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One-dimensional ordered growth of magneto-crystalline and biocompatible cobalt ferrite nano-needles



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ABSTRACT

In this letter, we have reported a novel synthesis of CoFe_2O_4 nano-needles by a co-precipitation method using precursors of ferric chloride and cobalt nitrate at 80 °C. The structural and magnetic properties of as-grown needle-like CoFe_2O_4 nanostructures exhibit cubic spinel structure. CoFe_2O_4 nano-needles have an average diameter of 15 nm with an aspect ratio of 30:50, which was depicted by High-resolution transmission electron microscopy (HRTEM). Superconducting Quantum Interference Device (SQUID) confirmed the property of superparamagnetism. The magnetic measurement illustrated that the coercivity (H_c) of CoFe_2O_4 nano-needles increased from -145.84 Oe at 5 K to -25.38 Oe at 312 K. The cell viability studies of CoFe_2O_4 nano-needles were performed in the concentration range of 5–1000 $\mu\text{g}/\text{ml}$ on L6 (Skeletal muscle cell lines) and Hep-2 (Larynx carcinoma) cells using 3-(4,5 dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay. There was more than 50% cell viability for both the cell lines, but Hep-2 cells were more prone to killing as compared to L6 cells. Such biocompatible nanostructures can be used as drug-delivery systems for cancer therapeutics.

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1. Introduction

Magnetic nanomaterials have intrigued the scientific community to enhance its mechanical hardness and biological activity. In the past decade, the synthesis of magnetic nanomaterials have been intensively studied due to the wide applications in biosensing, medical [1], and magnetic storage media [2]. The chemical routes for the synthesis of magnetic nanoparticles mainly include co-precipitation [3], microemulsions [4], sol-gel [5], and hydrothermal or solvothermal reactions [6]. The electrical, magnetic, thermal, chemical, and biomedical properties of nanomaterials strongly depend upon the structure and morphology of the particles. Hence, many efforts have been devoted to the manipulation of these factors to meet the needs for different applications. One-dimensional (1D) nanoscale materials have stimulated considerable interest recently because of their small dimension and thermodynamic stability [7]. Cobalt ferrite is a well-known hard

magnetic material with high coercivity, moderate magnetization, high electromagnetic performance, excellent physical and chemical stability, mechanical hardness and high cubic magneto-crystalline anisotropy. There are many conventional techniques for preparation of cobalt ferrite but all of them have the disadvantage of agglomeration [8,9]. In this paper, we have presented one-pot synthesis of cobalt ferrite nano-needles by the co-precipitation method. The size and size distribution was regulated by controlling the nucleation and growth rates. When the nucleation rate was higher than the growth rate, smaller and uniformly distributed nano-needles were obtained during synthesis [10]. Cytotoxicity assay of such nanostructures were performed on L6 (Skeletal muscle cells) and Hep-2 (Larynx Carcinoma) using MTT for the comprehension of toxicity as well as their significance in the field of Nanomedicine.

2. Experimental section

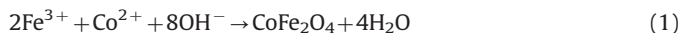
The chemical reagents used for nano-needle synthesis were ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), Cobalt (II) nitrate Hexahydrate

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($\text{CoN}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$), Sodium Hydroxide (NaOH) and Hydrochloric acid (HCl). All the chemicals were purchased from Sigma-Aldrich and were directly used without any further purification.

In a typical synthesis, 50 mL of degassed 1.5 M NaOH solution was used as a reducing agent under constant stirring. Then 10 mL of deionised water was degassed with nitrogen gas and then 0.0018 M of $\text{CoN}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$, 0.0036 M of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.85 mL of HCl were added. The solution mixture was then added to NaOH solution under constant stirring with nitrogen atmosphere at 80°C for 1.5 h. The reaction is as follows:



Nitrogen gas was passed through the solution throughout the experiment to prevent the formation of hematite as well as to deaerate the system [12]. Later, black solid powders were separated by using a magnet. The particles were then washed with distilled water for three times. The final product was dried in a desiccator for 24hrs.

3. Results and discussions

X-ray diffraction (XRD) pattern (Fig. 1A) suggested the formation of cobalt ferrites with well-defined lattice planes of (111), (220), (311) and (400), which are signature markers of cobalt ferrite. The significance of nitrogen gas was proved by the absence of any hematite peak in XRD. The crystal size determined by Scherrer equation with XRD data is 14.8 nm, which is close to the particle size calculated from TEM images (14.6 nm). This indicates that CoFe_2O_4 is nanocrystalline in nature.

Transmission electron microscopic observation of black colored cobalt ferrites apparently showed formation of needle shaped morphologies (Fig. 2A). The aspect ratio of the needles is in the range of 30–50 with sharp tips. Furthermore, evidence of the nanostructure was given in Fig. 2B from HR-TEM micrographs and Inverse Fast Fourier Transform (IFFT) diffractogram (inset of Fig. 2B). They display well-crystallized cobalt ferrite nano-needles with a lattice fringe of 0.25 nm, which is very close to the interplanar spacing of (311) plane of the ferrite crystal phase.

Energy dispersive X-ray (EDX) spectrometer analysis confirmed the stoichiometric ratio of $\sim 2:1$ for Fe and Co (Fig. 2C). In addition, selected area electron diffraction (SAED) patterns in Fig. 2D show several discernible concentric rings, which revealed crystalline spinel phase structure of the needles.

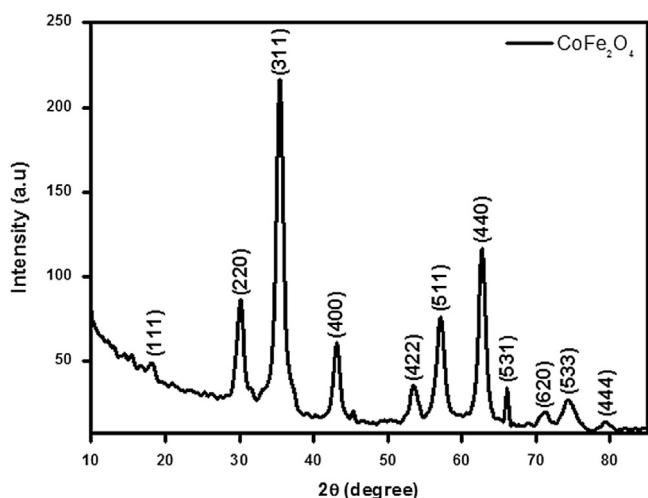


Fig. 1. XRD patterns of the CoFe_2O_4 nano-needles synthesized by the co-precipitation.

The UV-visible spectrum of CoFe_2O_4 nano-needles is shown in Fig. S1 (see in Supplementary information). Examination of the spectra shows that the solution has absorption in the entire range of UV-vis spectrum, and absorption increases gradually with decrease in wavelength.

The magnetic properties of pure CoFe_2O_4 nano-needles were evaluated by SQUID. Typical magnetization hysteresis loops are shown in Fig. 3A and saturation magnetization (M_s), magnetic remanence (M_r), H_c values at 5, 300 and 312 K are presented in Table 1. The Hysteresis curve at 5 K suggest an analogous behavior to what is shown by a classic ferromagnet, with $M_s=74$ emu/g, and $M_r=7.53$ emu/g. However, the ratio of $M_r/M_s=0.1$ is lower than the one reported for ferromagnets with cubic anisotropy (magnetocrystallinity) of $M_r/M_s=0.8$, and was lower than the one observed on systems of nanostructures with a uniaxial anisotropy, $M_r/M_s=0.5$. This feature suggests that there is magnetocrystalline anisotropy acting over the relaxation of the magnetic moment of the nanostructures. This could be co-related to the shape of the needle-like morphology of the nanostructures. This suggests that the response of material to the applied field is dominated by the interactions of the particles, which seems to be of demagnetizing nature. On the other hand, the curves obtained at 300 and 312 K show an absence of measurable hysteretical characteristics, which suggests that at these temperatures the system is still under the superparamagnetic regime. This fact is based on the observation that both curves superimpose on each other almost perfectly. Thus, it suggests that the response of magnetization is dominated by the interactions among particles, such as the ones related to core-surface exchange in particles and not to surface phenomenon [5].

In the case of ZFC (Zero Field Cooling) curve (Fig. 3B), it can be noticed that no maximum can be observed which is normally attributed to the blocking temperature. This temperature indicates the value above which the system starts to show superparamagnetic characteristics. Moreover, it can be noticed that the FC (Field Cooling) curve shows irreversibility with respect to the ZFC curve [11]. The behavior of both curves is congruent with the observations made with respect to the response of the sample's magnetization as a function of applied field. This explains us that when the size of the magnetic materials is smaller than the superparamagnetic critical dimension, just above the blocking temperature, the thermal fluctuation of the particles will surely circumvent the anisotropy. This will cause rotation of the moments among the different easy directions and superparamagnetism is shown. The demagnetizing interactions within particles might be responsible for dipolar coupling among magnetic moments that are close enough to form a multidomain-like magnetic ordering in nano-needles.

Room temperature Raman spectra of as-synthesized cobalt ferrite samples showed in Fig. S2 (see in Supplementary information) show broad peaks at 474, 564, 636 cm^{-1} and a strong peak at 682 cm^{-1} which clearly indicates cubic structure, thus depicting four Raman active modes [$A1g(2)+A1g(1)+T2g(3)+T2g(2)$]. Due to difference in ionic radii of Co and Fe ions in CoFe_2O_4 , where Fe alone occupies the tetrahedral site as well as Co and Fe occupies octahedral site, the Fe–O, Co–O bond distance redistribute between both the sites resulting in doublet like structure.

The biological property of these nanostructures for the application in the field of drug-delivery was analyzed using various concentrations of cobalt ferrite nano-needles ranging from 5–1000 $\mu\text{g}/\text{ml}$ and then MTT assay was performed. Fig. 4 demonstrates more than 50% viability for both L6 and Hep-2 cells. Cancer cell lines (Hep-2) were more prone to killing by cobalt ferrite nanostructures as compared to normal cell lines, which explains its biocompatibility. This corroborates that such nanostructures can be exploited as drug-delivery vehicles for cancer therapeutics.

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