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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

aqueous medium alone or a mix of water/ethanol medium produces higher crystallinity of the $CoFe_2O_4$ NPs than that of alcohol medium only. In addition, since the crystallite size is inversely proportional to the full width at half maximum (FWHM), the sharper peaks and corresponding smaller peak broadenings of the sample (S3) compared to the FWHMs of (S1 and S2) resulted in larger crystallite size for that sample.

3.2. Morphology characterization

The work presented here is based on the modified ultrasonics sonochemistry technique which was previously reported by our group for the synthesis of uniform magnetite nanocube [13]. In this method, the chemical reaction was driven by intense ultrasonic waves which are strong enough to produce cavitation while causing oxidation, reduction, dissolution, decomposition and hydrolysis [16–19]. Furthermore, the free radicals of $H^{\bullet}$ and $OH^{\bullet}$, which could be generated from the ultrasonic irradiation of aqueous liquids [20], are combined to produce H_2 and H_2O_2, and these resultant strong oxidants and reductants in turn are utilized for the synthesis of NPs [12]. Thus, the proposed mechanism for formation of $CoFe_2O_4$ NPs will be as follows: At first, the two precursors of metals ($FeSO_4 \cdot 7H_2O$ and $CoSO_4 \cdot 7H_2O$) we used in our experiment for iron and cobalt, respectively, decompose as a result of these unusual extreme conditions to form the divalent cations of Fe^{+2} and Co^{+2} (Eqs. (1)–(4)). Then, the H_2O_2, which was generated as a consequence of combining the two radicals of H. and OH., is suggested to initiate the oxidation of both the divalent cations of Fe^{+2} and Co^{+2} to form Fe^{+3} (Eq. (2)) and cobalt oxide (Eq. (5)), respectively. And finally, both these products recombine under the influence of ultrasound to form the final structure of cobalt ferrite ($CoFe_2O_4$) nanoparticles (Eq. (6)).

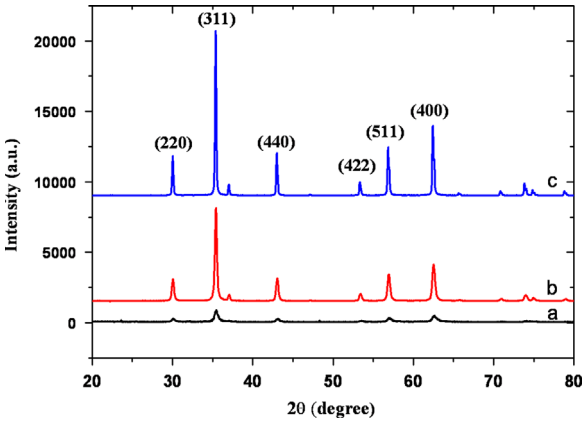

Fig. 1. XRD patterns of cobalt ferrite NPs synthesized by sonochemical method in (a) aqueous medium (S1), (b) alcohol medium (S2), and (c) Water: Ethanol (1:1) (S3).

$$FeSO_4(s) \rightarrow Fe^{2+}_{(aq)} + (SO_4)^{2-}_{(aq)} \quad (1)$$

$$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^- \quad (2)$$

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O \quad (3)$$

$$CoSO_4(s) \rightarrow Co^{2+}_{(aq)} + (SO_4)^{2-}_{(aq)} \quad (4)$$

$$Co^{2+} + H_2O_2 \rightarrow CoO + H_2O \quad (5)$$

$$Fe_3O_4 + CoO \rightarrow CoFe_2O_4 \quad (6)$$

The shapes and sizes of the as-prepared cobalt ferrite nanoparticles synthesized by sonochemical reaction with different solvents used in our experiment are shown in Figs. 2–4 observed by transmission electron microscopy (TEM). It is apparent that different shapes and sizes of $CoFe_2O_4$ NPs are formed according to the solvent used. Fig. 2 shows the well resolved TEM images of $CoFe_2O_4$ NPs synthesized in aqueous medium with nearly uniform sizes in spherical shape, and the nanoparticles also appear monodisperse with good crystalline structure which agree well with the XRD results discussed earlier. The average size of the particles estimated from the images is about 100 nm with a narrow size distribution. When ethanol is used as solvent, a dramatic decrease in the particle size is obtained to be in the range of 20 nm with evolution of shape from spherical to cubic (Fig. 3a–c). The reason for such a difference in shape and size of the particles obtained, when we used water and ethanol medium separately as a solvent medium in our reaction, could be due to the high reducing properties of ethanol with respect to water, where the ethanol molecules were probably adsorbed onto the crystal surfaces and thus limit the growth rate, thus leading to a decrease in the particle size and a change in particle shape. Similar results of decreasing the particle size while using ethanol as solvent medium in sonochemical reaction have been reported in the study of magnetite (Fe_3O_4) nanoparticles [11].

On the other hand, when we used a mixed solution of water and ethanol as a reaction solvent, a very highly crystalline and

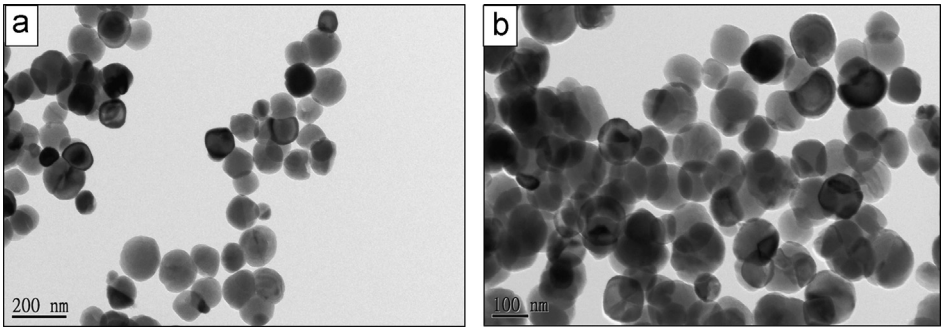

Fig. 2. TEM images of cobalt ferrite ($CoFe_2O_4$) NPs synthesized in aqueous medium (S1).

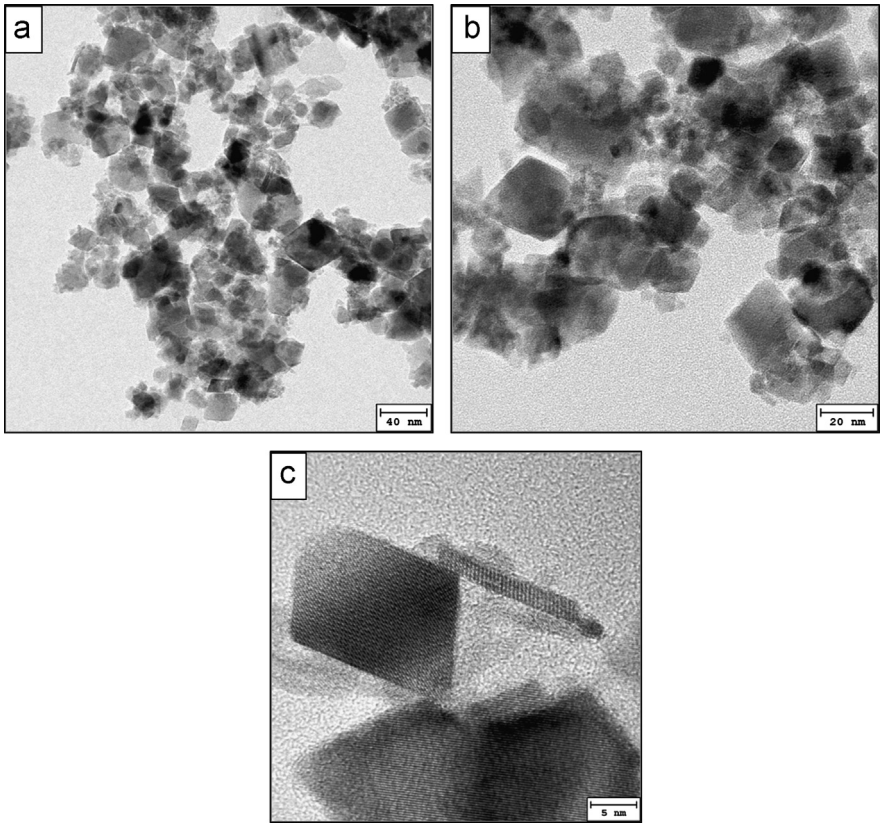

Fig. 3. TEM images of cobalt ferrite ($CoFe_2O_4$) NPs synthesized in alcoholic medium (S2).

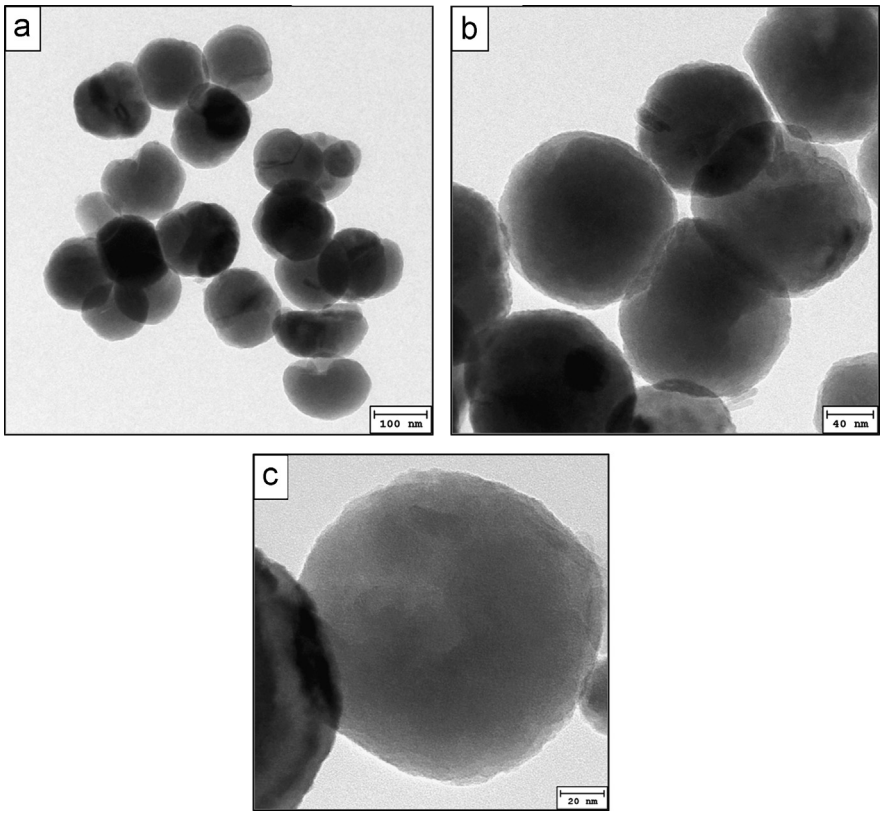

Fig. 4. TEM images of cobalt ferrite ($CoFe_2O_4$) NPs synthesized in a mixed solution of Water/Ethanol in 1:1 volume ratio (S3).

monodisperse structure of cobalt ferrite nanoparticles were resulted (Fig. 4). Furthermore, the particles obtained in this case have a uniform sphere shape distribution with an average particle size of 110 nm. The improvements in crystalline structure and monodispersity of the synthesized $CoFe_2O_4$ NPs in case of using mixture of water and ethanol solution as solvent media may be attributed to an increased rate of oxidation of Fe^{2+} and consequently an acceleration rate of formation of nanoparticles. Enomoto and coworkers reported the same results in the sonochemical synthesis of ferrite NPs with an increased reaction rate when they used a mixture of water and ethanol rather than using only aqueous medium [11].

In order to study the effect of capping agent in the synthesis process of cobalt ferrite nanoparticles by the sonochemical technique, we added one gram of polyvinyl pyrolidone (PVP) to the aqueous solution prior to the reduction process with sodium hydroxide as a stabilizing polymer. Choosing the PVP as a capping agent in our study is based on its hydrophilic properties and consequently the possibility for its solubility in the aqueous medium. Fig. 5 shows the TEM images of the cobalt ferrite nanoparticles obtained after using the PVP. The average size of the particles was dramatically decreased from 100 nm in case of using only aqueous medium to be in the range of 20–40 nm when PVP was added. Such a decrease in size in this case may perhaps be attributed to the addition of a large quantity of PVP (one gram in our case) to the mixture which greatly diminishes the Ostwald ripening process because the additional PVP present in the solution caps many of the free metallic surface sites in the nanoparticles. Consequently, since there are available only a fewer sites for the Ostwald ripening process, the nanoparticles do not increase in size [21].

The composition of as-synthesized $CoFe_2O_4$ NPs was confirmed by EDS analysis for different samples. Fig. 6 reveals that there are mainly three elements of Fe, Co and O only present in the sample with desired ratios and thus indicates that the composite is $CoFe_2O_4$ NPs in the three samples. However, the obtained Cu and C peaks in the spectra are due to carbon copper grid employed in the measurements. Further experimental confirmation is obtained through the FTIR spectra for three different samples (S1, S2 and S3), as shown in Fig. 7. All the three samples contain large peak around 542 cm^{-1} which related to the vibration of Fe–O functional group matching well with the characteristic peak of ferrite [22]. Also, all the curves contain another peak at around 3500–3000 cm^{-1} which could be attributed to the stretching of OH groups.

3.3. Magnetic properties

The magnetic properties of the samples of $CoFe_2O_4$ NPs (S1, S2, S3 and S4) were measured at room temperature using VSM in an external magnetic field ranging from –13 kOe to + 13 kOe, as shown in Fig. 8. It can be seen from the loops that the applied field is not enough to obtain saturation of magnetization for any of the samples. However, saturation magnetizations for all these samples were calculated by using the linear fits of M versus 1/H curves as 77.01, 37.78, 92.57 and 75.81 emu/g for S1, S2, S3 and S4 samples respectively, and the same were shown in the inset of Fig. 8 for different samples. On the other hand, the maximum magnetizations were estimated from the loops for the four samples (S1, S2, S3 and S4) as 71, 33.8, 87 and 70.5 emu/g, respectively. Indeed, the magnetization values of S1 and S4 are close to the theoretical value of bulk cobalt ferrite ($CoFe_2O_4$) of 73 emu/g [23] and that of S3 sample is even higher than the

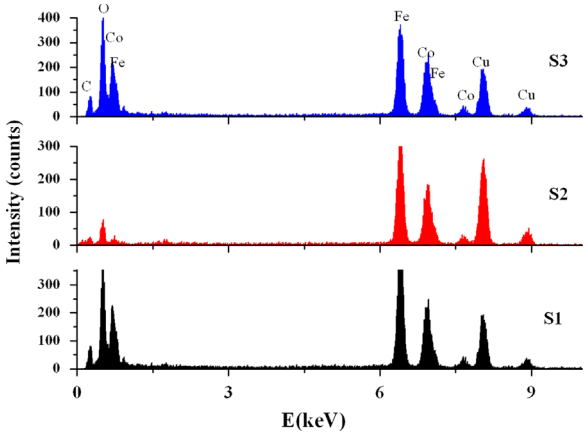

Fig. 6. EDS patterns of cobalt ferrite NPs synthesized by sonochemical method in aqueous medium (S1), alcohol medium (S2), and Water:Ethanol (1:1) (S3).

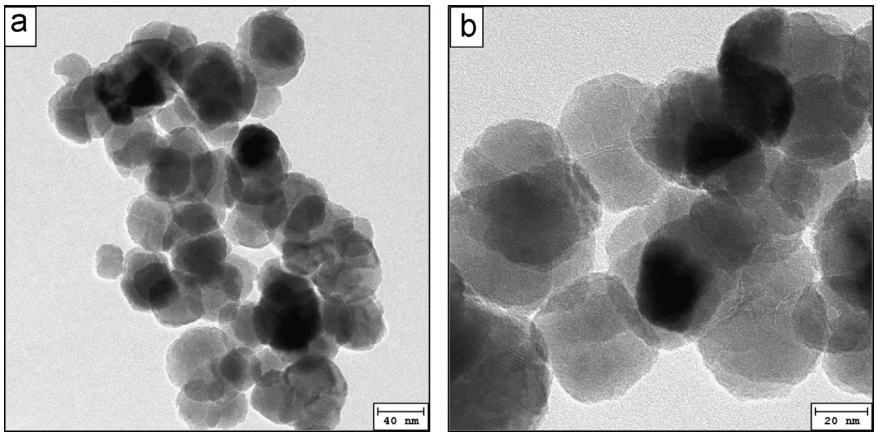

Fig. 5. TEM images of cobalt ferrite ($CoFe_2O_4$) NPs synthesized by adding 1 g of PVP to the aqueous solution.

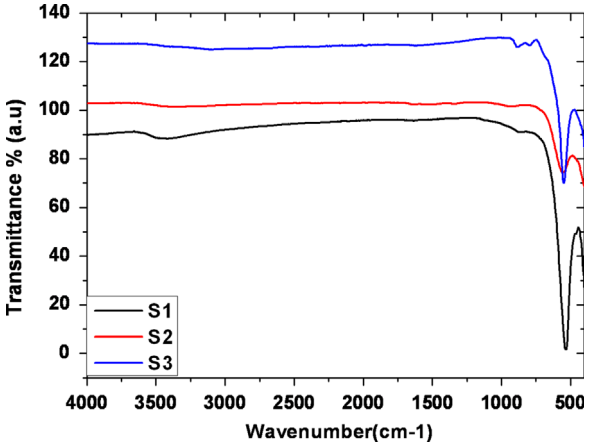

Fig. 7. FTIR spectra of cobalt ferrite NPs synthesized by sonochemical method in aqueous medium (S1), alcohol medium (S2), and Water:Ethanol (1:1) (S3).

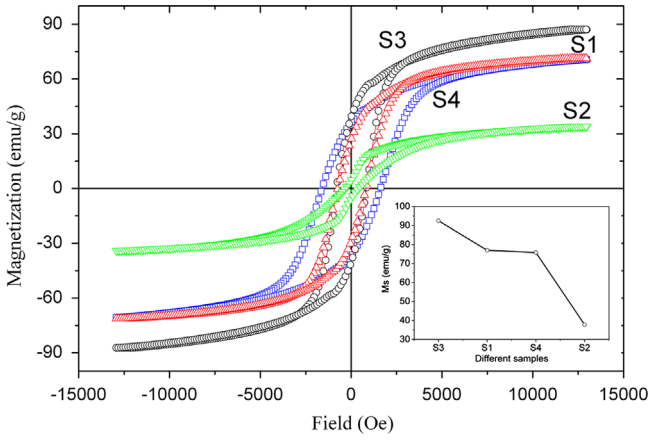

Fig. 8. Magnetization curves of cobalt ferrite NPs synthesized in aqueous medium (S1), alcohol medium (S2), mixed solution of Water:Ethanol (1:1) (S3), and PVP added to the aqueous solution (S4). The inset represents the calculated values of saturation magnetization for the four samples using M versus 1/H linear fitting curves.

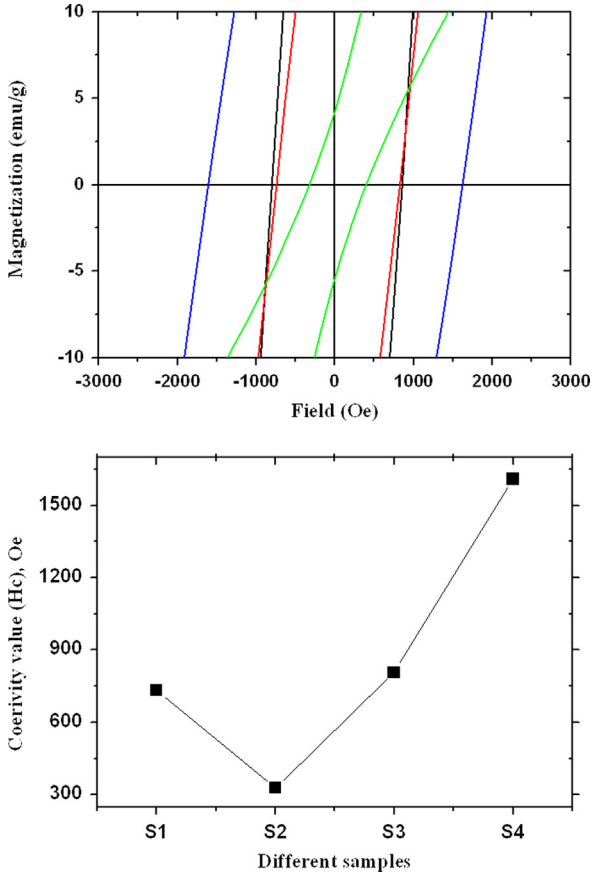

Fig. 9. Magnified view of the curves near low magnetic field and corresponding coercivities of different samples.

theoretical bulk value. This higher value may be ascribed to the larger particle size with negligible surface spin disorder. This argument is well supported by the higher degree of the crystallinity of these synthesized $CoFe_2O_4$ NPs, as observed through their corresponding XRD patterns, resulting in negligible surface spin canting and thus justifying the higher values of magnetization [24,22]. At the same time, the dramatic decrease in the magnetization value of the sample synthesized in alcohol medium (S2) is mainly attributed to its small particle size and poor crystallinity since it is well known that the magnetization value is very much sensitive to the size and crystallinity of the particles. Further, decrease in the particle size leads to an increase in surface to volume ratio [25], which in turn causes more surface spin disorder [26], and consequently a significant reduction in the magnetization value obtained.

Fig. 9 shows a magnified view of the curves near low magnetic field to make the coercivity value more clear for different samples of synthesized $CoFe_2O_4$ NPs, and the inset represents the values of coercivity for the same samples (732, 328, 807 and 1610 Oe for S1, S2, S3 and S4 samples, respectively). The samples which used aqueous medium in full or part exhibit similar values of coercivity at 732 Oe (S1) and 807 Oe (S3), whereas the PVP added sample (S4) displays maximum value of coercivity at 1610 Oe. Interestingly, rather low value of coercivity is obtained for S2 sample at 328 Oe. The reason for such a huge difference in the coercivity value among different samples may be ascribed to surface pinning that arises due to missing coordination of oxygen atoms and the shape effect of the nanaoparticles. Unlike the curved topography in spherical $CoFe_2O_4$ NPs which display larger coercivities, the cubic $CoFe_2O_4$ MNPs are hypothesized to fewer missing oxygen atoms and less surface pinning, resulting in lower coercivity for the cubic structures [27]. Song et al. reported similar results of variations in coercivity with shape structure from sphere to cube [28]. Thus, it may be pointed out that the shape effect plays an important role in determining the coercivity similar to the size effect on the magnetization value of these nanoparticles.

Nevertheless, in order to emphasize the advantages of our sonochemical synthesis method, an attempt has been made by comparing the properties of our cobalt ferrite nanoparticles with the same materials prepared by other methods. Table 1 shows a comparison of $CoFe_2O_4$ NPs properties synthesized

Table 1
A comparison of $CoFe_2O_4$ NPs properties synthesized by our sonochemical method and different methods by other groups.

Synthesis method of $CoFe_2O_4$ NPs	Surfactant	Calcination temperature (°C)	Ms (emu/g)	Crystallinity	Dispersion	References
Chemical method	Used	–	57	Not well crystalline	Some aggregation	[29]
Electrochemical method	Used	–	87	Not well crystalline	Some aggregation	[7]
Citrate gel method	Used	800	79	Not well crystalline	Good dispersion	[30]
Hydrothermal method	–	300	74.8	Good crystalline	Some aggregation	[1]
Sol–gel method	Used	600	62	Good crystalline	Some aggregation	[31]
Sonochemical (our method)	–	–	92.5	Highly crystalline	Good dispersion	-

by our sonochemical method and other different methods. Saso Gyergyek et al. and Mazario et al. synthesized $CoFe_2O_4$ NPs using chemical and electrochemical methods to obtain high magnetization value of 57 and 85 emu/g, respectively [29,7]. In other studies, Goh et al. and Girgis et al. and Sajjia et al. prepared $CoFe_2O_4$ NPs using hydrothermal and sol–gel method and the reported value of magnetization of their nanoparticles were 79 and 62 emu/g [1,30,31]. Though these studies were successful in synthesizing $CoFe_2O_4$ NPs with good magnetic properties, most of these nanoparticles suffer from the aggregation and are not well crystalline to be promising for various applications. Moreover, most of the research groups mentioned above used much amount of surfactant in their experiments and consequently involve high costs in their execution. Some of the studies even used calcination process at a higher temperature to improve crystallinity of their samples. In contrast, we used a facile sonochemical route without the need for using any kind of surfactant or subsequent calcination process to obtain highly crystalline $CoFe_2O_4$ NPs with high magnetization value of 92.5 emu/g within only 70 min of the reaction time; thus making our method highly feasible and attractive for synthesizing monodisperse nanoparticles with good magnetic properties suitable for bioapplications.

4. Conclusion

In summary, we succeeded to synthesize a highly crystalline, monodisperse $CoFe_2O_4$ NPs with uniform shape and size using rapid single-sonochemical reaction and without any kind of surfactant and deoxygenated protection or subsequent calcination process. Also, different morphological structures of spherical and cubic shape with different particle sizes were obtained by changing the synthesis solvent medium. Saturation magnetization values of 77.01, 37.78, 92.57 emu/g were obtained for the samples synthesized in aqueous medium, alcoholic, and mixed solution of water and ethanol in 1:1 volume ratio, respectively. Further, on adding PVP to the aqueous medium, the particles size has been observed to decrease with the corresponding decreases in the degree of crystallinity as well as in saturation magnetization to obtain the value of 75.81 emu/g. In view of the obtained results of high crystalline structure, high magnetization value and good dispersion properties, we consider our $CoFe_2O_4$ NPs carry enough significance for use in various bioapplications.

Acknowledgment

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