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One-pot synthesis of high magnetization air-stable FeCo nanoparticles by modified polyol method

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ABSTRACT

High magnetization FeCo nanoparticles with different Fe/Co ratios have been successfully synthesized by surfactant free simple modified polyol method. Polyethylene glycol (PEG) was used as solvent and reducing agent simultaneously in this synthesis process. All the synthesized samples of FeCo nanoparticles were annealed at 600 °C before characterizations. X-ray diffraction (XRD) data on the samples confirm formation of a body-centered-cubic single phase structure in all the compositions. Transmission Electron Microscopy (TEM) data suggest that the annealed FeCo nanoparticles are of 50–90 nm in size. The use of PEG and the annealing procedure employed ensure that the obtained nanoparticles are stable in air. This observation is well supported by both the analysis of Energy Dispersive Spectrometry (EDS) and the images of TEM which establish the formation of a thin passive oxide layer over the FeCo nanoparticles thereby resulting in the stability of the nanoparticles. The physical Property Measurement System (PPMS) reveals that the $Fe_{60}Co_{40}$ composition among all the samples exhibit highest saturation magnetization of 230.14 emu/g at 5 K.

1. Introduction

Magnetic nanoparticles with high saturation magnetization are considered to be very important for magnetic energy, data storage, magnetic separation, drug delivery and imaging applications [1–5]. Particularly, magnetic nanoparticles used in hyperthermia and targeted drug delivery require high saturations magnetizations for their easy manipulation through magnetic field assistance. Similarly, magnetic labels for biosensor applications should possess high magnetic moments for efficient translocation of the functionalized labels to the specific sites on the sensor surface [6,7]. Thus, the quest for identifying suitable materials for the said purpose points towards the most feasible body centered cubic (bcc) FeCo magnetic nanoparticles due to their high saturation magnetization (Ms = 240 emu/g), high Curie temperature and permeability properties [8,9].

Several investigations were reported on FeCo nanoparticles synthesized using different techniques such as, thermal decomposition [10–13], wet chemical processes (by means of a reducing agent such as borohydride) [14,15], and chemical vapor deposition [16]. Among the various wet chemical methods, the polyol process which involves reduction of a metal salt with a diol, typically ethylene glycol, or diethylene glycol, or a mixture of both [17], is believed to be one of the most appropriate methods, as it inherits the possibility to control the experimental conditions kinetically and to scale up the nanoparticle size easily [18]. Also, the polyol process is preferred over the others for simple reason that it does not emit toxic gases like carbon monoxide as in the case of thermal decomposition or contaminate the product as in the case of borohydride reduction [19,20].

Recently, there have been some reports on the synthesis of FeCo nanoparticles using polyol method [9,21–23]. Even though these studies provide high saturation magnetization, which reaches in some case to 221 emu/g, their particle sizes are relatively larger (> 100 nm) after annealing implying an amount of lesser control on the growth of the particles. This may be disadvantageous for some applications such as targeted drug delivery in which the larger particles are likely to be obstructed by endothelial barriers. Hence, by optimizing the Fe/Co ratio, concentration of the hydroxyl ions and the reaction condition in a surfactant free facile one-pot modified polyol method, we herein successfully synthesized size-controlled and air stable FeCo nanoparticles with high saturation magnetization. The crystalline structure and shapes of the synthesized nanoparticles were examined by XRD, TEM, EDS and the saturation magnetization was measured using PPMS.

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2. Experimental

The powders of FeCo nanoparticles with different chemical compositions such as $Fe_{20}Co_{80}$, Fe_{50} Co_{50}, $Fe_{60}Co_{40}$, and $Fe_{70}Co_{30}$ were prepared by modified polyol method. High purity analytical grade iron chloride tetra hydrate ($FeCl_2 \cdot 4H_2O$), cobalt acetate tetra hydrate ($Co(Ac)_2 \cdot 4H_2O$), polyethylene glycol (PEG), sodium hydroxide (NaOH) and ethyl alcohol were purchased from Sigma Aldrich and were used in synthetic reaction without any further treatment.

2.1. Synthesis of FeCo nanoparticles

At first, mixtures of ($FeCl_2 \cdot 4H_2O$) and ($Co(Ac)_2 \cdot 4H_2O$) in desired proportions with suitable amounts of PEG were prepared in round bottom flasks. For all the compositions, the pH of the solutions was adjusted in between 10 and 11 by adding NaOH prior to the reduction process. Then the PEG-metal salts solution was gradually heated up to 300 °C while stirring continuously using a magnetic stirrer, and refluxed at this temperature for 2 h. During this process, it was observed that the solution turned black in all the cases within a few minutes after reaching the refluxing temperature. The solutions were then cooled down to room temperature, ultrasonicated for about 20 min, washed several times using ethanol and water and finally collected by using a magnet. The synthesized powders were subsequently annealed for 2 h at 600 °C in the presence of hydrogen before characterizations.

3. Results and discussion

Crystalline structures of the synthesized FeCo nanoparticles were examined by X-ray powder diffraction (XRD) technique using Rigaku RiNT 2200. The size and morphology of the nanoparticles were characterized using transmission electron microscopy (Tecnai G2 F20). Energy dispersive spectroscopy (EDS), which was embedded on TEM, was used for elemental analysis. The magnetic properties of the nanoparticles were measured by Physical Property Measurement System (PPMS-VSM, Quantum Design Inc.) in an external magnetic field ranging from −30 kOe to +30 kOe.

3.1. Structure characterization

The X-ray diffraction patterns of the synthesized FeCo nanoparticles are shown in Fig. 1. It is apparent that three characteristic peaks indexed at 2θ values of 44.82, 65.2 and 82.66° corresponding to the crystal planes of (110), (200) and (211) were observed for all FeCo of different compositions. The strong and sharp diffraction patterns match only with that of the α-FeCo of body centered cubic structure (bcc) consistent with the standard data for FeCo (JCPDS card no. 00-044-1433), and no additional peaks for iron oxide or cobalt oxide were observed. Typical EDS analysis of the annealed FeCo samples in Fig. 2 reveal that the materials are mainly composed of Fe and Co metals only while displaying a small percentage (~2–3%) of oxygen for all the samples with different Fe/Co ratios. Since the weight percentage of the oxygen is so small, it perhaps could not be sufficient enough to be identified as an additional oxide phase through XRD patterns.

3.2. Morphology characterization

Typical TEM images of the as-prepared FeCo nanoparticles are shown in Fig. 3(a,b). The images reveal that the as-synthesized nanoparticles are monodisperse and spherical in shape with

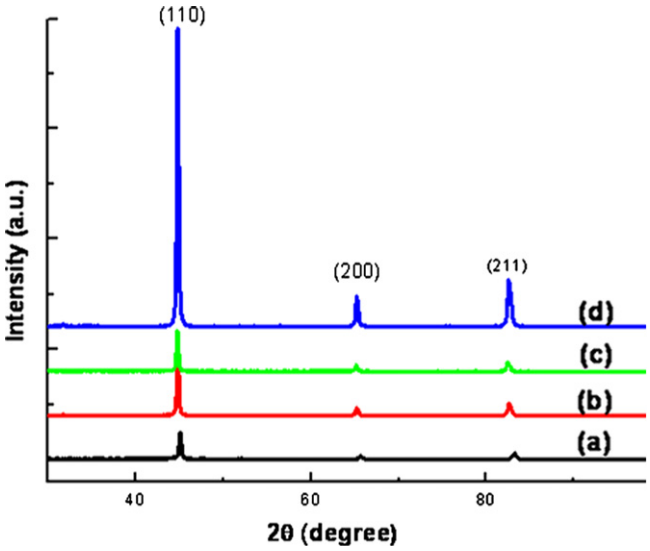

Fig. 1. XRD patterns for different compositions of the 600 °C annealed FeCo nanoparticles: (a) $Fe_{20}Co_{80}$, (b) Fe_{50} Co_{50}, (c) $Fe_{60}Co_{40}$, (d) $Fe_{70}Co_{30}$ and (e) $Fe_{80}Co_{20}$.

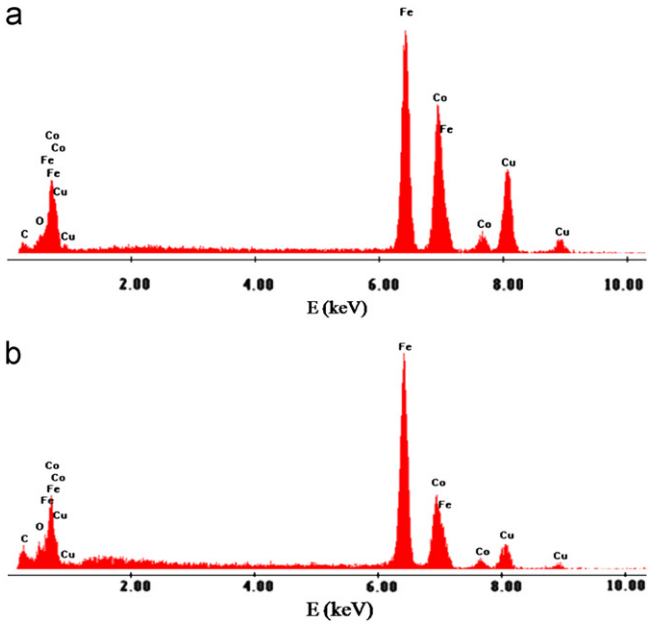

Fig. 2. EDS patterns of: (a) $Fe_{60}Co_{40}$ and (b) $Fe_{80}Co_{20}$ nanopaticles annealed at 600 °C showing the presence of Fe and Co and very small percent of oxygen elements in the nanoparticles (Cu and C peaks are due to carbon copper grid).

average size of about 10 nm. The smaller size of the FeCo nanoparticles, in the present study, has been successfully obtained mainly by controlling the reaction conditions such as reaction time, PEG, Fe/Co ratio, optimization of the concentration of hydroxyl ions, and the ultrasonication procedure. The optimum choice of the concentration of hydroxyl ions is not only important in size control but also in prohibiting the material from formation of additional phases. For example, we found that by decreasing the concentration of hydroxyl ions in solution, a cobalt ferrite phase was formed in the reaction solution. Also, when the reaction time is increased for more than 2 h, it resulted an increment in particle size to more than 100 nm. This has been clearly demonstrated in Fig. 3(c,d) which shows the TEM images of the annealed sample where the particles were still spherical in shape but with increased sizes to about 50–90 nm.