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# One-pot synthesis of magnetic $\gamma$-Fe$_2$O$_3$ nanoparticles in ethanol-water mixed solvent

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Maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticles were synthesized via a low-temperature solution-based method using ferric chloride hexahydrate and ferrous chloride tetrahydrate as precursors in the mixed solvent of ethanol and water. X-ray diffraction, energy-dispersive X-ray spectroscopy, and Fourier transform infrared spectroscopy revealed that the obtained product was pure $\gamma$-Fe$_2$O$_3$. Transmission electron microscopy showed the morphology of the nanoparticles to be approximately spherical in shape with an average diameter of 11 nm. Magnetization measurements indicated the dry powders exhibit ferromagnetic behavior with a maximum saturation magnetization of 41.1 emu/g at room temperature.

Keywords: *nanoparticles; magnetic materials; synthesis; FTIR; X-ray techniques*

## 1. Introduction

In recent years, iron oxide and ferrite nanomaterials have attracted a great deal of interest due to their unique electrical, optical, biological, magnetic properties and their technological importance in the nanotechnologies for information storage, magnetic resonance imaging contrast agents, and ferro fluids [1–6]. Maghemite ($\gamma$-Fe$_2$O$_3$) in nanophase has been especially interesting because of its non-toxicity, thermal and chemical stability and favorable hysteric properties, which is considered as a valuable material for modifying biologically active compounds, bio-tagging of drug molecules, hysteretic heating of malignant cells, magnetic recording systems, gas sensors, in catalysis, etc. [7–10].

The development of maghemite nanoparticles applications imposes the need for the synthesis of $\gamma$-Fe$_2$O$_3$ with well-controlled size and morphology by simple ways. Up to now, various approaches [11–15] have been employed to prepare $\gamma$-Fe$_2$O$_3$ nanostructures. Among all the synthetic methods, the chemical co-precipitation may be the most promising one because of its simplicity and productivity. As a classic example, Lee and

co-workers reported the synthesis of maghemite nanoparticles by co-precipitation technique [11]. The synthetic process involves the formation of Fe$_3$O$_4$ from a mixed solution containing Fe$^{2+}$ and Fe$^{3+}$ and the oxidization of magnetite to Fe$_2$O$_3$ at 300 °C. As you see, the technique involves a "fussy multi-step" procedure and higher temperature. It is of great research interest to develop a simple and easy-handling procedure for the fabrication of $\gamma$-Fe$_2$O$_3$ nanostructures at lower temperature. In this work, we propose a novel one-pot route for the synthesis of $\gamma$-Fe$_2$O$_3$ nanoparticles, which includes heating of alcohol-aqueous salt solution followed by the addition of ammonia. Using this method, the maghemite nanoparticles with the average particle size of about 11 nm can be successfully synthesized.

## 2. Material and methods

All chemicals used in this experiment were analytical grade and were used without any further purification. Ferric chloride hexahydrate (FeCl$_3$·6H$_2$O, $\geqslant$ 98 %), ferrous chloride tetrahydrate (FeCl$_2$·4H$_2$O), absolute alcohol and ammonium hydroxide solution (NH$_3$·H$_2$O, 28 – 32 % of ammonia) were purchased from Sigma-Aldrich.

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Urea was received from Fluka Company. The water used in this work was deionized water.

A typical preparation procedure was as follows: a stoichiometric ratio of 1:2 ferrous $FeCl_2 \cdot 4H_2O$ (0.01 mol) and $FeCl_3 \cdot 6H_2O$ (0.02 mol) were introduced into a beaker containing 80 ml absolute alcohol and 20 ml deionized water under constant magnetic stirring until a clear solution was obtained at room temperature. Then the solution was transferred to a flask with a reflux condenser, which was maintained at 80 °C for 60 min. After one hour, about 20 ml 28 % ammonium hydroxide was injected into the solution, followed by another 60 min reflux at 80 °C. The resulting solution was cooled to room temperature and the reddish-brown precipitate was separated and washed thoroughly with deionized water for 3 times to remove the reaction residues. Then it was washed two times with ethanol and dried at room temperature.

The iron oxide powders were characterized by X-ray diffraction (XRD, X'Pert, PHILIPS) using Cu K$\alpha$ radiation with graphite monochromator. The diffraction patterns were measured step by step (0.02° in 2 theta range). The particle size and morphology were characterized via transmission electron microscopy (TEM, JEM-1400 model, JEOL) with accelerating voltage of 100 kV. The elemental analysis of the sample was performed with SEM equipped with an energy dispersive X-ray spectroscopy (EDS, XL30, PHILIPS, with accelerating voltage of 25 kV). The particle size distribution of the obtained maghemite nanoparticles was investigated with Microtrac Nanotrac 150 based on dynamic laser scattering (DLS). FTIR was recorded on a Bruker tensor 27 FT-IR spectrometer with RT-DLATGS detector, in the range of $400 - 4000$ cm$^{-1}$ with a spectral resolution of 4 cm$^{-1}$ in transmittance mode. The magnetic properties were measured using the vibrating sample magnetometer (VSM) model EV7 with an applied magnetic field of 20,000 Oe at room temperature.

## 3.   Results and discussion

Fig. 1 presents the XRD results for the obtained red-brown product. The broad reflection peaks due to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0)

planes were in accordance with the characteristic peaks of $\gamma$-$Fe_2O_3$ (Powder Diffraction file, JCPOS card no. 25-1402). The crystallite size was determined to be approximately 9.7 nm, calculated by Scherrer's equation and the half width of the $\gamma$-$Fe_2O_3$ maximum intensity (311) plane after correction for the instrumental broadening [16]. However, XRD analysis did not provide discrimination between magnetite and maghemite because both had the same spinel structure and their XRD diffraction patterns overlapped. Further investigations were carried out as follows. First, the colors of our samples were the characteristic color of $\gamma$-$Fe_2O_3$ (red-brown) which was significantly different from that of $Fe_3O_4$ (black). Second, as shown in Fig. 2, the FT-IR spectra of the nanoparticles had three peaks centered at the wavelengths of around 561, 581 and 632 cm$^{-1}$, associated with the stretching and torsional vibration modes of the maghemite Fe–O–Fe bonds in maghemite [17, 18]. Third, the stoichiometric composition of the obtained nanoparticles was measured with EDS as shown in Fig. 3 which includes the EDS spectrum and the result of quantitative analysis. According to the spectrum, the prepared nanoparticles were composed of only Fe and O elements, no other elements were present. Based on the elemental analysis of the sample (Fe = 30.53 wt.%, O = 69.47 wt.%), the atomic Fe/O ratio could be calculated to be 0.65, which was close to the theoretical value (0.667) of $Fe_2O_3$ while there was a significant difference from the value of $Fe_3O_4$ (0.75). Based on XRD/EDS/FT-IR investigations, we could confirm that the produced powder was pure $\gamma$-$Fe_2O_3$ rather than $Fe_3O_4$.
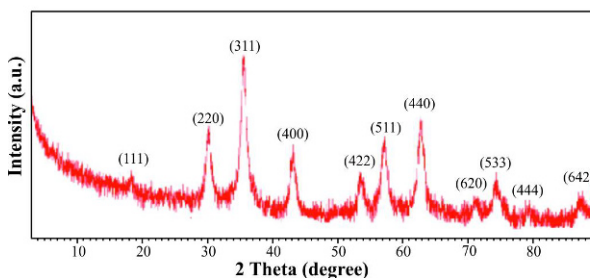


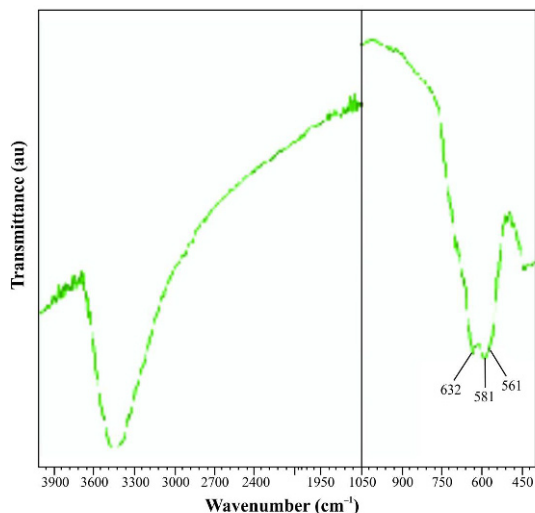Fig. 1. X-ray diffraction pattern of the obtained $\gamma$-$Fe_2O_3$ nanoparticles.

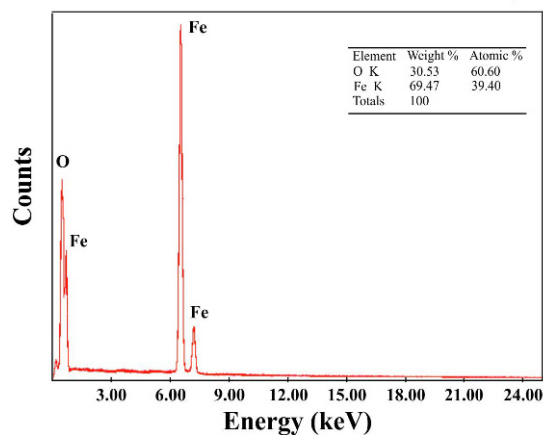Fig. 2. FT-IR spectra of the obtained $\gamma$-Fe$_2$O$_3$ nanoparticles.



Fig. 4. TEM of the obtained $\gamma$-Fe$_2$O$_3$ nanoparticles.



Fig. 3. EDS of the obtained $\gamma$-Fe$_2$O$_3$ nanoparticles.



Fig. 5. Particle size distribution of the obtained $\gamma$-Fe$_2$O$_3$ nanoparticles by DLS.

Fig. 4 depicts a representative TEM for the $\gamma$-Fe$_2$O$_3$ nanoparticles. The TEM image of the sample shows light clumping of spherical primary particles with an average diameter of 8 to 15 nm. The light clumping can be attributed to the magnetic interaction between the nanoparticles. The particle size distribution obtained from DLS is shown in Fig. 5. It may be seen that the particle size distribution is narrow with most of the particles having size between 7 and 14 nm and the average particle size is close to 11 nm. This is comparable to the particle size obtained from TEM analysis.
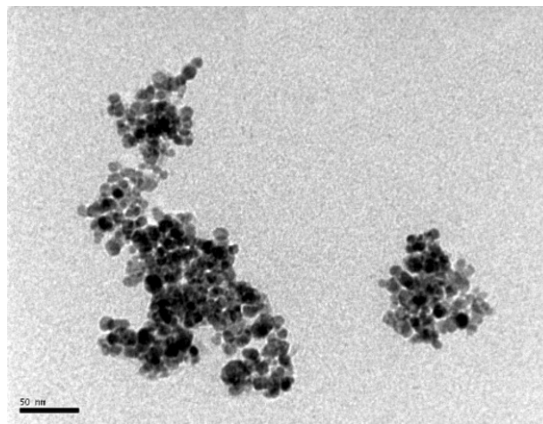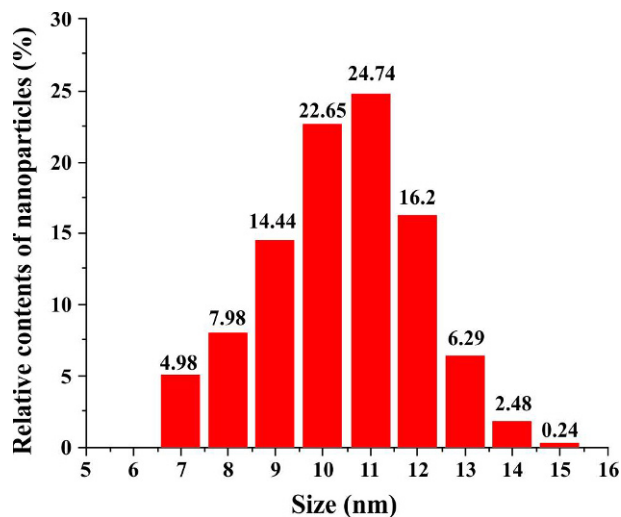
In order to obtain the magnetic properties of the synthesized maghemite nanoparticles, the room temperature magnetization curve as a function of applied magnetic field was registered. Fig. 6 shows a narrow hysteresis curve. The saturation magnetization (M$_s$), remanent magnetization (M$_r$) and the coercivity (H$_c$) were determined as 41.1, 13.2 emu/g (41.1, 13.2 Am$^2$/kg) and 143 Oe, respectively. This result indicates that the prepared nanoparticles exhibit typical ferromagnetic behavior. The inset in Fig. 6 demonstrates that the obtained $\gamma$-Fe$_2$O$_3$ nanoparticles in aqueous solution could be readily separated and collected by a magnetic field within a few seconds. The M$_s$ result

was close to the reported data in the literature which was about 30 emu/g for the same particle size [19, 20] but much less than the known value of 73 – 74 emu/g for the magnetization of the bulk sample at room temperature [21]. The reasons for the reduced value are likely due to the existence of nonmagnetic surfactant on the surface with reduced magnetization and some diamagnetic contribution from the surfactant shell [22].
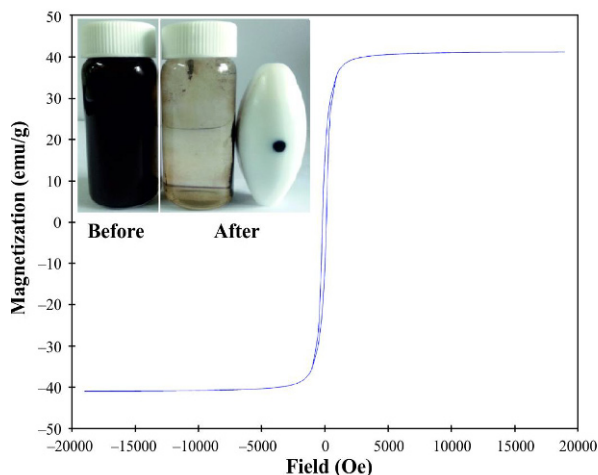


Fig. 6.  M-H curve measured at 300 K for the obtained maghemite.

## 4.    Conclusions

From the results of this study, it could be pointed out that by applying this innovative single step method, pure maghemite ($\gamma$-$Fe_2O_3$) nanoparticles with a narrow size distribution could be prepared simply, effectively and cheaply. The obtained $\gamma$-$Fe_2O_3$ nanoparticles were almost spherical in shape with an average size of 11 nm. The coercivity and the saturation magnetization values were of 143 Oe and 41.1 emu/g (41.1 $Am^2$/kg), respectively. The new approach was proven to be a fast, easy to operate, efficient in terms of energy consumption and environmentally friendly method to prepare maghemite nanoparticles. We postulate that it would be a novel approach for the potentially large-scale synthesis of maghemite nanoparticles.

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