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One-step synthesis of maghemite (γ-Fe_2O_3) nano-particles by wet chemical method

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ABSTRACT

Maghemite (γ-Fe_2O_3) nano-particles were produced by an innovative one-step method at room temperature and characterized using X-ray diffraction (XRD), Brunaure–Emmet–Teller analysis (BET), infrared spectrum (IR), scanning electron microscope (SEM), energy dispersive spectra (EDS), and photon correlation spectroscopy (PCS). The average particle size of the maghemite was estimated to be 45 and 57 nm, by SEM and PCS, respectively. The SEM image showed that the γ-Fe_2O_3 nano-particles were of approximately spherical shape and a size below 50 nm.

1. Introduction

Nano-particles have become the focus of modern materials science because of their potential technological importance, which stems from their unique physical properties [1]. Their electronic, magnetic and optical properties contribute attractive prospects in the design of new electronic and optical device, information storage, color imaging, bio-separation, magnetic refrigeration, ferro fluids, gas sensors, etc. In these latter fields of application, small particles of metal oxide are particularly important [1,2]. Various methods have been reported for the synthesis of maghemite nano-particles, such as co-precipitation [3], sol–gel synthesis [4], microemulsion [5], flow injection synthesis [6], flame spray pyrolysis [7], decomposition of organic precursors at high temperatures, and the oxidation of magnetite nano-particles [8]. Industrially, maghemite nano-particles are usually prepared in two steps. In the first step, magnetite is synthesized by chemical co-precipitation of ferric and ferrous ions in an alkali solution, and in the second step, magnetite is oxidized by aeration at 200–400 °C (reaction (1)) [3,9–11]. During the heat transfer, the particles are subjected to agglomeration which results in a larger particle size distribution:

$$FeCl_2 + FeCl_3 \rightarrow Fe_3O_4 \xrightarrow{\text{Oxidation } (200\text{–}400\,^{\circ}\text{C})} \gamma\text{-}Fe_2O_3 \qquad (1)$$

In this paper, an innovative and simple one-step method for the synthesis of γ-Fe_2O_3 nano-particles is presented. This method dose not required organic solvents and heat treatment. Pure maghemite with an average particle size below 50 nm can be produced without any hematite and magnetite impurities.

2. Materials and methods

The synthesis procedure was as follows: $FeCl_3$ and $FeCl_2 \cdot 4H_2O$ were dissolved in a 2 M hydrochloric acid to form a solution with the concentration of 1 M for $FeCl_3$ and 2 M for $FeCl_2 \cdot 4H_2O$. The $NH_3 \cdot H_2O$ solution (2 M) was dropped to this solution with vigorous stirring at room temperature for 2 h. The final pH was 9.73. The brown precipitate was then collected by filtration and rinsed three times with deionized water and ethanol. Finally, the washed precipitate was dried at 70 °C overnight. The synthesis procedure has been summarized in Fig. 1.

The crystalline structure of the nano-particles was characterized by X-ray diffraction (XRD, PHILIPS, X' pert-MPD system) using Cu Kα (λ = 1.54 Å) radiation. The particle size distribution of the nano-sized maghemite was measured by photon correlation spectroscopy (PCS) at 25 °C using a Malvern nano-sizer/zeta sizer® nano-zs, model ZEN 3600(Malvern instrument, UK). Samples of 0.1 g maghemite in 1000 ml of deionized water were prepared. The analysis was preformed three times and a mean value was presented. IR spectra were recorded on a Bruker tensor 27 FTIR spectrometer with RT-DLATGS detector, in the range of 400–1100 cm^{-1} with a spectral resolution of 4 cm^{-1} in transmittance mode. The KBr pellet technique with about 1 wt% of sample was used for sample preparation. The specific surface area of nano-sized maghemite particles was estimated by the Brunaure–Emett–Teller (BET) method. The morphology and average particle size of maghemite nano-particles

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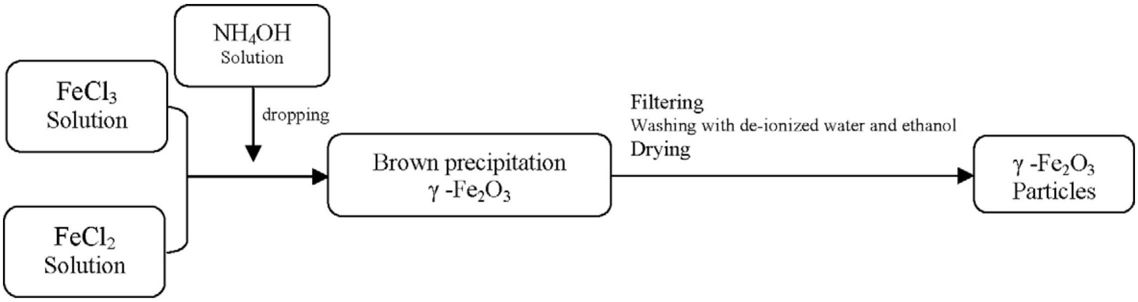

Fig. 1. Schematic of the experimental procedure.

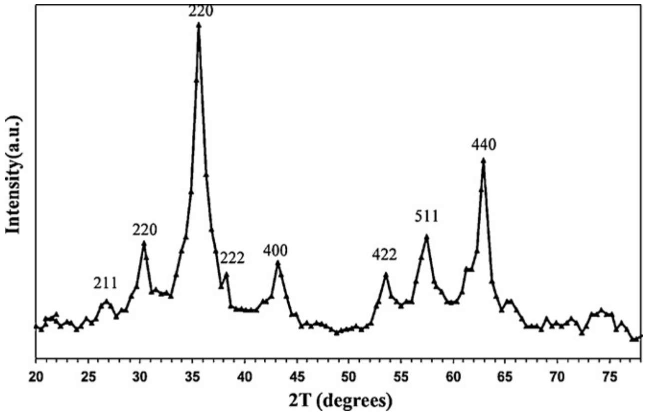

Fig. 2. X-ray diffraction patterns of γ-Fe_2O_3 nano-particles by wet chemical at room temperature.

were further investigated by a scanning electron microscope (SEM, Tescan Vega-II). All of the chemicals were of analytical grade.

3. Results and discussion

X-ray diffraction patterns of a representative sample produced material are presented in Fig. 2. The peaks in the XRD pattern could be in consistent with the standard structure (JCPDS card No. 39-1346). The results showed that the products consisted of pure phases. The mean crystallite size of maghemite nano-particles was calculated to be about 13 nm using Scherrer's Eq. (2):

$$D = \frac{0.9\lambda}{\beta \cos\theta_{\circ}} \qquad (2)$$

where D is the mean crystalline size (nm), λ is the wavelength of Cu Kα (0.154 nm), β is the full width at half maximum intensity (FWHM) in radian and θ° is the Bragg angle (°) [12,13]. Surface area of nano-particles was measured to be 31 m^2/g (N_2, BET). The average crystalline size of nano-sized γ-Fe_2O_3 powders was also figured out by using Eq. (3):

$$d_{\mathrm{BET}} = \frac{6000}{\rho S_{\mathrm{BET}}} \qquad (3)$$

where d_{BET} is the crystalline size (in nm), ρ is the density of nano-sized γ-Fe_2O_3 powder (in g cm^{-3}) and S_{BET} is the BET specific surface area [14]. In this study, a d_{BET} of 39 nm could be obtained by using the 4.98 g cm^{-3} powder density. The inconsistency of γ-Fe_2O_3 crystalline size determined by the BET methods and the XRD Scherrer formula indicated that there was conglomeration in the nano-sized γ-Fe_2O_3 powder. The FTIR spectra have provided information on the nature of the produced maghemite. The analysis was performed using a mixture of 0.2 mg the produced maghemite nano-particles with 250, 300 and 350 mg KBr. A typical FT-infrared (FTIR) spectrum of the sample is shown in Fig. 3. The absorption peak at 587 cm^{-1} could be related to the vibration of γ Fe–O [13–18], and the other peaks at 454, 632, 795 and 892 cm^{-1} are pure maghemite.

SEM image of γ-Fe_2O_3 nano-particles and relevant EDS spectra of the marked area of sample are shown in Fig. 4. The EDS spectrum reveals that only Fe and O elements are detected in the prepared γ-Fe_2O_3 powder, as shown in Fig. 4(B1). Based of the elemental analysis of sample (Fe = 33.95%, O = 66.05%), the atomic Fe/O ratio can be calculated to be 0.52, which is close to the value calculated for γ-Fe_2O_3. The results of EDS analysis also confirm that the produced powder is γ-Fe_2O_3, which is in agreement with the results of XRD and FTIR. The morphology of the nano-sized γ-Fe_2O_3 particles showed an approximate spherical shape. The size distribution of the nano-particles measured by PCS and SEM analysis is given in Fig. 5. It can be pointed out that the average particle size determined by PCS and SEM analysis is around 57 and 45 nm, respectively.

The surfaces of γ-Fe_2O_3 suspension are generally covered with hydroxyl groups that vary in forms at different pHs. There is a relationship between the pH value and zeta potential of γ-Fe_2O_3 nanofluid. The zero point of charge, pH_{zpc}, of maghemite nano-particles is around 6.3 [19]. When the pH value of nano-particle suspension is 6.3, the zeta potential is 0 mV (i.e.p), but when the pH value is higher than 6.3, it becomes a negative. From this, when the pH value is far greater or smaller than 6.3, the particles can hardly agglomerate because the nano-particle suspension has a high surface potential. When the nano-particles were dispersed in deionized water with the pH value of 7, closed to i.e.p (pH 6.3), the nano-particles become unstable and aggregate within short period because of the larger surface area and electrostatic force between particles.

A qualitative ranking of the magnetic susceptibility of the maghemite nano-particles has been demonstrated in a simple laboratory setup with a hand-held magnet as shown in Fig. 6. The

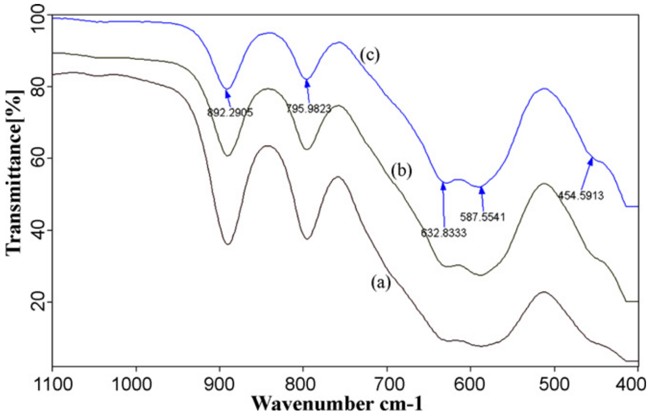

Fig. 3. FT-infrared spectra of γ-Fe_2O_3 nano-particles performed by 200 mg (a), 250 mg (b) and 300 mg (c) KBr.

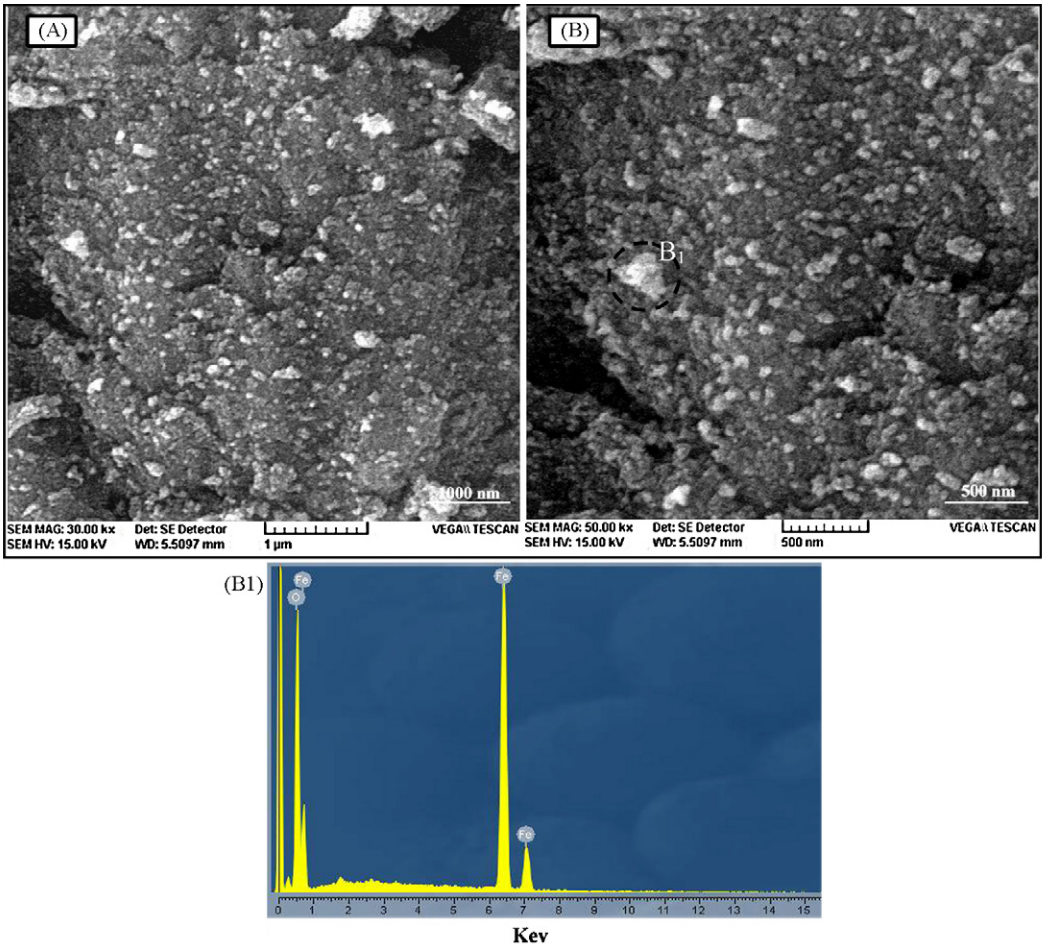

Fig. 4. SEM image of the γ-Fe_2O_3 nano-particles at (A) 30,000× and (B) 50,000× magnification; the relevant EDS spectrum of the circled area (B_1) in (B).

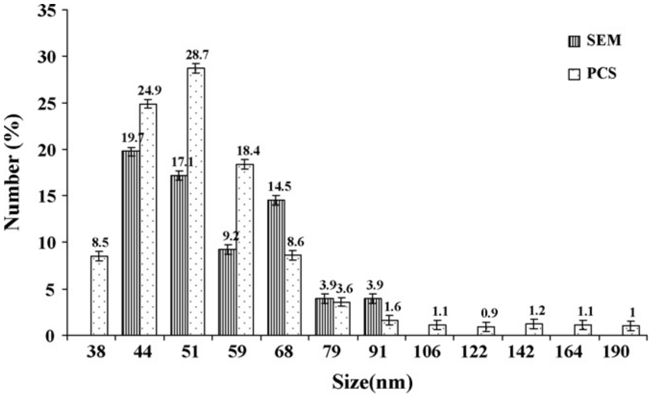

Fig. 5. Particle size distribution of the γ-Fe_2O_3 nano-particles.

meso-porous maghemite (>200 nm) could be completely separated from the aqueous solution within 5 min, while the separation time of maghemite nano-particles with a size of about 10 nm is more than 5 h [20].

4. Conclusions

From the results of this study, it can be pointed out that applying this innovative single step, wet chemical method, pure γ-Fe_2O_3 nano-particles can be produced at room temperature. XRD, EDS and FTIR data analysis confirmed the absence of hematite and magnetite in the synthesized γ-Fe_2O_3 powder. The mean particle size of γ-Fe_2O_3 nano-particles determined by SEM and PCS analysis was about 45 and 57 nm, respectively. The difference in average particle size determined by PCS and SEM analysis is due to the elec-

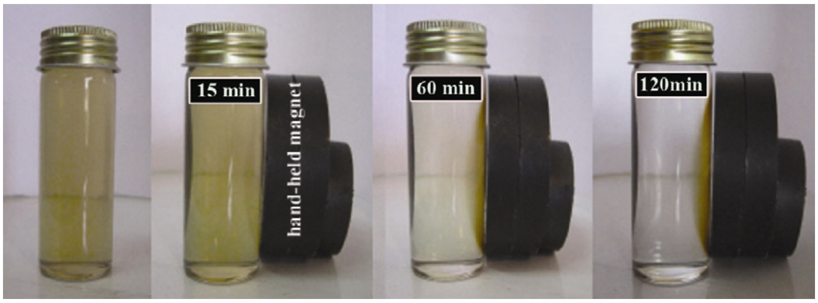

Fig. 6. γ-Fe_2O_3 dispersed in ethanol in a hand-held magnet field at different periods of time.

trostatic forces between particle and their agglomeration. It could be demonstrated that pure γ-Fe_2O_3 nano-particles in a single step using this easy, cheap and nontoxic method. It is quite promising for the mass production of γ-Fe_2O_3 nano-particles.

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