

Synthesis and Structural Characterization of Iron Oxide-silica Nanocomposites Prepared by the Solgel Method

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Abstract: Nano iron oxide powders have been synthesized by solgel method at 700°C (3-12h), using X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) have been employed to characterize the magnetite nanoparticles. The results reveal that the magnetite nanoparticles have a tunable diameter range of ~ 20-42 nm. The particles don't make any agglomeration, and show us an excellent monodisperse property. The influences of the reaction time and filled value on the particle size of the products have been studied.

Keywords: Thermal Treatment, Magnetite, Hematite, Nanocrystallites.

1. INTRODUCTION

Magnetic nanoparticles are gaining increasing attention in biomedical applications [1-4]. Most interests in the clinical use of magnetic nanoparticles have focused on magnetite nanoparticles [5-7]. This is because of the chemical stability, biological compatibility, and relative ease of manufacture and recycling of magnetite. To date, magnetite nanoparticles have already been approved for clinical use as MRI (magnetic resonance imaging) contrast agents [3-4], biological separation and magnetite nanoparticles-aided drug delivery [8-12] is still a work-in-progress. The phase and structure of nanomaterials are prime controlling parameters, which play very important role in tailoring most of the properties required for various applications. These prime parameters mostly depend on the precursors and their molar ratio and also on method of preparation. Magnetic (ferrite) powders are generally prepared by traditional high temperature ceramic method, which is associated with several limitations, including poor control of particle size, morphology and microscopic homogeneity. Chemical methods, e.g. co-precipitation, solgel, hydrothermal and colloid emulsion techniques, allow efficient control of the morphology and chemical composition of the prepared powders. Solgel, hydrothermal and colloid emulsions are time consuming and involve highly unstable alkoxides and therefore, sometime difficult to maintain reaction conditions.

Recently, the present authors [7] prepared $\text{Nd}_2\text{O}_3:\text{SiO}_2$ composite using solgel technique and shown that thermal annealing played a pivotal role to obtain its nanocomposite structure. However in the present investigation, solgel

technique has been used to synthesize iron oxide nano powder, because solgel technique is more versatile. Moreover, it provides good homogeneity, fine and uniform particle size with non agglomerate or weakly agglomerate particles at low reaction temperature. Beside, this technique is easy scale-up, low cost and time saving process [7]. Despite of all these, there is still a major challenge to develop a technologically simple, cost effective and the most versatile solgel synthetic route for preparation of nanostructured materials with desired chemical composition. In the present paper it is shown that the phase and structure of the iron oxide nano powder can be tailored by heat treatment. Thermal annealing of iron oxide powder at temperature 700°C (12h) leads to direct transition of Fe_3O_4 (magnetite) phase to $\alpha\text{-Fe}_2\text{O}_3$ (hematite) phase with a well defined morphology and size. To the authors knowledge, the direct transition of nanocrystallite Fe_3O_4 (face-centered cubic) to nanocrystallite $\alpha\text{-Fe}_2\text{O}_3$ (hexagonal rhomb-centered), prepared by solgel technique, has not been reported so far.

2. EXPERIMENTAL

2.1. Sample Preparation

Magnetite nanoparticles were synthesized by a solgel method. The high purity reagents: 10 wt% Fe_2O_3 at mixed hydrolysis ratio. The sols were prepared by dissolving ferric chloride hexahydrate (Aldrich 99.99%), in a mixture of deionized water-ethanol and subsequently adding of tetraethoxysilane drop wise under continuous stirring for 40 minutes. The pH of the resultant solution was 0.9. To this end, hot solution was allowed to cool at room temperature and diluted to double of its initial volume after cooling. The

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solutions was filtered, washed many times with deionized water and acetone and finally allowed to dry in air. The samples were ground to very fine powder. The powder sample calcined in muffle furnace (KSL 1600X, MTI) in air at different heating rates i.e. from room temperature up to 700°C(3h) and 700°C(6h) at 2°C/h and 700°C(12h) at 4°C/h.

2.2 Characterization

Complementary methods were used to characterize the structure and phase of heat treated samples. X-ray diffraction pattern of samples were carried out by a Philips X-ray diffractometer PW/1710; with Ni filter, using monochromatic CuK α radiation of wavelength 1.5418Å at 50KV and 40mA. Scanning electron microscopy (SEM) of the samples was done with JEOL-JSM-T330-A 35 CF microscope at an accelerating voltage of 20KV. Infrared spectra were collected by using Fourier transform infrared spectrometer (Perkin Elmer 1600) ranging 2500-500 cm⁻¹.

3. RESULTS AND DISCUSSION

3.1. XRD

The XRD patterns of magnetite nanoparticles obtained with different reaction time is showed in Fig 1. The powder sample calcined at 700°C (3h) shows one strong and three weak diffraction peaks at 2 θ ~ 35.6° and 30.2°, 57.5°. This diffraction pattern reveals that sintering of the sample around 700°C (3h) plays effective role in developing crystalline phase of the powdered iron oxide sample. The diffraction peaks appeared at angle 2 θ ~ 30.2° (220), 35.6° (311), and 57.5° could be attributed to Fe₃O₄ face-centered cubic structure [JCPDS file no 85-1436]. Here it is worth mentioning that Fe₃O₄ has an inverse spinel structure with a phase centered cubic unit cell of 32 O²⁻ ions with a lattice constant of 0.839 nm in which 1/3 of iron ions occupy the tetrahedral sites (all Fe³⁺) while 2/3 of the iron ions occupy both the octahedral and tetrahedral sites [8]. When the annealing time was increased for 6 hours, no drastic change in the diffraction pattern was observed, but when the diffraction pattern was minutely examined we noticed that sharpness in the diffraction peak around 2 θ ~ 35.7° was increased while its intensity slightly reduced. It is expected that the sharpness of the diffraction peak arises because individual nano structure merged together and as a result the activation energy become larger. Beside, those peaks, a new but weak peak was also appeared around 2 θ ~33.1° which may be ascribed by hematite phase of Fe₂O₃. Debye-Scherrer formula was employed to obtain the average size of Fe₃O₄ and was found to be 20 nm and 30 nm for the sample sintered at 700°C (3h), 700°C (6h), respectively. This result shows that the crystallite size increases with increasing calcination time, which is well in agreement with reported results [9].

Finally, the sample was fired at 700°C (12) study the effect of prolonged sintering time on structural evolution of iron oxide powder. Under this condition many peaks appeared in the diffraction pattern. Interestingly, characteristic peaks of Fe₃O₄ disappeared while new peaks appeared around 2 θ ~ 24.1°, 40.8°, 49.4°, and 54°. In addition, strengthening of the characteristic peak (2 θ ~33.1°) of α -Fe₂O₃ was observed, which confirms artifact of α -Fe₂O₃ crystallite. The diffraction peaks, centered at 2 θ ~24.1°(012), 33.1° (104), 35.6° (110), 40.8° (113), 49.3° (024), and 54° (116) may be assigned to hexagonal rhomb-centered α -Fe₂O₃ (hematite) [JCPDS File no.72-0469]. Hematite is an antiferromagnetic insulator with corundum structure in which Fe³⁺ ion are octahedrally coordinated by O²⁻ ions which are organized in hexagonal structure [10]. Above result suggests that phase and structure of iron oxide can be tailored by the thermal treatment and the direct transition from Fe₃O₄ (magnetite) to α -Fe₂O₃ (hematite) can be achieved by sintering at temperature 700°C (12h). The strong and sharp diffraction peak around 2 θ ~ 33.1° was employed to estimate mean crystallite size of α -Fe₂O₃ using Debye-Scherrer formula and found to be ~ 42 nm.

3.2. FTIR

The infrared absorption spectra of the sample provide some important information about the structural changes. Fig. 2 shows FTIR transmittance spectra (range 2500-500cm⁻¹) of the heat treated sample at temperature 700°C (3h); discrete medium peaks appeared at 695cm⁻¹. In this low frequency region of FTIR spectra, a medium peak appeared at 552 cm⁻¹ and this is indicative peak of the Fe-O stretching vibration in iron oxide. Beside, the peak centered about 635 and 694 cm⁻¹ may be assigned to α -FeOOH and β -FeOOH phase, respectively. In addition, the peak centered at 1384 cm⁻¹ can be ascribed to C-H bending vibration mode [11]. The weak band centered around 1641cm⁻¹ is due to the bending mode of H-O-H adsorbed at the Fe₃O₄ surface. When the sample was annealed at temperature 700°C (6h), no drastic change in FTIR spectra, ranging 500-695 cm⁻¹, was observed. The close look of the peak centered at 552 cm⁻¹ shows broadening in absorption line. The broadening in absorption line may be due to combination of factors such as degeneracy of vibration state, thermal broadening of lattice dispersion band and mechanical scattering from the powdered samples. Beside, the weak band at 1384 cm⁻¹ and broad bands centered around 1641cm⁻¹ completely disappeared. The disappearance of these characteristic bands is due to elimination of volatiles hydrocarbon, water molecules and leads to densification of the nanopowders. At temperature 700°C (12h), the peaks of α -FeOOH and β -FeOOH completely disappeared and a new strong peak appeared at 533 cm⁻¹ which is the characteristic peak of α -Fe₂O₃ [12]. This result confirms that the thermal annealing at temperature 700°C (12h), decomposes α -FeOOH and β -FeOOH into final α -Fe₂O₃ product. FTIR results also support the XRD data.

3.3. SEM

The morphology of iron oxide powder, synthesized by chemical technique (solgel) and revealed by SEM observation (Fig. 3), showed some difference in shape and size of the particles when samples were heated at constant temperatures and calcined for different time periods. Micrograph (a) shows the morphology of the sample calcined at 700°C (3h). The white patches in the micrograph reveal the crystallization of the samples. In this image one may also see clearly that particles have lamellar structures of irregular shapes and different size in the range 17-35 nm. Image also exhibits weak aggregation of particles, which was expected due to the technique used for the sample preparation. The weak agglomerate structure indicates development of super paramagnetic structure. When the sample was annealed at 700°C (6h), SEM image 'b' reveals marginal change in the morphology when it compared with the micrograph 'a'. Both micrographs of the particles also support the results of XRD data of the corresponding condition. Micrograph 'c' (700°C (12h)) shows sharp grain boundaries and well defined morphology. The shape of the structure is roughly spherical with size between 25 to 35 nm. Moreover, an increase in the densification in the structures may be clearly seen. The SEM data also supports the XRD data.

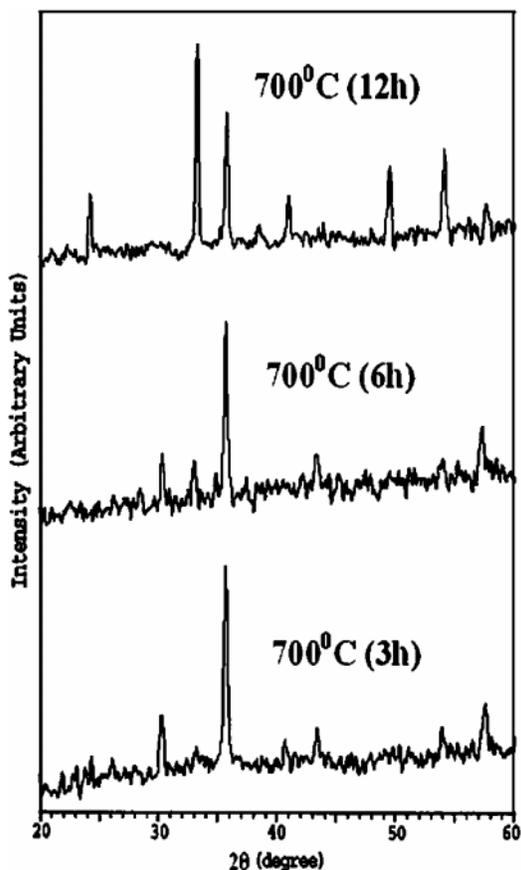


Figure 1: XRD Pattern of the Iron Oxide Powder Sample Annealed at 700°C (3h), 700°C (6h) and 700°C (12h).

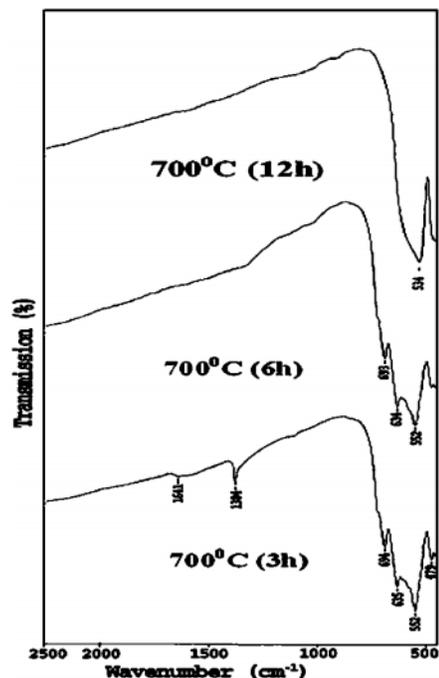


Figure 2: FTIR Spectra of Iron Oxide at Different Temperatures: 700°C (3h), 700°C (6h) and 700°C (12h).

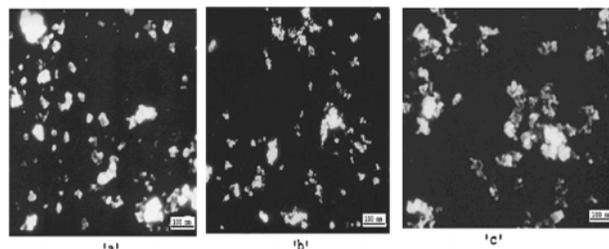


Figure 3: SEM Photograph of Iron Oxide at 700°C (3h), 700°C (6h) and 700°C (12h), Respectively.

4. CONCLUSIONS

In summary, the chemical method (solgel) has been used to successfully produce the magnetite nanoparticles. This approach provides a simple, general, and economical method for the preparation of monodisperse magnetic nanoparticles with a diameter range of 20–42 nm. We believe that these hydrophilic and biocompatible nanoparticles will have important applications not only in advanced magnetic materials and ferrofluid technology, but also in biomedical fields such as biomolecular separations, targeted drug delivery, cancer diagnosis and treatment, as well as magnetic resonance imaging.

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