A rapid and efficient thermal decomposition approach for the synthesis of manganese-zinc/oleylamine core/shell ferrite nanoparticles

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Abstract

This paper presents the effect of adding different amounts of zinc into the composition of Zn-Mn/oleylamine core/shell ferrite nanoparticles (NPs). For this purpose, acetylacetonate as a main precursor, oleylamine as a surfactant and surface modifier, and stearyl alcohol as a co-surfactant were used for thermal decomposition synthesis of this ferrite. Monodispersed core/shell ferrite NPs synthesized with several compositions. The X-ray diffraction (XRD) patterns and transmission electron microscopy (TEM) images showed single-phase nanoparticles around 10 nm without any impurities. Fourier Transform Infrared Spectroscopy (FTIR) confirmed single-phase spinel with ultra-thin layers of oleylamine on the surfaces that make the particles separated from each other. Thermo gravimetric studies could also measure the amount of surfactant around the NPs. Moreover, the DC magnetic properties of the samples were studied using the vibrating sample magnetometer (VSM). The M-H curves for all the samples showed negligible hysteresis loops indicating the superparamagnetic behaviour of the NPs. Furthermore, maximum saturation magnetization was measured for the

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sample with $\text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ with 45 amu.gr^{-1} , suggesting that this composition could be an excellent candidate for biomedical applications such as hyperthermia and imaging.

Keywords: Magnetic nanoparticles; ferrite; Thermal decomposition; Superparamagnetic

1. Introduction

Currently, synthesis of high-quality superparamagnetic nanoparticles (NPs) with fine distribution, reproducible properties and production with short processing time are some of important matters in NPs investigation. In all structures, spinel ferrites have gained significant attention because of their ability in controlling and improving the properties for specific applications [1, 2]. Manganese (Mn) and Zinc (Zn), as substitute spinel-type ferrites, have many potential biomedical applications. This is due to their outstanding properties such as chemical and physical stability, moderate saturation magnetization, lack of toxicity and soft-magnetic behavior at room temperature [3, 4]. It has been further shown that the substitution of Zn ions instead of base ions (Co, Zn, Fe, Ni) can potentially improve their properties for more specific applications. The inverse ferrite spinels have a $(\text{Fe}^{3+})^{\text{A}} [\text{Me}^{2+} \text{Fe}^{3+}]^{\text{B}} \text{O}_4$ formula, in which " Me^{2+} " is a metal cation, that can be Mn, Co, Ni, Zn, Fe and Cu. A is the symbol of tetrahedral and B octahedral sites. In MnFe_2O_4 , 80% of the Mn fill the A site and the remaining 20% remain sites fill with the spinel lattice. If we now replace the Mn ions with diamagnetic Zn, the curie temperature will be further reduced. In such system, although the overall magnetization may increase, the cation distribution is not altered [1]. The substituted Zn gives the higher paramagnetic coefficient to magnetic NPs making them suitable for magnetic fluid hyperthermia and magnetically guided drug-delivery agents [5, 6]. In magnetic fluid, hyperthermia based on heating the magnetic NPs with electromagnetic field irradiation the particle under AC field, the transformation efficiency is mostly dependent

on the properties of the magnetic NPs. In tumor therapy, modifications and optimizations in the physical and magnetic properties of the NPs are crucial for effectiveness and reliability [7]. For example, in magnetic fluid hyperthermia, the specific power absorption for monodispersed magnetic NPs is higher than polydispersed particles [4].

In order to improve the efficiency of magnetic NPs for individual applications, various methods have been employed such as co-precipitation method, hydrothermal precipitation processing, sol-gel synthesis, and micro emulsions routes [8]. Controlled synthesis and subsequent assembly of magnetic nanomaterials with specific size, shape and arrangement are important steps in the fabrication of novel nanostructured devices with unique magnetic properties [9]. Among different methods, thermal decomposition synthesis is known as one of the most important methods in which the system is perfectly under control. The particle size of the materials synthesized with this method fits within a log normal distribution lead to standard deviation between 0.1 and 0.15, which is much lower than that of particles synthesized via a conventional co-precipitation method (0.2-0.4) [10].

More recent studies have shown that decomposition of organometallic precursor's modified magnetic samples could demonstrate superior advantages compared with conventional methods, such as suitable size control, narrow distribution range, and excellent crystallinity of individual NPs. This method is also suitable for mass production [11]. However, the high cost of precursors/surfactants and their possible toxicity in this method should be evaluated first. Furthermore, absolute controlling of size, shape, and distribution in this method is very difficult and the formation mechanism of the fabricated magnetic NPs is vague [12, 13]. To decreasing the cost and toxicity, Sun *et al.* [14] have recently used iron acetylacetonate as inorganometallic compounds and stearyl alcohol as a non-toxic low cost surfactant for the synthesis of magnetite. They successfully synthesized magnetite in various sizes ranging from 16 to 60 nm with narrow size distribution. Roca *et al.* [15] also

investigated the effects of some parameters such as nature of the precursor, ligand precursor ratio and the decomposition temperature on shape, size and formation mechanism of magnetic NPs. This investigation showed that higher temperatures, larger iron concentrations, and capping groups could significantly affect the reaction rate of nanocrystals and induce the formation of smaller particles.

Many researches have worked on the effects of precursor, solvent, surfactant and other ingredients in final characteristics of NPs. As shown, solvent is one of the important parts in the synthesis process of NPs in all methods, which can control the temperature of the reaction. Oleylamine is one of the best solvents for thermal decomposition reaction not only because of the ability to solve many of organic and inorganic compounds and high working temperatures but also it can act as a good surfactant and even mild reducing agent. A recent report also showed that oleylamine could be used in the synthesis of spherical iron and iron oxide NPs under 10 nm and in large scale [16].

The present study shows a new fabrication method for producing superparamagnetic NPs with narrow size distribution and appropriate magnetic properties suitable for a wide range of biomedical applications. For this purpose, three different compositions with variance in Mn value were selected and then synthesized with metal acetylacetonate benzyl ether as a solvent and oleylamine as a surface modifier with stearyl alcohol as a co-surfactant. Then, all samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR) and vibrating sample magnetometer (VSM).

2. Experimental method

2.1. Materials

Zinc(II) acetylacetonate ($\text{Zn}(\text{acac})_2$), Mn(II) acetylacetonate ($\text{Mn}(\text{acac})_2$), and Iron(III)

acetylacetonate ($\text{Fe}(\text{acac})_3$) were purchased from Merck Co. and other contents such as oleylamine, stearyl alcohol and Benzyl ether obtained from Sigma Aldrich Co. The organic solvents acetone, hexane, and ethanol were purchased from Samchun. All chemicals were used as received without any further purification.

2.2. Synthesis

All of the monodispersed Mn-Zn ferrite magnetic NPs were synthesized by thermal decomposition of $\text{Fe}(\text{acac})_3$ (2 mmol), $\text{Mn}(\text{acac})_2$ (1-x mmol), $\text{Zn}(\text{acac})_2$ (x mmol) with stoichiometric value for each composition (x=0.3, 0.4, 0.5 mmol). Inorganic compounds and stearyl alcohol (15 mmol) added to the reactor. Then, 10 ml benzyl ether as a solvent and 30 ml oleylamine as a high boiling point precursor added. The complex heated with mantle to 60 °C for solving stearyl alcohol then vacuumed for 15 min. After that, the mixture heated to 100 °C; then, vacuumed for 2 min. The mixture heating and stirring to reflux (at ≈ 330 °C) with 20 °C per min heating rate. The mixture was maintained under nitrogen atmosphere for 30 minutes. This time duration was sufficient to form monodisperse spinel ferrite. The NPs were separated with magnet. Then, washed several times with ethanol and acetone and dried as a powder. The samples were coded based on the chemical compositions as shown in Table I.

(Table I)

2.3. Characterization

The samples were characterized by XRD using Philips diffractometer (Co $K\alpha$ radiation) for phase specification and measuring the crystallite size. The scans of the selected diffraction peaks were carried out in the step mode (step size 0.01 °, measurement time 0.5 s,

measurement temperature 25 °C, and standard: Si powder). All the samples were also analyzed by Atomic Absorption Spectroscopy (AAS) to characterize the compositions. The FTIR spectrum was recorded on disks (samples mixed with KBr) in the range of 400–4000 cm^{-1} by using (Perkin Elmer FTIR, 1403, USA) spectrophotometer. The particle's size and shape were examined by TEM using a 200-keV Philips microscope. The TEM samples were prepared by placing one drop of a diluted suspension of ferrite NPs in hexane on a carbon coated copper grid and allowing the solvent to evaporate at room temperature. For thermogravimetric analysis, Simultaneous Thermal Analysis (STA) was used to measure the amount of solvent and surfactant with (1640, polymer laboratories). The samples were heated up to 600 °C in air atmosphere. The magnetic measurements of the synthesized powders were determined using a vibrating sample magnetometer (VSM - Meghnatis Daghigh Kavir Co.)

3. Results and discussion

3.1. Structural Analysis

Fig. 1. shows the XRD patterns of the synthesized NPs, analyzed and indexed by Xpert. The XRD patterns showed (220), (311), (400), (422), (511) and (440) diffraction peaks for all patterns with same peaks. The deviation in the intensity of the peaks can be an indicator for the variance in the composition of NPs. The characteristic peaks indicated that a single-phase spinel with no detectable impurities was formed in all samples. The peak broadening observed in this figure could be the result of nano-sized crystallites [17].

(Figure 1)

In order to calculate the structural data, crystallite size and lattice constant were evaluated using both Scherrer method and Rietveld refinement technique. Fig. 2. shows a typical

Rietveld refinement performed on $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. Also, crystallinity of all samples were calculated with Material Studio. The results obtained from XRD patterns were shown in Table II. As can be seen, the maximum crystallinity observed for the sample with 0.6 Mn. The lattice constant value was about 8.4 Å for all calculations. The results also showed that the lattice constant calculated for the synthesized samples were lower than that of the bulk samples due to the size effect of the samples [18]. However, in some cases a little increase was observed as a result of interfacial energy [19]. It should be noted that the observed lattice constant value was in accordance with the previously reported work by Dunlap *et al.* in which the typical value was 8.476 Å [20]. Furthermore, the crystallite size for all compositions calculated from both methods were approximately equal and near 10 nm without any significant differences. To confirm the stoichiometry, calculations were performed on the ratios obtained from AAS, as shown in Table III. The experimental and theoretical data showed that there was an agreement between these two values.

(Figure 2)

(Table II)

(Table III)

FTIR spectra of the synthesized samples were recorded in the 4000-400 cm^{-1} region at room temperature, shown in Fig. 3. These FTIR spectra revealed the characteristic peak of spinel structure, metal-oxygen stretching modes of tetrahedral and octahedral symmetries at 568 cm^{-1} and 418 cm^{-1} , respectively [21]. Two absorption bands at 1631 cm^{-1} and 1459 cm^{-1} were due to $-\text{C}=\text{C}$ and $-\text{CH}_3$ bending vibrations from oleylamine, in that order. The bands at 1593 cm^{-1} and 795 cm^{-1} in the IR spectrum of oleylamine was due to the bending vibration NH_2 , which shifted to 719 cm^{-1} and 1541 cm^{-1} in oleylamine-capped Mn-Zn ferrite NPs

caused by absorption of N–H groups onto the magnetic NPs surface due to van der Waals interactions [19, 22]. The peaks at 2849 cm^{-1} and 2918 cm^{-1} were attributed to symmetric stretching vibration and asymmetric stretching vibration of C–H methylene groups in turn for stearyl alcohol adsorbed on the surface of NPs [23]. For M5 and M7 samples, the peak located at 2360 cm^{-1} could be ascribed to C=O vibrations in CO₂ molecules originated from atmospheric carbon dioxide [24].

(Figure 3)

3.2. Morphological characterization

The TEM images of the NPs for each composition are shown in Fig. 4. These images approved the uniform spherical shape NPs with size about 10 nm. The average particle sizes were calculated from ten images and different regions of the images. This homogeneity in particle size and shape raised from the temperature of solvent (oleylamine) [25]. The observed average particle size was in agreement with that obtained from the XRD analysis. This coordination between particle size and crystallite size could indicate synthesis of near single crystal NPs.

(Figure 4)

3.3. Thermo-gravimetric analysis

The thermal behaviour of Mn-Zn NPs was investigated by STA (see Fig. 5), in which the samples were heated with a rate of $5^{\circ}\text{C}/\text{min}$. The thermal behaviour of NPs with increasing the temperature can be divided into three stages. The first stage of weight loss corresponds to the evaporation of adsorbed solvents, occurred at around $30\text{--}200^{\circ}\text{C}$. After that, due to the

physical absorption of oleylamine molecules and stearyl alcohol on the surface of NPs, a sharp peak appeared in the DSC curve about 280-340 °C. In addition, at the range of 420-440 °C, the chemical absorbed surfactant of the particles was decomposed and all of organic compounds were removed. Moreover, the weight loss at high adsorption temperature approved strong chemical bindings between the surfactant and NPs. The weight loss of NPs until this step was around 25% [4, 26].

(Figure 5)

3.4. Magnetic properties characterization

When the dimension of magnetic particles decreases, there is a reduction in the number of magnetic domains per particle. Below a critical particle size, each particle cannot hold more than one domain, due to, energetically unfavourable for a domain wall to exist, so that the magnetic particles have only a single domain. Superparamagnetism can be expressed as an important property of single domain magnetic NPs. This property originates from fluctuations in spin directions as result of the thermal energy. When the external magnetic field was applied, magnetic moments aligned along the field direction produced a net magnetization [27, 28]. However, with removing it, the magnetization shifted to the zero. Superparamagnetic NPs have frequently shown to be attractive for biological imaging and therapeutic applications due to high surface-to-volume ratio and superparamagnetism properties [29, 30]. The magnetization curves (M-H) for all samples measured at room temperature are shown in Fig. 6. Ulrich *et al.* [31] have recently shown that by replacing of 0.4 of "Mn" sites in the structure of MnFe_2O_4 with zinc ions, magnetic properties of ferrite NPs could be increased. It can be seen that maximum magnetization attributed to the M6 sample with 45 emu.gr^{-1} saturation magnetization, showing the effect of zinc in the increase

of magnetic properties. The unsaturated magnetization state and negligible coercivity (< 2 O_e) for all samples are listed in Table IV. These properties provided adequate support for the superparamagnetic behaviour of the Mn-Zn ferrite magnetic NPs at the room temperature.

(Figure 6)

4. Conclusion

Monodispersed Mn-Zn ferrite NPs have been synthesized by thermal decomposition method using oleylamine as a surface modifier, and stearyl alcohol as a co-surfactant and acetylacetonate as the main precursor in various values of Zn. The XRD patterns showed a single phase spinel without impurities and suitable crystallinity. The FTIR patterns confirmed the formation of single phase spinel NPs coated with oleyl film for all samples. The TEM images revealed separated spherical shape particles with narrow size distributions (≈ 10 nm). The images also revealed that the crystallite size calculated from XRD patterns and particle size from TEM were nearly equal. In this method, it was observed that as the Zn values changed in the composition, no significant changes were observed in the particle size. In addition, the STA pattern showed 25% weight loss which was attributed to the physical and chemical absorbed oleylamine in several stages. The magnetic measurements exhibited no major hysteresis loop with low coercivity (≈ 1 O_e) that showed superparamagnetic behavior of the synthesized NPs. The maximum magnetization observed in the sample with maximum crystallinity, M6 with 63 emu.gr^{-1} saturation magnetization. Further characterizations proved that M6 sample was the most suitable composition for magnetic applications.

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Figure captions:

Figure 1. XRD patterns of different synthesized compositions of Mn–Zn ferrite NPs

Figure 2. Rietveld refinement of XRD pattern for M5 sample.

Figure 3. FTIR spectra of different compositions of Mn–Zn ferrite NPs.

Figure 4. TEM images with average particle size and size distribution for: a) M5, b) M6, c) M7 NPs.

Figure 5. STA (DSC/TG) pattern of M6 sample.

Figure 6. Low and high magnifications M–H curves of different synthesized samples as a) and b), respectively.

Tables:

Table I. The detailed component of the synthesized samples.

Sample name	composition
M5	$\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$
M6	$\text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$
M7	$\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$

Table II. The calculated XRD crystallite size via Rietveld refinement (R_D), XRD crystallite size via Scherrer method (S_D), lattice parameter (a), degree of crystallinity and figures of merit obtained at different samples during Rietveld refinement.

Samples	R_D (nm)	S_D (nm)	a (Å)	Degree of crystallinity (%)	R_{wp} (%)	R_p (%)	χ^2 (%)
M5	8.9	9.2	8.4486	68.3	10.15	7.75	0.86
M6	9.3	9.4	8.4627	75.4	9.54	7.28	1.19
M7	9.1	9.3	8.4718	72.9	10.73	7.89	0.96

Table III. Theoretical and experimental compositions of the synthesized samples from AAS measurements.

Theoretical	Experimental
$\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$	$\text{Mn}_{0.54}\text{Zn}_{0.46}\text{Fe}_2\text{O}_4$
$\text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$	$\text{Mn}_{0.65}\text{Zn}_{0.35}\text{Fe}_2\text{O}_4$
$\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$	$\text{Mn}_{0.73}\text{Zn}_{0.27}\text{Fe}_2\text{O}_4$

Table IV. Saturation magnetization (M_s), magnetic remanence (M_r) and coercivity of different samples.

sample	M_s (emu.gr ⁻¹)	M_r (emu.gr ⁻¹)	H_c (Oe)
M5	28	0.008	0.45
M6	45	0.047	1.1
M7	34	0.012	0.45

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6