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Effects of hydrothermal process parameters on the physical, magnetic and thermal properties of $Zn_{0.3}Fe_{2.7}O_4$ nanoparticles for magnetic hyperthermia applications

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ABSTRACT

Effects of hydrothermal temperature and time on physical, magnetic and thermal properties of Zn-substituted magnetite nanoparticles ($Zn_{0.3}Fe_{2.7}O_4$) were assessed. The magnetic nanoparticles were synthesized via citric acid-assisted hydrothermal reduction route at temperatures of 150, 175 and 200 °C for duration of 10, 15 and 20 h. The nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), vibrating sample magnetometer (VSM) and specific loss power (SLP) measurements. The results showed that temperature and time of the hydrothermal process both had significant effects on nanoparticles composition and properties. It was observed that at 150 °C, heat generation was insufficient to produce activation energy required for nucleation of $Zn_{0.3}Fe_{2.7}O_4$ spinel nanoparticles, even after a long time. At 175 °C, although temperature was low, but the suitable condition for nucleation of nanoparticles was made and spinel nanoparticles with the size of about 13 nm were formed after 15 h. Nonetheless, since crystallinity and SLP of the nanoparticles was low, they showed weak performance for magnetic hyperthermia. At 200 °C, the required activation energy was provided for nanoparticles nucleation; however, the spinel was oxidized to hematite, resulting in a decrease in thermal and magnetic properties. In overall, the nanoparticles synthesized at 200 °C for 15 h possessed the best characteristics of reasonable purity, saturation magnetization of about 35.9 emu/g and SLP of 18.7 W/g.

1. Introduction

Magnetic nanoparticles (MNPs) have wide applications in industry and medicine due to their unique chemical, thermal and magnetic properties [1,2]. They can be used as catalysts [2], energy storage materials, magnetic data storage materials [3], ferro-fluids [4], magnetic adsorbents [5], and image contrast agents [6]. One of the exclusive properties of the ferro-magnetic materials is the super-paramagnetic property [7,8], based on which MNPs are widely used in biomedicine, drug delivery, magnetic resonance imaging (MRI), and hyperthermia for cancer therapy [1,2,9,10].

Magnetic hyperthermia is a promising method for non-invasive or low-invasive treatment of tumors, which is used by itself or as a help to chemotherapy, radiotherapy and photodynamic therapy [11]. In this method, nanoparticles are injected to the tumor where by applying an alternating magnetic field, the tumor is warmed up to 41 °C and consequently destroyed [1]. In fact, the single domain MNPs attract the power from the magnetic field by magnetic relaxation process which consists of either physical rotation of particles (Brownian motion), or motion of magnetic moments without particle moving (Néel relaxation theory) [8,12]. In 1957, Gilchrist et al. used MNPs to heat a tissue for the first time in a 1.2 MHz magnetic field [8,13–15]. The best choice for hyperthermia is a magnetic material which is bio-compatible with high magnetic saturation (M_s) and Curie temperature (T_c). This material may generate adequate heat without reaching to a temperature that is harmful for human body. Moreover, this property acts like a switch to turn off the heat; once reaching to Curie temperature, MNPs lose their magnetic property; so in the presence of magnetic field they cannot generate heat anymore which is harmful for body [11]. Ferrites with general formula of AB_2O_4, are a group of chemically and thermally stable materials [16]. Magnetite (Fe_3O_4) is a ferrite with a reverse spinel cubic structure which shows unique magnetic and electric properties due to electron displacement between Fe^{+2} and Fe^{+3} ions in octahedral positions [3].

Magnetite is the most popular and applicable material in biomedicine which possesses high magnetic saturation [16], good bio-compatibility, and low cost [8,9]. It is difficult to characterize magnetite in a ferro-fluid from iron oxides in blood hemoglobin [1]. In addition, the

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magnetic saturation of magnetite will be reduced by decreasing the size of MNPs in the range of 10–20 nm [17]. In order to solve this problem, the use of combined ferrites (MFe_2O_4 where M=Co, Mn, Ni, Zn) is suggested [1], since substituting some Fe^{2+} ions with M^{2+} in the magnetite structure would increase its magnetic saturation [18]. Due to high bio-compatibility and low toxicity, Zn^{2+} can be a proper ion to be substituted instead of Fe^{2+} [6,19]. Furthermore, Zn^{2+} has shown better properties than other combinations, when doped in magnetite [11]. Behdadfar et al. showed that MNPs substituted by Zn ($Zn_{0.3}Fe_{2.7}O_4$ (had higher intrinsic loss power (ILP) than commercial nanoparticles [20].

For the hyperthermia application, it is important to synthesize super-paramagnetic nanoparticles with diameter less than 15 nm and narrow particle size distribution [21]. Magnetic properties of materials significantly depend on the amount and crystallographic position of divalent and trivalent cations. One of the most common problems in the synthesis of sub-micron particles is how to monitor the particles and to prevent them from aggregation and agglomeration, since they have high tendency to reduce their large surface energy [22]. Therefore, the magnetic (especially super-paramagnetic), physical, and chemical properties of MNPs depend on their chemical composition and microstructural features, and consequently their synthesis process [2,4,21,23–25]. In order to achieve the desired properties, various methods for producing MNPs are used including self-propagating combustion synthesis [26], co-precipitation [27], microbial preparation [10], polymer matrix templated synthesis [22], microwave hydrothermal flash synthesis [23], thermal decomposition [6], simple thermal treatment [15], polyol synthetic process [25], solvothermal [21] and hydrothermal [28] reduction methods. The goal is to prepare nanoparticles with arbitrary particle size, appropriate size distribution, and strong magnetic properties with a simple fabrication process [21,23,24]. The hydrothermal technology is simple and cheap in which non-toxic raw materials are used, and therefore is a useful tool for the fabrication of MNPs. In hydrothermal process, raw materials including oxide and hydroxide precursors with water are placed in a tightly closed chamber at temperatures above the normal boiling point of the water (100 °C). Under the supercritical condition, the chamber pressure is increased, and the required hydrothermal reactions are conducted. Special care should be taken, as the chamber pressure might go up too much [30]. The size, morphology and other characteristics of particles can be controlled by adjusting the reaction temperature, time, pH, additives and other parameters [21,28–31]. Different reducing agents have been reported in literature for this method including hydrazine [32], sodium borohydride ($NaBH_4$) [33], carbon monoxide (CO) [34], and dimethyl formamide (DMF) [35]. All of these are reactive chemicals and pose potential environmental and biological risks. Recently regenerative bio-compatible agents have been used such as ascorbic acid [36], tartaric acid [37], aspartic acid [38], α-D glucose [39], and citric acid [20]. The hydrothermal reduction process using citric acid as a reducing agent is an easy, one-step and environment-friendly approach to produce hydrophilic MNPs. The citric acid is not only used as a reducing agent, but also as a hydrophilic cover on the nanoparticles surface [20,40,41]. The aim of the present work is to investigate effects of temperature and time in the citric acid-assisted hydrothermal process on different characteristics of the Zn-substituted MNPs which are aimed to be used in hyperthermia applications.

2. Materials and experimental procedures

2.1. Materials

All raw materials, including $Fe(NO_3)_3{\cdot}9H_2O$, NH_4OH 25%, $ZnCl_2$ and $C_6H_8O_7{\cdot}H_2O$ were purchased from Merck Co. with minimum purity of 99%.

Table 1
The hydrothermal process parameters used to synthesize different samples.

Samples codes	Temperature (°C)	Time (h)	pH after adding (NH_4)OH
S15010	150	10	9.20
S15015	150	15	9.30
S15020	150	20	9.50
S17510	175	10	9.56
S17515	175	15	9.96
S17520	175	20	9.35
S20010	200	10	9.87
S20015	200	15	9.58
S20020	200	20	9.80

2.2. Synthesis

To synthesize Zn-substituted MNPs of $Zn_{0.3}Fe_{2.7}O_4$, 11.8 mmol of $Fe(NO_3)_3{\cdot}9H_2O$ and 1.3 mmol of $ZnCl_2$ were dissolved in 25 ml deionized distilled water. The solution was continuously stirred by a magnetic stirrer for 20 min. After that 25 ml deionized distilled water was added to basic solution followed by stirring. Then a solution of NH_4OH 25% was added slowly to reach a pH medium of 9–10. Vigorous stirring continued for another 20 min until a reddish-brown slurry was formed. The slurry was washed and centrifuged for 10 min at the speed of 5000 rpm three times with deionized distilled water, in order to eliminate excess ions in solution such as ammonium and nitrate ions. Citric acid was then added to the mixture and it was stirred vigorously for 30 min.

The prepared solution was transferred into a 325 ml volume teflon-lined autoclave and filled up to only 200 ml of its total volume. The autoclave was kept at different temperatures of 150, 175 and 200 °C for various durations of 10, 15 and 20 h (Table 1) and then free-cooled to room temperature. The sample code was SXY, where X is temperature and Y is time. For powder characterization, the precipitate was washed with acetone several times and then dried at 100 °C.

2.3. Characterizations

The surface morphology, shape, size and size distribution of the synthesized nanoparticles were investigated using a Philips XL30 scanning electron microscope (SEM) and a Philips 208S transmission electron microscope (TEM) with the working voltage of 100 kV. Mean particle size was calculated from SEM images by measuring the size of at least 250 particles via Image J software. The data were fitted by a log-normal distribution curve and then the mean size was obtained.

Phase identification was carried out using a Bruker diffractometer, D8 ADVANCED model, with CuKα radiation (λ=0.15406 nm). To calculate the average crystallite size, Scherrer equation (Eq. (1)) was used:

$$d = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

where λ is the wavelength of X-ray, β the peak width at half of the maximum intensity, and θ the Bragg peak angle [42].

The magnetic properties of a material including magnetization and magnetic admissibility are changed by altering the applied magnetic field. Magnetic susceptibility of a material, χ_i, is the ratio of magnetization to the applied magnetic field to that material, as shown in Eq. (2) [43]:

$$\chi_i = \frac{M(H, T)}{H} \quad (2)$$

The magnetic susceptibility is a function of two variables of H (magnetic field) and T (temperature). The magnetic susceptibility can be determined in terms of the applied magnetic field through vibrating sample magnetometer (VSM) [43]. Magnetic characterizations were