscopic data was taken in the range from 4000 to 400 cm^{-1}. The magnetic properties of the synthesized nanoparticles were measured by vibrating sample magnetometer (VSM, Lake Share 7400) with an external magnetic field ranging from −15 kOe to +15 kOe.

3. Results and discussion

3.1. Structure characterization

The X-ray diffraction patterns of cobalt ferrite NPs synthesized in aqueous medium (S1), alcohol (S2) and mixed solution of water/ethanol in 1:1 ratio (S3) are shown in Fig. 1. It is found that all the peaks in the three patterns could be indexed to a cubic inverse spinel structure of $CoFe_2O_4$ NPs, which are consistent with the standard data for ferrite phase (JCPDS card no. 00-019-0629). Further, no peaks were detected in the patterns for any impurities which indicate the synthesis process produces high purity cobalt ferrite nanoparticles in a single reaction. Besides, the strong and sharp intensity peaks in case of (S1, S3) samples compared to the peak intensities of (S2) sample imply that the use of either the