Controllable Preparation of Ternary Superparamagnetic Nanoparticles Dual-Doped with Mn and Zn Elements

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Superparamagnetic iron oxide nanoparticles (SPIONs) with high saturation magnetization are successfully synthesized via thermal decomposition method by doping Mn and Zn elements simultaneously. The synthesis procedure was modified according to the thermal stabilities of the precursors, in order to ensure that the stoichiometry of the synthesized samples can be retained exactly from the starting ratios of the Fe/Mn/Zn in the initial precursors. As a result, the saturation magnetization of the dual-doped nanoparticles increased about 23% compared to that without the dopants. The superparamagnetic nanoparticles had narrow size distribution and the average diameter was about 8 nm. XRD and HRTEM analyses also indicated that the materials had a cubic spinel structure.

Keywords:

1. INTRODUCTION

When the size of magnetic nanoparticles (MNPs) is less than 20 nm,1 they are superparamagnetic with a series of special properties. Among these, spinel ferrites represent a very important class,2-5 which have been extensively studied for their fundamental properties for a wide range of applications, such as magnetic data storage, targeted drug delivery and magnetic resonance imaging (MRI) etc. The saturation magnetization of the MNPs is desired to be as high as possible to achieve high sensitivity in most applications.4-5 It is also critical for these MNPs to be monodisperse and nonagglomerate in solvents for homogeneous physical and chemical properties. In order to prevent agglomeration, MNPs used as ferrofluids are often covered with organic or inorganic surfactants,6-8 which would result in the loss of the magnetization. Therefore, it has been a very important and challenging task to develop effective strategies to increase the magnetization properties for the MNPs.

As reported previously,9 the magnetic and electrical properties of MFe2O4 (M = Mn, Co, etc.) nanoparticles can be varied by changing the identity of the divalent M2+ cation or by partial substitution. Different kinds of metal elements and their locations,10 and the preparation methods11 would influence the magnetic properties significantly. The thermal decomposition method is the most common and the best method to synthesize the ferrite materials.12-15 In the past decades, many researchers have synthesized binary system of MFe2O4 through thermal decomposition of different metal precursors, such as metal acetylacetonates,12 metal oleates,16-17 and metal pentacarbonyls,18 where M = Co, Ni, Mn, Zn, etc. Among the cations, Mn has the best effect to improve the magnetic property of the MNPs. Given that the cation distribution is not altered, the partial replacement of Mn by Zn will reduce the Curié Temperature by interfering the interactions between the tetrahedral sites (A sites) and the octahedral sites (B sites), thereby increasing the overall magnetization.19 Furthermore, the Zn doped nanoparticles has lower toxicity than that of the Mn doped.20 Therefore, Mn2+ and Zn2+ have been drawn more attention to be doped into the iron oxide to increase the magnetic properties.21-22 For the first time, Parekh et al.23 described the synthesis of the monodispersed Mn0.5Zn0.5Fe2O4 ternary compound through thermal decomposition technique with a magnetization of 51 emu g⁻¹ at 300 K, based on Sun’s reported method.22 However, in the above procedure, the same decomposition temperature was applied to the three different kinds of precursors introduced. This would result in that the ratio of Fe/Mn/Zn could not be controlled exactly when the ions were doped into the iron oxide consequently, since the thermal stability of precursors will crucially influence the synthesis process.24

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In this research, we systematically studied the ternary system of the superparamagnetic nanoparticles doped with Mn and Zn through a modified thermal decomposition method by controlling the reaction temperatures sequentially to dope Mn and Zn elements with improved efficiency and control of doping compositions. Furthermore, the saturation magnetization of the superparamagnetic nanoparticles was increased compared with the previous reports.

2. EXPERIMENTAL DETAILS

2.1. Materials

Iron (III) acetylacetonate (Fe(acac)3), manganese (II) acetylacetonate (Mn(acac)2), zinc acetylacetonate (Zn(acac)2), 1,2-hexadecanediol (97%), benzyl ether (BE, 99%), oleic acid (90%) and oleylamine (>70%) were purchased from Sigma Aldrich. Tetracosane (TC) was obtained from Alfa-Aesar. The other reagents were all analytical grade. All chemicals were used as received without further purification.

2.2. Synthesis Procedure

A series of superparamagnetic nanoparticles were synthesized referring to the previously reported procedures by Sun et al. and Parekh respectively.12,25 Firstly, Fe(acac)3 and M(acac)2 (M = Mn, Zn) were mixed with 1,2-hexadecanediol (5 mmol), oleic acid (3 mmol), and oleylamine (3 mmol) in benzyl ether (10 ml) under dry and deoxidized argon atmosphere. The mixture was then heated to 200 °C at a heating rate of 3 °C/min for 2 h and then heated to reflux (300 °C) for another 1 h.

To dope the metal elements completely, we modified the synthesis method as in Scheme 1. In our modified method, the precursors firstly were heated to 200 °C for 1 h, and then heated to 250 °C for 1 h, at last refluxed in TC (tetra-cosane) for another 1 h. The solution was then precipitated and centrifuged consequentially with ethanol, hexane in the presence of oleic acid and oleylamine, and ethanol, respectively. The black products were finally dispersed in hexane.

Table I shows the products prepared through the methods above respectively. The MNPs without dopants and with only Mn element doped were synthesized according to the previous method by Sun, and were defined as Sample-1 (S-1) and Sample-2 (S-2) respectively. Sample-3 (S-3) was dual-doped with Mn and Zn elements according to the method by Parekh. Sample-4 (S-4) and Sample-5 (S-5) were doped with Mn or Mn-Zn elements through our modified method.

2.3. Characterization

Size distribution of superparamagnetic nanoparticles dispersed in hexane was characterized by dynamic light scattering (DLS) using a Nanosizer (Zetasizer Nano ZS, Malvern, U.K.). Fe, Mn and Zn elemental analysis of nanoparticle powders were performed using inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Fisher Scientific ICP-IRIS Advantage). Samples for transmission electron microscopy (TEM, JEM 2100) analysis were prepared by drying a dispersion of the nanoparticles in hexane on amorphous carbon coated copper grids. The crystal structures were identified using powder X-ray diffraction (XRD, X’Pert Pro MPD, Philips, Netherlands) at 40 kV and 25 mA with Cu/Kα (λ = 0.154 nm) radiation source.

The thermogravimetric analysis (TGA) was employed by a simultaneous thermal analysis (STA 449 C Jupiter, NETZSCH) from 35 °C up to 500 °C at a heating rate of 10 °C/min under a dynamic N2 flow. The saturation

<table>
<thead>
<tr>
<th>Samples</th>
<th>Initial Fe/Mn/Zn ratio</th>
<th>Holding temperature and time</th>
<th>Solvent</th>
<th>Reflux temperature</th>
<th>Final cation concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>Fe only</td>
<td>200 °C for 2 h</td>
<td>BE</td>
<td>280 °C</td>
<td>Fe3O4</td>
</tr>
<tr>
<td>S-2</td>
<td>2.0/1.00</td>
<td>200 °C for 2 h</td>
<td>BE</td>
<td>280 °C</td>
<td>Fe2Mn0.5O4</td>
</tr>
<tr>
<td>S-3</td>
<td>2.0/0.7/0.3</td>
<td>200 °C for 2 h</td>
<td>BE</td>
<td>280 °C</td>
<td>Fe2Mn0.5Zn0.5O4</td>
</tr>
<tr>
<td>S-4</td>
<td>2.5/0.3/0.2</td>
<td>200 °C for 1 h; 250 °C for 1 h</td>
<td>TC</td>
<td>340 °C</td>
<td>Fe2Mn0.5Zn0.5O4</td>
</tr>
<tr>
<td>S-5</td>
<td>2.0/1.00</td>
<td>200 °C for 1 h; 250 °C for 1 h</td>
<td>BE</td>
<td>280 °C</td>
<td>Fe2Mn0.5O4</td>
</tr>
</tbody>
</table>
magnetization was measured within a field range of $-20 \sim +20$ kOe using a vibrating sample magnetometer (VSM, 7410 vibrating Sample Magnetometer) at 300 K.

3. RESULTS AND DISCUSSION

3.1. Size Distribution and Morphology

Figure 1 shows the DLS data of the four kinds of nanoparticles with the exception of S-5. The mean hydrodynamic diameter of all samples is about 8 nm with a narrow size distribution. TEM analysis (Fig. 2) shows the above-mentioned MNPs are spherical and monodisperse, no matter through which method they are synthesized and whether or not they are doped. The TEM size is about 6 nm which is smaller than the results of DLS because of the oleic acid coating on the surface of the MNPs.

3.2. Chemical Composition and Crystal Structure

The chemical compositions of S-2, S-3, S-4 and S-5 were characterized by ICP-AES, as shown in the formula of $\text{Fe}_2\text{Mn}_3\text{O}_4$, $\text{Fe}_2\text{Mn}_3\text{Zn}_2\text{O}_4$, $\text{Fe}_2\text{Mn}_3\text{Zn}_2\text{O}_4$ and $\text{Fe}_2\text{Mn}_3\text{O}_4$ respectively. Figures 3(a) and (b) show the high-resolution TEM (HRTEM) images of S-3 and S-4, indicating that both dual-doped particles are highly crystalline. According to the XRD analysis in Figure 4, for all of the samples curves, there are six characteristic peaks at $30.56^\circ$ (220), $35.84^\circ$ (311), $43.46^\circ$ (400), $53.90^\circ$ (422), $57.38^\circ$ (511) and $63.26^\circ$ (440). The lattice spacing of all the rings and peaks match well with the standard XRD pattern of the bulk magnetite, which means that the particles are consisted of $\text{Fe}_3\text{O}_4$ phase. From the XRD curves and the selected area electron diffraction pattern of S-3 shown in Figure 3(c), it could be found that the crystal structure of the samples is not changed when doped with Mn or Zn element.

3.3. Thermal Stability of Precursors

Figure 5 shows the weight losses of the three kinds of precursors used in this study: $\text{Fe(acac)}_3$, $\text{Mn(acac)}_2$ and $\text{Zn(acac)}_2$, for the thermal stability of precursors dramatically influence the magnetic $\text{MnFe}_2\text{O}_4$ spinel nanocrystals. For both $\text{Fe(acac)}_3$ and $\text{Zn(acac)}_2$, the thermal decomposition stage both take place at about $200^\circ$C, while the $\text{Mn(acac)}_2$ is about $250^\circ$C. During the synthesis procedure when the temperature was raised to $200^\circ$C at a heating rate of $3^\circ$C/min and with a holding time of 2 h for nucleation, $\text{Fe(acac)}_3$ and $\text{Zn(acac)}_2$ could decompose.
totally, as a result, the iron and zinc elements might participate the reaction in the form of ions. Unfortunately, when the temperature was remained at 200 °C, the Mn(acac)$_2$ could not decompose completely, leading to the incomplete doping of Mn element into the MNPs as in S-2 and S-3. Accordingly, the synthesis was modified by prolonging the maintenance time at 250 °C with the same solvent for 1 h in order to promote the decomposition of Mn(acac)$_2$ as completely as possible.

But during the synthesis process, we found that even though the increase of decomposition temperature to 250 °C for Mn(acac)$_2$ could facilitate more Mn to be doped into the system, the Mn element was still not retained as the initial ratio as shown in S-5 under the reflux temperature of 280 °C. Therefore, the solvent with much higher boiling point, such as tetracosane (TC) was introduced. The reflux temperature was kept at 340 °C for 1 h, 90 °C higher than the maintenance temperature of 250 °C to ensure the complete doping of the Mn element, as indicated in S-4 (shown in Table I). That is, when the reactants ratio of Fe/Mn/Zn is 2.5/0.3/0.2, and the Fe$_2$Mn$_{0.5}$Zn$_{0.2}$O$_4$ is controllable obtained. Consequently, the stoichiometry of the samples we synthesized can be achieved definitely by the Fe/Mn/Zn ratio of initial precursors.

### 3.4. Magnetization Properties

Figures 6 and 7 illustrate the magnetization properties of S-1, S-2, S-3 and S-4. Since there is no remanent magnetization in the absence of an external field, all the MNPs are superparamagnetic at room temperature. However, the magnetization values with different cation concentration
are different. The saturation magnetization values of the four kinds of MNPs are 45, 53, 58 and 58 emu g$^{-1}$ (mass), and 96, 106, 118 and 118 emu g$^{-1}$ (mass of metal atoms), respectively. Obviously, the values of the as-synthesized nanoparticles are much lower than that of the bulk materials, and much research has been carried out in this issue.\textsuperscript{3} A detailed study suggests that the loss of magnetization of magnetic nanoparticles with nanoscale diameter might be caused by magnetic anisotropy energy constant or a spin canting surface effect, and the surface modification with non-magnetic materials could also result in decrease in magnetic saturation values.

In the cubic spinel structure of MFe$_2$O$_4$, or M$\cdot$Fe$_2$O$_3$, the oxygen forms an fcc close packing, and M$^{2+}$ and Fe$^{3+}$ are located at either the tetrahedral (A site) or octahedral (B site) interstitial sites.\textsuperscript{12} The magnetic spins in A sites are in parallel with the direction of external magnetic field while those in B sites are anti-parallel.\textsuperscript{5,20} The magnetic susceptibility of MnFe$_2$O$_4$ is the highest with magnetic spins of 5 $\mu_B$ while $i$ magnetic spins are 4 $\mu_B$, 3 $\mu_B$, 2 $\mu_B$ and 0 $\mu_B$ respectively when $M$ = Fe, Co, Ni and Zn in MnFe$_2$O$_4$.\textsuperscript{3} And at the same time, when Zn participates the synthesis, the interactions between A and B sites will be affected and the magnetization value will be increased accordingly, supposing that the cation distribution is not altered.\textsuperscript{19} Therefore, when dual-doped with Mn and Zn elements, the saturation magnetization value of the nanoparticles can be increased greatly.

When Mn$^{2+}$ substitute for the Fe$^{3+}$ in Fe$_3$O$_4$ completely to form MnFe$_2$O$_4$, the magnetic spins will increase from 4 $\mu_B$ to 5 $\mu_B$. In principle, the saturation magnetization value of MnFe$_2$O$_4$ will increase 25 \% to 125 emu g$^{-1}$ compared with that of Fe$_3$O$_4$. However, the measured values
are only 106 emu g\(^{-1}\) for Fe\(_{2.5}\)Mn\(_{0.3}\)O\(_4\), and 118 emu g\(^{-1}\) for Fe\(_{2.5}\)Mn\(_{0.3}\)Zn\(_{0.2}\)O\(_4\), which might because that the metal atoms are not all located at the desired sites as we expected. While there is no definite data on the exact ratio of Fe/Mn/Zn with the highest magnetization, it is reasonable to deduce that there would be an optimal ratio of Fe/Mn/Zn for the highest saturation magnetization, and the content of Zn cannot be too high.\(^{20}\)

4. CONCLUSION

According to the different thermal stability of the precursors, we have modified the thermal decomposition method with different solvent and reaction temperature to ensure the complete doping of Mn and Zn elements into the iron oxide nanoparticles. Consequently, the stoichiometry of Fe/Mn/Zn in the precursors. The synthesized MNPs had a narrow size distribution and good crystallinity. Furthermore, the saturation magnetization value of the superparamagnetic nanoparticles is increases about 23% compared to that without dopants.

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References and Notes


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