A Mild Hydrothermal Route to the Synthesis of $\gamma$-Fe$_2$O$_3$ Nanorod

F. Aghazadeh$^1$, M. Aghazadeh$^2$, S. Kharrazi$^3$

Research Institute of Applied Science (ACECR), Shahid Beheshti University, Tehran, Iran.
Department of Physics, Faculty of Science, Islamic Azad University, Karaj Branch, Karaj, Iran.
Department of Physics, Faculty of Science, Shahid Beheshti University, G. C., Evin, Tehran 1983963113, Iran.

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ABSTRACT

Magnetic iron oxides have always been attractive to scientists due to great potential applications in different areas. This paper reports on a mild hydrothermal route for the synthesis of $\gamma$-Fe$_2$O$_3$ nanorods, when the hydrothermal temperature was 125 °C. The uniqueness of the method lies in the use of ferrous ammonium sulphate, in conjugation with FeCl$_2$, which helps maintain the stability of Fe$^{2+}$ state in the reaction sequence thereby controlling the phase formation. Hexamine was added as the stabilizer and hydrolyzing agents. The particle size was 70nm in width and 400nm in length. The magnetic behavior of the particles was like the typical behavior of superparamagnetic particles, so smaller particles can improve the magnetic properties and decreasing the coercivity.

1. Introduction

Novel synthesis routes and applications of nanomaterials have recently gained enormous importance. Iron oxide nanoparticles with their wide range of applications have always attracted a lot of interest. Magnetic iron oxides like maghemite and magnetite have been used for many biomedical applications such as targeted drug delivery, separation of biomedical products, cell separation, in cancer therapy, magnetic induced hyperthermia, MRI contrast agent, immunomagnetic separation IMC and others. The magnetic properties of maghemite play an important role in different applications of health care. A large number of materials in bulk as well as in the form of nanoparticles have been created for a variety of photochemical and photo electrochemical applications [1-7]. To design any application for such nanoparticles, it is necessary to find a synthesis route which provides good control on particle size with

* Author to whom all correspondence should be addressed
Fatemeh Aghazadeh
Lecturer - Research Institute of Applied Science (ACECR), Shahid Beheshti University, Tehran, Iran.
E-mail: aghazadeh_ch@yahoo.com
Tel.: 0098-261-4316125 Mobile: 0098-912-7679538
narrow size distribution in addition to being quick and low cost. Each application requires specific material properties. The size and the shape of the magnetite nanocrystals are important for their strong influence on the magnetic behavior of the particles. The magnetic single-domain ranges of size from 30 to 120 nm. For crystals smaller than 30 nm the magnetization spontaneously changes its direction because of thermal fluctuations. These grains are superparamagnetic. Crystals larger than 120 nm are multi-domain and have lower remanent magnetization than single-domain crystals. In general, the more elongated the crystals, the better constrained is the direction of the magnetic induction, particularly if the elongation and the easily magnetisable direction are parallel to each other [8]. Gamma Fe₂O₃ (maghemite) is the ferromagnetic cubic form of Fe (III) oxide and it differs from the inverse spinel structure of magnetite through vacancies on the cation sublattice. Maghemite has the same crystalline structure like magnetite. Main distinct features of maghemite are the presence of vacancies in Fe position with symmetry reduction. Gamma and epsilon type Fe₂O₃ are ferromagnetic, alpha-Fe₂O₃ is a canted antiferromagnetic while beta type Fe₂O₃ is a paramagnetic material [7].

Various methods for preparation of iron oxide nanoparticles, such as oxidation of iron nanoparticles [9], spray pyrolysis [10-11], microwave irradiation [12], electrodepositing [13], co-precipitation [14,15] and hydrothermal [16-17] have been reported in the literature [18-20].

The hydrothermal method used hydrolyzing agents such as sodium hydroxide, sodium hydroxide + hexamine, ammonia, ammonia + formaldehyde [21]. Hexamine is known to assist anisotropic growth of metal oxides and the same is also found to be true for magnetite nanosynthesis. It elucidates the role of hexamine and other precursors in the formation of magnetite nanorods by the hydrothermal route and their stoichiometry [21-22]. Hydrothermal synthesis of iron oxide nanorod can be performed by using different precursors under various temperature-pressure conditions. For the first time, we report the hydrothermal synthesis of maghemite nanorods by using ferrous ammonium sulfate (FAS), as the source of ferric ions and hexamine is known stabilizer and hydrolyzing agents. We are also studied the role of hexamine in the formation of maghemite nanorods by the hydrothermal method.

2. Experimental

For the synthesis of γ-Fe₂O₃ nanorods, ferrous ammonium sulphate (FAS) (analytical grade, Merck, Germany) was used as the source of ferrous ions and hexamine (Merck, Germany) was used as a stabilizer and hydrolyzing agent. A typical synthesis involved 15 ml, 0.1 M solution of FAS, mixed with 7g Hexamine in 50 ml water. The mixed solution was put in a 100 ml Teflon lined reaction vessel autoclave. The reaction was carried out at 125 °C, for duration of 1-3 hours. After the completion of reaction a brownish precipitate was formed. The product was separated by exposing the solution to a 1 Tesla magnetic field, followed by centrifugation and the precipitate was washed with water for several times and was finally dried in oven.

The structure and phase purity of as-synthesized samples were examined by using powder X-ray diffraction (Philips, PW-3710) with Cu kα radiation as the source of X-rays. The size and the morphology of the particles were investigated by using transmission electron microscope (TEM), model ZEISS,
CEM 902A operating at 100 KV. Magnetic measurements were carried out by using an alternating gradient force magnetometer (AGFM). Fourier transform infrared (FT-IR) spectra of the samples were taken with KBr pellets using a Bruker IF,66/5, range \( \lambda = 400-4000 \text{Cm}^{-1} \).

3. Results and Discussion

The structure of \( \gamma \)-Fe\(_2\)O\(_3\) is similar to that of Fe\(_2\)O\(_4\), but with cation vacancies at the octahedral site of the spinel lattice [23, 24]. The ordering of these vacancies can occur in different forms leading to different crystal symmetries. It has been shown that the cation vacancy distribution depend on the preparation method of \( \gamma \)-Fe\(_2\)O\(_3\). The low temperature methods of synthesis usually lead to the formation of disordered phase.

The phase purity and crystal structure of the synthesized nanoparticles were investigated by powder X-ray diffraction (XRD), as shown in Fig.1. As it could be observed, the samples are well crystalline but the structure and phases vary in these samples, depending on the reaction conditions. In samples \( S_1 \) and \( S_2 \), where the reaction time increases from 1 hour to 3 hours, the phase purity improves drastically, showing peaks attributed to the tetragonal \( \gamma \)-Fe\(_2\)O\(_3\) phase.

FTIR spectroscopy was carried out to find out the precursors’ residue in the samples. As it could be seen in Fig.2, for sample \( S_1 \), the presence of peaks related to precursors indicates that the reaction time has not been long enough for the completion of the reaction. In sample \( S_2 \) a broad peak between 3000 and 3500 \text{cm}^{-1} \) is related to the overlapping of the \( \text{–NH stretching and –OH bending. The peak at } \approx 1600 \text{ cm}^{-1} \) is attributed to \( \text{–NH deformation and therefore the presence of –NH functional group on the surface of the nanoparticles are confirmed. The strong and broad bands found in the range 500-700 cm}^{-1} \), can be assigned to the antisymmetric FeO\(_6\) stretching vibration. The lower energy band at 440 cm\(^{-1}\) is related to deformational modes of same octahedral.

Fig. 1: XRD pattern of samples \( S_1 \) and \( S_2 \).

Fig. 2: FTIR spectra of samples \( S_1 \) and \( S_2 \).
TEM micrographs (Fig. 3) confirmed that sample $S_2$ consists of elongated rod shaped particles, mostly overlapping on the sides along the length, with an average width of 70nm and length in the range of 400nm. $\gamma$-Fe$_2$O$_3$ nanorod with similar morphology (elongated) was also reported by Fang et al. [25]. Sample $S_1$, on the other hand, contained particles which look larger and of arbitrary shapes with some elongated particles formed. This is in good agreement with XRD results which showed that $S_1$ was in more pure form and therefore of better reaction time.

Fig. 4 shows the magnetization as a function of magnetic field (M vs. H) recorded at 300 K. Both the samples show a measurable hysteresis even though the coercivity ($H_c$) is very small, 17.1 Oe in $S_1$ and 71.6 Oe in $S_2$. The saturate magnetization is higher in $S_2$ as the particles have grown larger in this sample. The coercivity of the nanorods increases with increasing particle size. In both the samples the magnetization rapidly increases with applied field but in $S_1$ hardly reaches saturation even in 8 KOe applied field whereas the magnetization of $S_2$ reaches saturation in about 6 KOe. The magnetic behavior of the samples is similar to that of superparamagnetic nanoparticles.
Fig. 4: Magnetization (M) versus applied magnetic field (H) isotherms at room temperature for samples $S_1$ and $S_2$.

4. Conclusions

It was shown that FAS and hexamine can be used as a precursor for the hydrothermal synthesis of $\gamma$-Fe$_2$O$_3$ nanorods. The nanoparticles were elongated with needle like shape. In samples, where the reaction time increases from 1 hour to 3 hours, the phase purity improves drastically, showing peaks attributed to the tetragonal $\gamma$-Fe$_2$O$_3$ phase. The particle size was 70nm in width and 400nm in length. Therefore, both the samples show a measurable hysteresis even though the coercivity ($H_c$) is very small, 17.1 Oe in $S_1$ and 71.6 Oe in $S_2$. The saturate magnetization is higher in $S_2$ as the particles have grown larger in this sample. The magnetic behavior of the particles was like the typical behavior of superparamagnetic particles, though achieving smaller particles can improve the magnetic properties of the particles namely decreasing the coercivity.

References


