SYNTHESIS AND CHARACTERISATION OF ROD-LIKE MAGNETIC NANOPARTICLES

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Magnetic rod-like particles have been prepared through two type hydrolysis. The influence of different conditions during synthesis on the size (length and diameter), structure and magnetic properties of the prepared nanoparticles was studied. The molar ratio of the reactants affects structure, shape and magnetic properties of particles. The prepared samples were characterized by a variety of methods: infrared spectroscopy, magnetization measurements, Transmission electron microscopy and Scanning electron microscopy.

Keywords: magnetic particles, nanorods, chemical synthesis, magnetic properties

1. INTRODUCTION

Properties of magnetic nanoparticles significantly depend on their size, shape and structure. Controlling the shape and size of nanoparticles is an ultimate challenge of modern material research. A number of techniques have been developed to synthesize magnetic nanoparticles such as the sol-gel method, hydrothermal method, co-precipitation in normal or reverse micelles, sonochemical reactions, microwave radiation, ball milling [1-9]. Up to date, magnetic nanoparticles have established their wide applications. These magnetic particles can be made so small that each particle becomes a single domain, exhibiting abnormal magnetic properties, known as superparamagnetism. Superparamagnetic particles have been widely studied and used in biomedicine and biotechnology as contrast agent in magnetic resonance imaging (MRI), as drug carriers for magnetically guided drug delivery, hyperthermia [10]. Many such superparamagnetic particles are metal ones which are not stable at room temperature and easily oxidized. Then their potential applications are greatly limited. On the contrary the corresponding metal oxides can overcome the limit and develop the applications further. In addition, the metal oxides are relatively inert and their magnetic properties can be controlled by controlling the size and shape through chemical synthesis. Of all the metal oxides, magnetite (Fe₃O₄) and hematite (α-Fe₂O₃) or maghemite (γ-Fe₂O₃) have aroused great interest in the magnetic material field.

Magnetite nanoparticles can be produced by co-precipitation of Fe(II) and Fe(III) ions by a base, usually sodium hydroxide or aqueous ammonia or they may be produced by thermal decomposition of alkaline solution of Fe(III) chelate in the presence of hydrazine and by sonochemical decomposition of hydrolyzed Fe(II) salt followed by thermal treatment. Direct synthesis of magnetite nanorods is difficult because of the great difference in deposition rate of Fe(II) and Fe(III) ions in aqueous solution. In addition, the isotropic structure of magnetite also cause difficulties in anisotropic growth of nanocrystal.

We report synthesis of magnetic rod-like particles (nanorods) through two type hydrolysis (A) of ferrous and ferric solutions containing urea and (B) ferrous solution containing urea. The influence of different conditions during synthesis on the size, morphology, structure and magnetic properties is described.
2. EXPERIMENTAL

(A) Nanorods with diameter from 3 to 20 nm and lengths from 20 to 110 nm were synthesized through hydrolysis of FeCl$_3$ and FeSO$_4$ solutions containing urea (different molar ratio Fe$^{2+}$/Fe$^{3+}$/urea) (Table 1). In a typical experiment FeCl$_3$·6H$_2$O, FeSO$_4$·7H$_2$O and (NH$_2$)$_2$CO were dissolved in demineralised water. To this mixture an oleic acid was added and then sonicated for 30 min. Amount of the oleic acid was the same in all experiments. This mixture was added to a flask with reflux condenser. They were heated in water bath for 12 hours at 85 - 95ºC. The dark precipitate was formed. Sample was cleaned several times by demineralised water, and then the sample was dried in a lower pressure at 50ºC for 3 hours.

(B) The second type of synthesis was similar to the first but without using Fe$^{3+}$ salt (Table 2). The nanorods with diameter from 2 to 70 nm and lengths from 6 to 400 nm were prepared by this method.

The morphology and size distribution of the prepared nanorods were determined by Transmission electron microscopy (TEM Tesla BS 500) and Scanning electron microscopy (SEM, JEOL 7000F). The Infrared (IR) spectroscopy was used to characterise the prepared nanorods. Attenuated Total Reflectance (ATR) measurements were carried out with an FTLA2000 instrument (ABB, resolution 4 cm$^{-1}$, Diamond window). Their magnetic properties were investigated by SQUID magnetometer (Quantum Design MPMS 5XL).

Table 1.
The reactant ratio, size of the prepared particles, structure and magnetic properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar ratio Fe$^{2+}$:Fe$^{3+}$:urea</th>
<th>Length (nm)</th>
<th>Thickness (nm)</th>
<th>Composition</th>
<th>Saturation magnetization (emu/g)</th>
<th>Hc (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>1.0 : 2.0 : 8.0</td>
<td>30 - 60</td>
<td>7 - 10</td>
<td>Fe(OOH)</td>
<td>para</td>
<td>60</td>
</tr>
<tr>
<td>HB</td>
<td>1.0 : 0.5 : 1.7</td>
<td>20 - 100</td>
<td>3 - 20</td>
<td>Fe(OOH), Fe$_3$O$_4$</td>
<td>0.5 (+para)</td>
<td>43</td>
</tr>
<tr>
<td>HC</td>
<td>1.0 : 1.0 : 2.4</td>
<td>110</td>
<td>15</td>
<td>Fe(OOH)</td>
<td>para</td>
<td>60</td>
</tr>
<tr>
<td>HD</td>
<td>1.0 : 1.0 : 2.7</td>
<td>20 - 60</td>
<td>4 - 10</td>
<td>Fe(OOH), Fe$_3$O$_4$, Fe$_2$O$_3$</td>
<td>22</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 2.
The reactant ratio, size, composition and magnetic properties of obtained nanorods.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar ratio Fe$^{2+}$:urea</th>
<th>Length (nm)</th>
<th>Thickness (nm)</th>
<th>Composition</th>
<th>Saturation magnetization (emu/g)</th>
<th>Hc (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HE</td>
<td>1.0 : 2.7</td>
<td>6 - 50</td>
<td>2 - 4</td>
<td>Fe(OOH), Fe$_3$O$_4$</td>
<td>0.7</td>
<td>33</td>
</tr>
<tr>
<td>HF</td>
<td>1.0 : 1.5</td>
<td>230 – 400</td>
<td>9 - 14</td>
<td>Fe(OOH), Fe$_3$O$_4$</td>
<td>43</td>
<td>32</td>
</tr>
<tr>
<td>HH</td>
<td>1.0 : 3.0</td>
<td>170 - 350</td>
<td>50 - 70</td>
<td>Fe(OOH), Fe$_3$O$_4$, Fe$_2$O$_3$</td>
<td>35</td>
<td>32</td>
</tr>
</tbody>
</table>
3. RESULTS

At the beginning of the reaction, urea after heating over 70°C decomposes to CO₂ and NH₃ (Eq. 1). In the reflux condition, CO₂ can be released, so only NH₃ reacts with water and produces hydroxyl ions (Eq. 2).

\[
\text{(NH}_2\text{)}_2\text{CO} + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2 \\
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- 
\]

(1) (2)

Then Fe³⁺ reacts with OH⁻ ions and yellow precipitate can be observed, indicating the generation of Fe(OH)₃ (Eq. 3).

\[
\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 
\]

(3)

Fe(OH)₃ is transformed into goethite Fe(OOH) (Eq. 4), which is usually in the shape of needle:

\[
\text{Fe(OH)}_3 \rightarrow \text{FeOOH} + \text{H}_2\text{O} 
\]

(4)

Since the solubility of Fe(OH)₃ is much smaller than Fe(OH)₂, with enhancement of the pH value, Fe(OH)₃ is first precipitated.

\[
\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 
\]

(5)

After reaction of goethite with hydroxide magnetite is formed (Eq. 6).

\[
2\text{FeOOH} + \text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} 
\]

(6)

During these processes, hematite Fe₂O₃ can be formed by oxidation of magnetite, but also by decomposition of goethite (Eq. 7., 8).

\[
4\text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow 6\text{Fe}_2\text{O}_3 \\
2\text{FeOOH} \rightarrow \text{Fe}_3\text{O}_3 + \text{H}_2\text{O} 
\]

(7) (8)

In Table 1 and Table 2 are summarised molar ratios of used reactants, the size, composition and magnetic properties of prepared samples by first and second synthesis, respectively. The size distribution was obtained from TEM, composition was determined from IR spectroscopy.

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**Fig. 1** TEM image of rod-like particles - sample HA.

**Fig. 2** TEM image of needle-like particles HB.
Rather short yellow paramagnetic particles (sample HA) have been prepared by hydrolysis of Fe$^{2+}$ and Fe$^{3+}$ in presence of urea ($\text{Fe}^{2+}/\text{Fe}^{3+} = 1/2$). Figure 1 shows TEM image of the prepared particles. It can be seen that the product is composed of uniform rod-like structures with the diameter of 7 – 10 nm and length of 30 – 60 nm. IR spectroscopy confirmed goethite (FeOOH) structure in the sample HA. Longer needles-like FeOOH/ Fe$_3$O$_4$ particles, with length up to 100 nm (sample HB, Figure 2), were obtained by using ratio Fe$^{2+}$/Fe$^{3+} = 2/1$. IR spectroscopy confirmed goethite as main component. By changing reactant ratio Fe$^{2+}$/Fe$^{3+}$ to value 1/1 (sample HC) uniform rod-like goethite particles with the diameter of 15 nm and length of 110 nm were obtained. In the next sample HD, increased urea amount caused formation of smaller FeOOH/ Fe$_2$O$_3$/Fe$_3$O$_4$ rod-like particles (Fe$^{2+}$/Fe$^{3+}$ remain the same as in the case HC) with the diameter of 4 – 10 nm and length of 20 – 60 nm.

Fig. 5. Infrared spectra of sample HH, oleic acid and sample HH coated by oleic acid. The spectra are shifted vertically for clarity.
In the next (B) series of the prepared samples as reactant were used only Fe$^{2+}$ ions and different urea amount (no Fe$^{3+}$ ions). Fe$^{2+}$/urea ratio was changed from 1/1.5 to 1/3. The longest needle-like particles and the highest value of the saturation magnetization was observed in the sample HF (Figure 3) with molar ratio of Fe$^{2+}$/urea was 1.0/1.5. In the sample HF was found also small fragment of the spherical particles. The long needle-like particles were obtained also by using reactant ratio Fe$^{2+}$/urea = 1/3 (sample HH). In all samples presence of FeOOH/Fe$_3$O$_4$ was observed.

Figure 5 shows infrared spectra of sample HH prepared without oleic acid, oleic acid and sample HH coated with oleic acid. The absorption bands in region from 793 cm$^{-1}$ to 891 cm$^{-1}$ corresponds to goethite. The absorption band at 586 cm$^{-1}$ and shoulder at 434 cm$^{-1}$ refer to magnetite and maghemite. Oleic acid is obvious in the sample. The absorption band at 1713 cm$^{-1}$ refers to the stretching C=O vibration of the undissociated (COOH) carboxyl group.

The magnetic measurements of the prepared nanorods reveal the significant dependence of the magnetic properties of the samples on the synthesis conditions. The results of these measurements realized at temperature 295 K are collected in Table 1 and Table 2 and in Figure 6.

The saturation magnetization clearly depends on the length of the nanorods in opposite to the coercive field $H_c$, which vary very lightly excluding sample HA. By IR measurements the sample HA is composed from goethite which is paramagnetic at room temperature. This fact is confirmed by magnetic measurements (see inset in Figure 6), but existence of coercive field indicate also small amount of the ferromagnetic phase in this sample. The results of sample HB reveal the mixture of two phases – ferro and paramagnetic with significant part of the ferromagnetic phase. The decrease of the magnetization with increasing of the magnetic field at sample HE is due to the diamagnetic contribution of the sample capsule which absolute value is comparable with the small value of the sample signal.

![Fig. 6. The hysteresis loops of the nanorods measured at temperature 295 K.](image-url)
4. CONCLUSION
The nanorods were successfully synthesized through hydrolysis of FeCl$_3$ and FeSO$_4$ solutions containing urea with oleic acid as stabilizer (different molar ratio Fe$^{2+}$/Fe$^{3+}$/urea) or hydrolysis of FeCl$_3$ solution containing urea (different molar ratio Fe$^{2+}$/urea). Depending on the experimental condition, nanorods of different size, composition and magnetic properties were prepared.

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LITERATURE