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Synthesis of monodisperse and high moment nickel–iron (NiFe) nanoparticles using modified polyol process

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ABSTRACT

Monodisperse NiFe nanoparticles with different compositions have been successfully synthesized by surfactant free simple modified polyol method. In the process, polyethylene glycol was used as a solvent media and it has been found to play a key role to act as a reducing agent as well as a stabilizer simultaneously. XRD, TEM, and EDS analysis techniques were used to characterize the synthesized nanoparticles. TEM images displayed formation of a thin oxide layer around the nanoparticles, and confirmed by detection of some oxygen element using EDS measurement. The magnetic properties of the synthesized NiFe NPs samples were measured by vibrating sample magnetometer (VSM) at room temperature, and the saturation magnetization value was found to be iron content dependent.

1. Introduction

Recently, the Ni–Fe nanoparticles have received great attention because of its diverse practical applications in the fields such as magnetic materials, catalyst, and medicine application [1]. Especially for bioapplications, the magnetic nanoparticles should be highly crystalline, monodisperse, have high magnetization value, and superparamagnetic properties so as to make them suitable for applications such as targeted drug delivery, hyperthermia and magnetic resonance imaging enhancement [2]. Furthermore, the nickel–iron nanoparticles containing 65–90 wt% nickel is well known as permalloy, and is important because of its magnetic permeability and low hysteresis loss [3].

Many groups have synthesized NiFe nanoparticles using different methods such as hydrothermal method, hydrogen reduction of Fe and Ni inorganic salts, reverse micelle techniques, and sonochemical decomposition [3–8]. Even though all these methods provide good benefits in synthesis of NiFe NPs with different structure and properties, but the obtaining of NiFe nanoparticles with highly crystalline structure, monodisperse, uniform shape and size distribution with good magnetic properties by easy process and without using of surfactant, and complicated procedures is still of high interest. However, the polyol method which involves reduction of metal salts with a diol, typically ethylene glycol, diethylene glycol, or a mixture of both is believed to be one of the most appropriate methods for synthesis of nanoparticles. Where, by using the polyol process we can dispense for using of surfactant, because the polyethylene glycol (PEG) plays a triple role as high-boiling solvent, reducing agent, and stabilizer to efficiently control the particle growth and prevent inter-particle aggregation due to steric interactions, in addition to its hydrophilic properties [9]. Also, the polyol method is not only used for synthesis of different kinds of magnetic nanoparticles like FeCo and Fe_3O_4 as we reported in our previous works [9,10], but also it is a useful method for synthesis of other different nanoparticles like Cu, ZnO, Au, and Ag [11–14].

Herein, we report a facile polyol method for the preparation of high magnetization and nearly superparamagnetic NiFe nanoparticles without using any surfactant and deoxygenated conditions, while realizing the possibility for controlling the compo sition of the nanoparticles by varying some of ratio between iron and nickel precursors. The structure, composition, size, shape, surface coating, and magnetic properties of the synthesized nanoparticles were examined in detail and discussed the obtained results.

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2. Experimental

2.1. Materials

High purity analytical reagent grade iron chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), nickel chloride hexa hydrate ($NiCl_2 \cdot 6H_2O$), polyethylene glycol (PEG), sodium hydroxide (NaOH) and ethyl alcohol were purchased from Sigma Aldrich and used in synthetic reaction without any further treatment.

2.2. Synthesis of NiFe nanoparticles

NiFe nanoparticles were prepared with different chemical compositions such $Ni_{20}Fe_{80}$, $Ni_{50}Fe_{50}$, and $Ni_{80}Fe_{20}$ based on our reported work [9] with some modifications. Firstly, in round bottom flasks, mixtures of ($FeCl_2 \cdot 4H_2O$) and ($NiCl_2 \cdot 6H_2O$) with a suitable amount of Polyethylene glycol (PEG) which was used as dispersing media was prepared in different compositions. For all the compositions, the pH of the solutions was adjusted in-between 10 and 11 by adding NaOH prior to reduction process. Then the PEG-metal salts solution was heated up to 200 °C for 30 min, then increase the temperature to 300 °C, and was continuously stirred using a magnetic stirrer, refluxed at this temperature for 2 h. Then the solutions cooled down to room temperature and washed several times using ethanol and water and then collected by using the magnet. The as-synthesized NiFe nanoparticles were annealed in presence of hydrogen for 2 h.

2.3. Characterization

Structural characterizations were performed by X-ray diffraction (XRD) analysis using Rigaku RiNT 2200, which was carried out at the voltage of 40 kV and the current of 40 mA, by employing a scanning rate of 2°/min and a step size of 0.01 in the 2θ range from 20 to 80° with Cu K_α radiation. The size and morphology of the synthesized nanoparticles were characterized using Tecnai G2 F20 Scanning/Transmission electron microscope (S/TEM) with field emission system operated at 200 kV. Energy dispersive spectroscopy (EDS), which was mounted on S/TEM, was used for elemental analysis. The magnetic properties of the synthesized nanoparticles were measured by vibrating sample magnetometer (VSM) with an external magnetic field ranging from −13 kOe to +13 kOe.

3. Results and discussion

3.1. Crystal structure

The X-ray diffraction patterns of the three compositions of NiFe nanoparticles which synthesized using different molar ratios of metal precursors are shown in Fig. 1a–c. The peaks can be mainly indexed at the crystal planes of (111), (200), and (220) which match well with the face-centered cubic (fcc) structure of bulk NiFe alloy. However, there is some peaks (marked by the asterisks in Fig. 1) for the composition with high iron content ($Ni_{20}Fe_{80}$) which cannot be indexed to fcc structure of NiFe. These diffraction peaks correspond well to those of spinel oxide ($(FeNi)_3O_4$) as reported by other group, where the high concentration of Fe precursor will result in the formation of oxide phases [1]. Furthermore, the oxide phase not only indicated from the XRD results but also clearly appear in the TEM images and also EDS analysis as we will be discuss later in the morphology part.

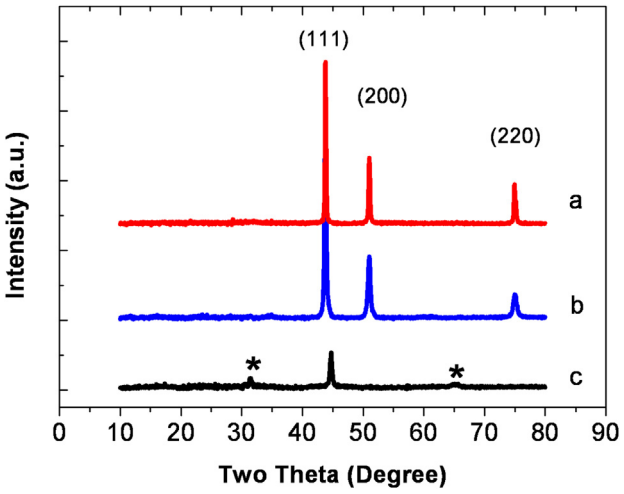

Fig. 1. XRD patterns of different compositions of nickel ferrite (NiFe) NPs, (a) $Ni_{80}Fe_{20}$, (b) $Ni_{50}Fe_{50}$, and (c) $Ni_{20}Fe_{80}$.

3.2. Morphology characterization

The shape and size of the as-synthesized and annealed NiFe nanoparticles are observed in Fig. 2 using TEM. Fig. 2a–c shows the typical TEM images of the as-prepared NiFe nanoparticles which reveal that the nanoparticles are monodisperse with 15 nm average size and have different shapes of flower-like and sphere shape depending on the composition of NiFe alloy (Fig. 2b). The such smaller size and excellent dispersion of the nanoparticles even we didn't used any surfactant or reducing agent in our reaction is mainly attributed to the using of polyethylene glycol (PEG). Hence, it acts not only as a solvent medium for the reaction but also as a reducing agent, where it is well known that the PEG is characterized by its strongest reducing properties, which lead to formation of a thin monolayer of the PEG (Fig. 2d) on the surface of the nanoparticles not only to stabilize the particles in the solution but also to act as a protective agent to inhibit the particle growth [9,10]. Furthermore, the condition used in our reaction of heating the PEG-metal salts solution firstly up to 200 °C for 30 min instead of direct heating the solution to the refluxing temperature of 300 °C is important step, where it is helpful for permitting slowly growth of the nanoparticles. On the other hand, annealing the as-synthesized NiFe nanoparticles resulted in an increment in particle size to be in the range of 50–150 nm with still the monodispersity there (Fig. 2e). Furthermore, formation of oxide shell around the particle was observed (Fig. 2f). This oxide shell is considered very important as a protective agent against oxidation. Same behaviors of oxide shell formation around the annealed nanoparticles within just exposure to the natural air have been reported with FeCo NPs and Fe NPs [9,15].

Further characterizations for the three different compositions of NiFe nanoparticles were obtained using EDS analysis (Fig. 3). Fig. 3a–c reveals that there are mainly two elements of Fe and Ni are detected, in addition to presence small percent of oxygen element which consider as an indicator about formation of the oxide shell around the nanoparticles. Meanwhile, we can see that an increase in the iron percent with increasing the iron on the composition and same with nickel metal. On the other hand, and especially in case of the bioapplications part we should mention that the NiFe nanoparticles without shells may, of course, display some toxic properties, but in our case the existence of a thin oxide layer around the NiFe nanoparticles, as evident from the TEM images in Fig. 2f, and also the PEG layer with high bio-compatibility may significantly decrease the toxicity levels and thus can be termed as less harmful if used in drug delivery as one kind of its application.