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Synthesis of acicular iron oxide nanoparticles and their dispersion in a polymer matrix

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An alternative forced hydrolysis approach for the synthesis of β-FeOOH of varying dimensions was achieved. The β-FeOOH particles were converted into γ-Fe_2O_3 in a colloidal process, which eliminated the agglomeration of γ-Fe_2O_3 particles. The acicular γ-Fe_2O_3 nanoparticles could be readily dispersed into an organic solvent. Preliminary studies have demonstrated that the dispersion of the γ-Fe_2O_3 nanorods in a polymer matrix is feasible leading to an organic-inorganic nanocomposite. *© 2001 Kluwer Academic Publishers*

1. Introduction

Acicular magnetic iron oxide (γ-Fe_2O_3) nanoparticles have been prepared by three different acicular modifications of iron oxide-hydroxides (α-, β-, γ-FeOOH) [1]. Among the oxide-hydroxides, the orthorhombic α-FeOOH (synthetic goethite) has been mostly used so far for the commercial production of γ-Fe_2O_3 particles as magnetic-recording material. The transformation process involves the solid-state reaction of the dehydration and reduction of oxide-hydroxides into magnetite (Fe_3O_4) at 300–800 °C, followed by oxidation of Fe_3O_4 into γ-Fe_2O_3 at temperatures in the range of 200–350 °C. As a result of the solid-state reaction, the acicular γ-Fe_2O_3 nanoparticles are agglomerates. Mechanical energy is required to break them up by the impact and shear forces in ball mills, sand mills and kneaders. Another oxide-hydroxide modification is β-FeOOH, which can be made in well-defined needles. Recently it has been made as small as 70 nm, with an aspect ratio of 7 [2]. Here we report an alternative forced hydrolysis approach for the synthesis of β-FeOOH of varying dimensions. The β-FeOOH particles were converted into γ-Fe_2O_3 in a colloidal process, which eliminated the agglomeration of γ-Fe_2O_3 particles. The acicular γ-Fe_2O_3 nanoparticles could be readily dispersed into an organic solvent.

2. Experimental

2.1. Materials

Iron (III) chloride hexahydrate (98%, Aldrich), Tetraethoxysilane (98% Aldrich), 2-hydroxyethyl ether (99%, Acros), Poly(methyl methacrylate) ($\sim$120,000, Aldrich), $NH_3{\cdot}H_2O$ (29%, Fisher Scientific), Methyl ethyl ketone (99.5%, Aldrich), and Methyl iso-butyl ketone (J. T. Bakers, Inc.) were used as purchased. Spectra/Porr® 7 membrane was used as dialysis tubing.

2.2. Characterization

The characterization by transmission electron microscope was carried out with Philips EM 300 at 80 KeV and a JEOL 2010 analytical microscope at 200 KeV with a resolution of 2.3 Å. High resolution images and their corresponding nanobeam diffraction patterns (NBDP) were obtained with the 2010 JEOL electron microscope at Scherzer condition in order to understand some structural details in both reciprocal and real spaces. The copper grids were coated with a thin layer of amorphous carbon. X-ray photoelectron spectra (XPS) were collected on a Physical Electronics (PHI) 5300 X-ray Photoelectron Spectrometer. The surface of the magnetic γ-Fe_2O_3 nanorods was characterized by diffuse reflectance Fourier transform infrared spectrometry (DRIFTS) with a Nicolet MAGNA-IR 560 spectrometer equipped with a MCTA cryodetector.

2.3. Preparation of acicular β-FeOOH nanoparticles

A 0.37 M ferric chloride aqueous solution was prepared by dissolution of 10.0 g of $FeCl_3{\cdot}6H_2O$ into 100 ml of deionized water. The ferric chloride solution was sealed in a pressure tube, which was heated to 60 °C in an oven. Initially, the ferric chloride solution was transparent, and became cloudy after several hours of hydrolysis. Towards the end of the hydrolysis, a yellow precipitate was observed at the bottom of the pressure tube. The hydrolysis was carried out in an oven for various periods to reach different particle sizes of β-FeOOH nanoparticles.

2.4. Silica coating of β-FeOOH particles

The β-FeOOH nanoparticles were redispersed by sonication, and placed into a regenerated cellulose dialysis tubing, and immersed in 1000 ml of ethanol under magnetic stirring. The ethanol was replaced with

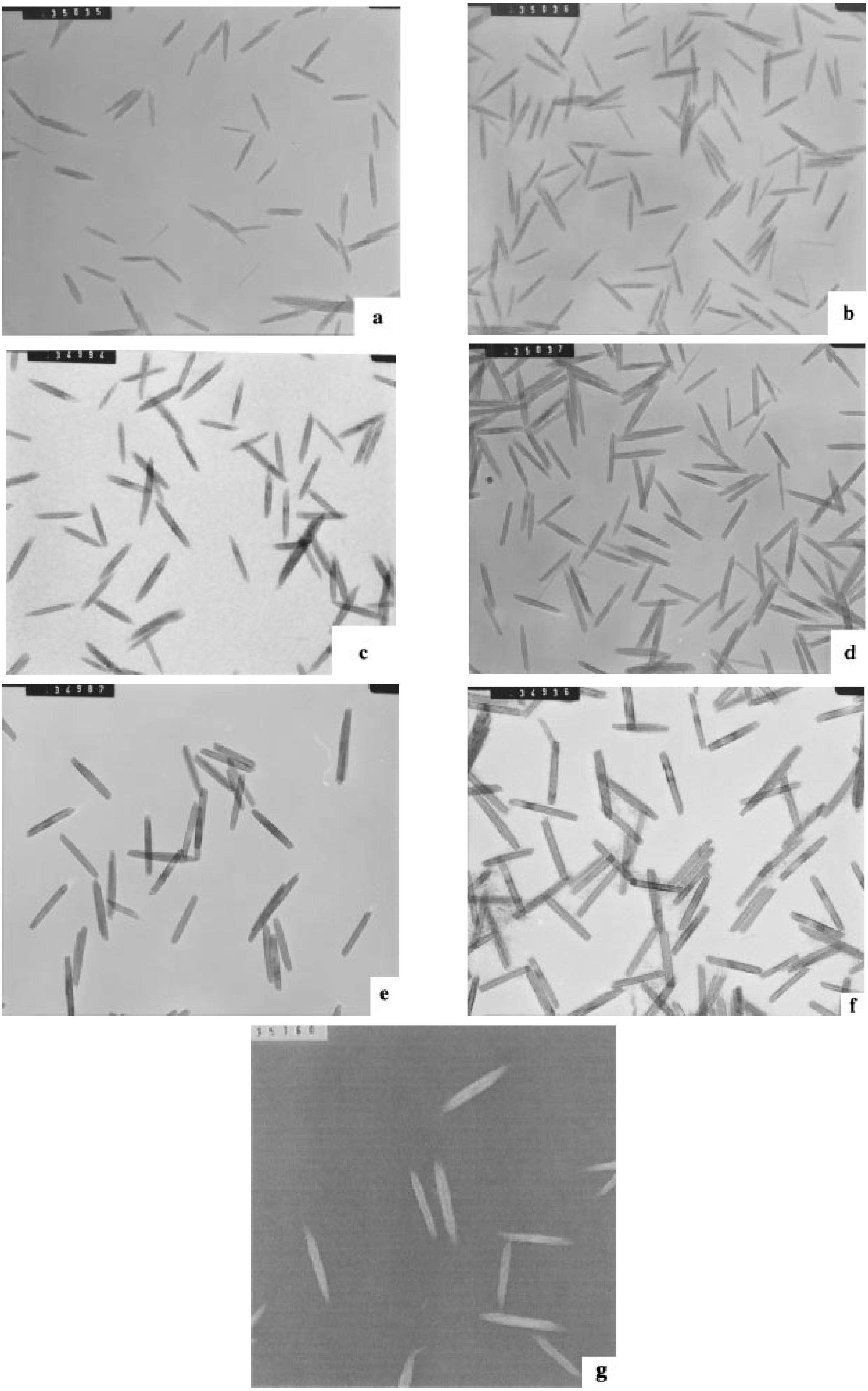


Figure 1 TEM images (X110,000) of β-FeOOH nanoparticles synthesized by various hydrolysis time, (a) 5 hours, (b) 6 hours, (c) 7 hours, (d) 8.5 hours, (e) 10 hours, (f) 16 hours, and (g) 24 hours.

fresh ethanol three times in a 3 day period. Next, the β-FeOOH product was transferred into 2000 ml of ethanol to reach a 0.05 g/L concentration, and redispersed into a colloidal solution by sonication. To the β-FeOOH ethanol dispersion was added 30 ml of 29 wt% NH_3 aqueous solution. Under mild magnetic stirring, 0.3–0.5 ml of tetraethoxysilane (TEOS) was added into the solution in small aliquots (for example, $\leq$0.1 ml) every 12 hours. In a different coating procedure, TEOS was added into the dispersion at once. At the end of the silica coating process, the silica coated β-FeOOH particles were retrieved by centrifugation at 5000 rpm, washed at least three times with ethanol, and then redispersed into a minimum amount of ethanol.

2.5. Transformation of silica-coated β-FeOOH into magnetic iron oxide nanorods

The silica coated β-FeOOH dispersion in ethanol was added into about 100 ml 2-hydroxyethyl ether to reach 0.1 g/L concentration, and redispersed by sonication. The dispersion was heated to 245 °C under mechanical stirring for 2 to 4 hours. The solution turned black when heated to 245 °C, and was cooled slowly to room temperature. The magnetic iron oxide nanorods were retrieved by centrifugation at 9000 rpm for 0.5 hour. The nanorods were washed with ethanol several times, and redispersed into ethanol.

2.6. Dispersion of acicular iron oxide particles in polymer (PMMA) matrix

Poly(methyl methacrylate), 0.6 g, was dissolved in 9.4 g of methyl ethyl ketone and methyl isobutyl ketone mixture (3 : 1) by overnight sonication. The PMMA concentration was 6 wt %. One half of the as-prepared acicular magnetic iron oxide nanorod ethanol dispersion (containing ~0.005 g nanorods) was centrifuged, and the supernatant was decanted. To the nanorods was added 8.3 g of 6 wt % PMMA solution, and the mixture was sonicated for several hours in an ice-water cooling bath. The concentration of the magnetic nanorods was about 1 wt % relative to the PMMA. The acicular iron oxide particle dispersion in PMMA solution was dip coated on a microscope cover glass (1″ × 1″). Solvent evaporation resulted in the polymer matrix solidification.

3. Results and discussion

The acicular β-FeOOH nanorod precipitates at the bottom of the pressure tube were readily redispersed by sonication. The dimensions of acicular β-FeOOH particles prepared by forced hydrolysis [3] were dependent on the hydrolysis time (Fig. 1). The longer the hydrolysis time, the larger the particle sizes of β-FeOOH nanoparticles as shown in Table I. The smallest particle dimension of β-FeOOH by this method was 72 nm in length and 10 nm in diameter, which was obtained by 5 hour hydrolysis at 60 °C. When the hydrolysis time was less than 5 hours, the β-FeOOH particles were thin and fragile (Fig. 2), and they tended to fragment into pieces under strong sonication for redispersion.

TABLE I The dependence of β-FeOOH nanoparticles upon the hydrolysis time

No.	Hydrolysis time (hours)	Length (nm)*	Diameter (nm)*
1	5	72	10
2	6	82	12
3	7	90	15
4	8.5	98	18
5	10	110	20
6	16	125	20
7	24	200	22

*Determined by Philips EM 300 at 80 keV and ×110,000 magnification.

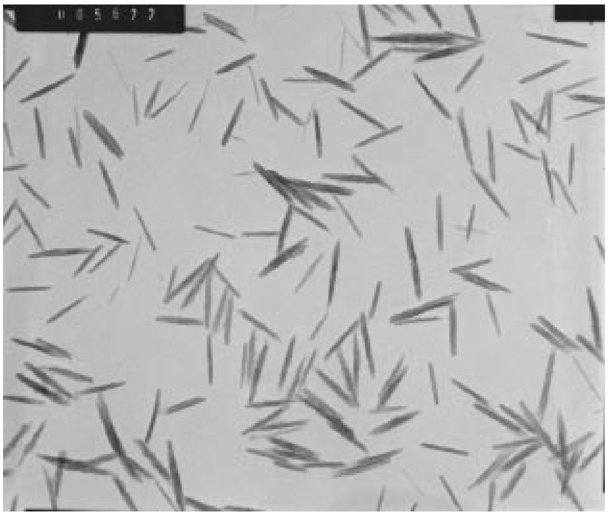
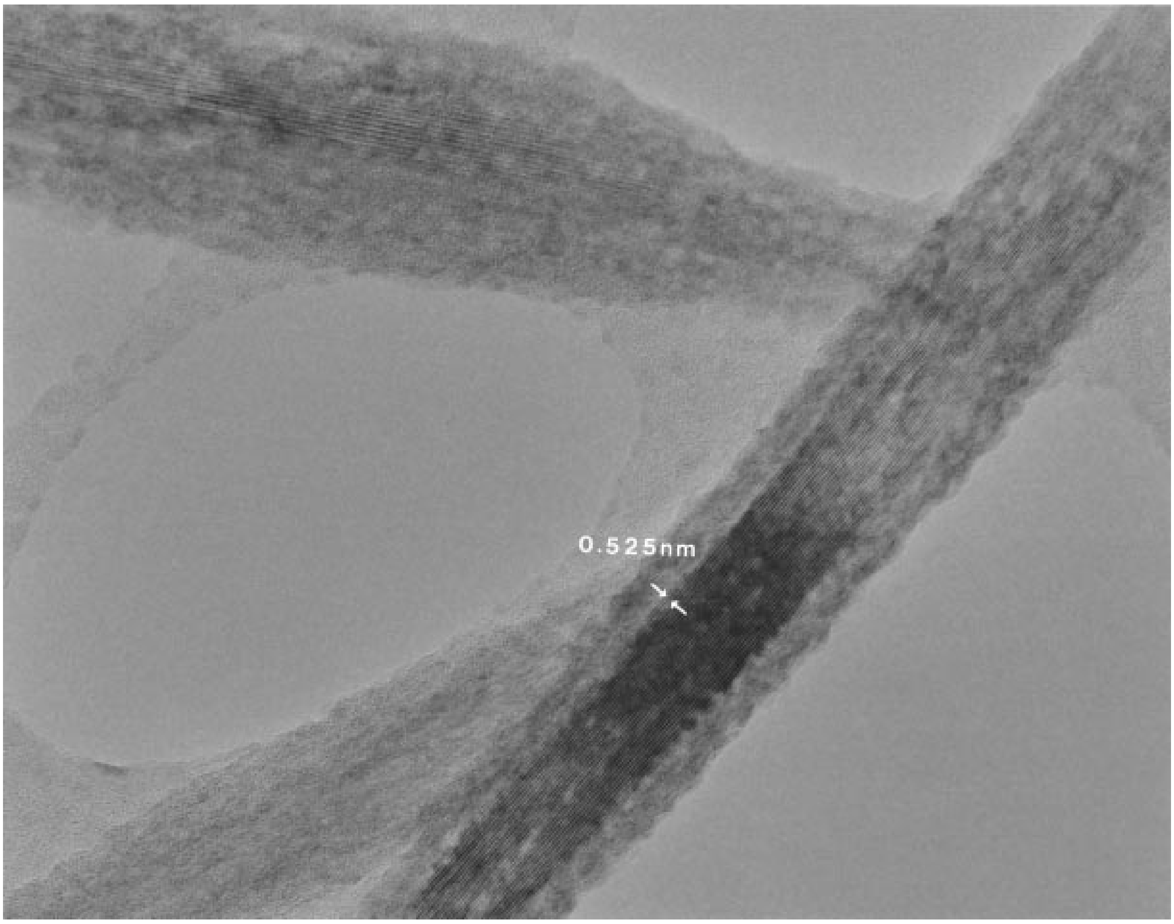


Figure 2 TEM images (X110,000) of β-FeOOH nanoparticles synthesized by 4 hour hydrolysis.

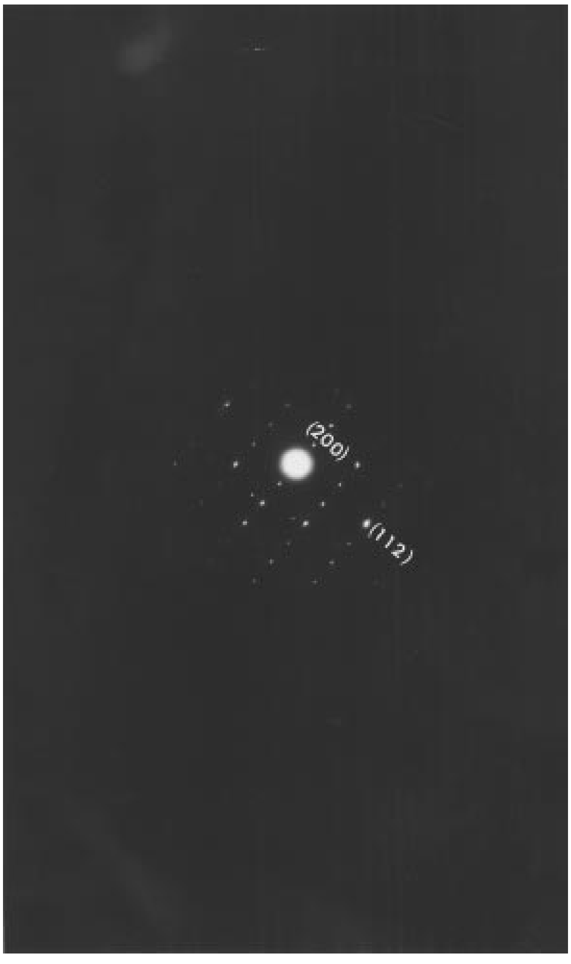
Fig. 3a shows a high resolution image from a β-FeOOH nanorod and its corresponding nanobeam diffraction pattern (NDBP) as shown in Fig. 3b. The fibers are observed from the direction perpendicular to the fiber axis(texture axis), therefore the 5.25 Å lattice fringes shown in Fig. 3a correspond to the [200] reflection in the NBDP reported for β-FeOOH. The length of the rods was assessed by HRTEM to be between 100 to 300 nm with a 30–50 nm width.

The β-FeOOH nanorods collapsed into spherical iron oxide particles (α-Fe_2O_3) when heated to higher temperature [4]. To retain their acicular particle morphology, these β-FeOOH particles were coated with an enforcing layer. The Stöber method is commonly used for coating SiO_2 onto nanoparticles [5], and it is carried out in ethanol reaction media. Therefore, the aqueous dispersion of β-FeOOH had to be changed into a dispersion in alcohol by solvent exchange. A dialysis procedure was used successfully to change the dispersion solvent from water to ethanol without causing any agglomeration. A direct dilution of aqueous dispersion of β-FeOOH into ethanol solvent gave rise to severe agglomeration of β-FeOOH particles (Fig. 4).

To reach a uniform layer of SiO_2 coating onto β-FeOOH acicular nanoparticles, small aliquots of TEOS were added into the dilute dispersion of β-FeOOH



(a)



(b)

Figure 3 (a) HRTEM micrograph of β-FeOOH nanorods. (b) NBDP of the β-FeOOH nanorod.

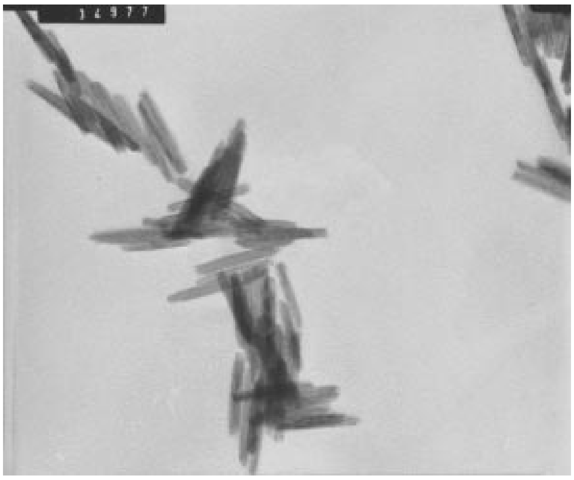


Figure 4 The agglomerated β-FeOOH nanoparticles when the aqueous dispersion was transferred into alcohol dispersion by simple dilution, magnification number = 110,000.

every 12 hours under magnetic stirring. The thickness of SiO_2 coating was controlled by the total amount of TEOS added into the reaction. When TEOS was added into the dispersion in excess amount in each aliquot (0.15 and 0.5 ml), SiO_2 self-nucleation and rough coating onto β-FeOOH nanoparticles occurred (Fig. 5).

It is possible to see in Fig. 6a that the β-FeOOH rods have been coated with silica in order to force the nanorods to maintain their shape through a higher temperature treatment. In this case, the silica formed a non-porous coating around the nanorods. Untill this point, no phase transformation occurred, as can be seen in the corresponding NBDP (Fig. 6b). The nanorods were stable under the electron beam.

The β-FeOOH phase is antiferromagnetic, and can be converted into the ferrimagnetic γ-Fe_2O_3 phase inside the SiO_2 matrix, when heated slowly up to 245–260 °C in an inert atmosphere and followed by exposure to hydrogen [6]. With a modification of lit. procedure [6], the SiO_2 coated β-FeOOH nanorods were transformed into SiO_2 coated γ-Fe_2O_3 nanorods (Fig. 7) in a colloidal solution of 2-hydroxyethyl ether solvent. The temperature of the solution was raised up to 245 °C for 2–4 hours under vigorous mechanical stirring. When the temperature of the colloidal solution was heated to as high as 245 °C, esterification of surface silanol groups (-SiOH) occurs forming ester groups (SiOR) on the surface of the nanorods [7].

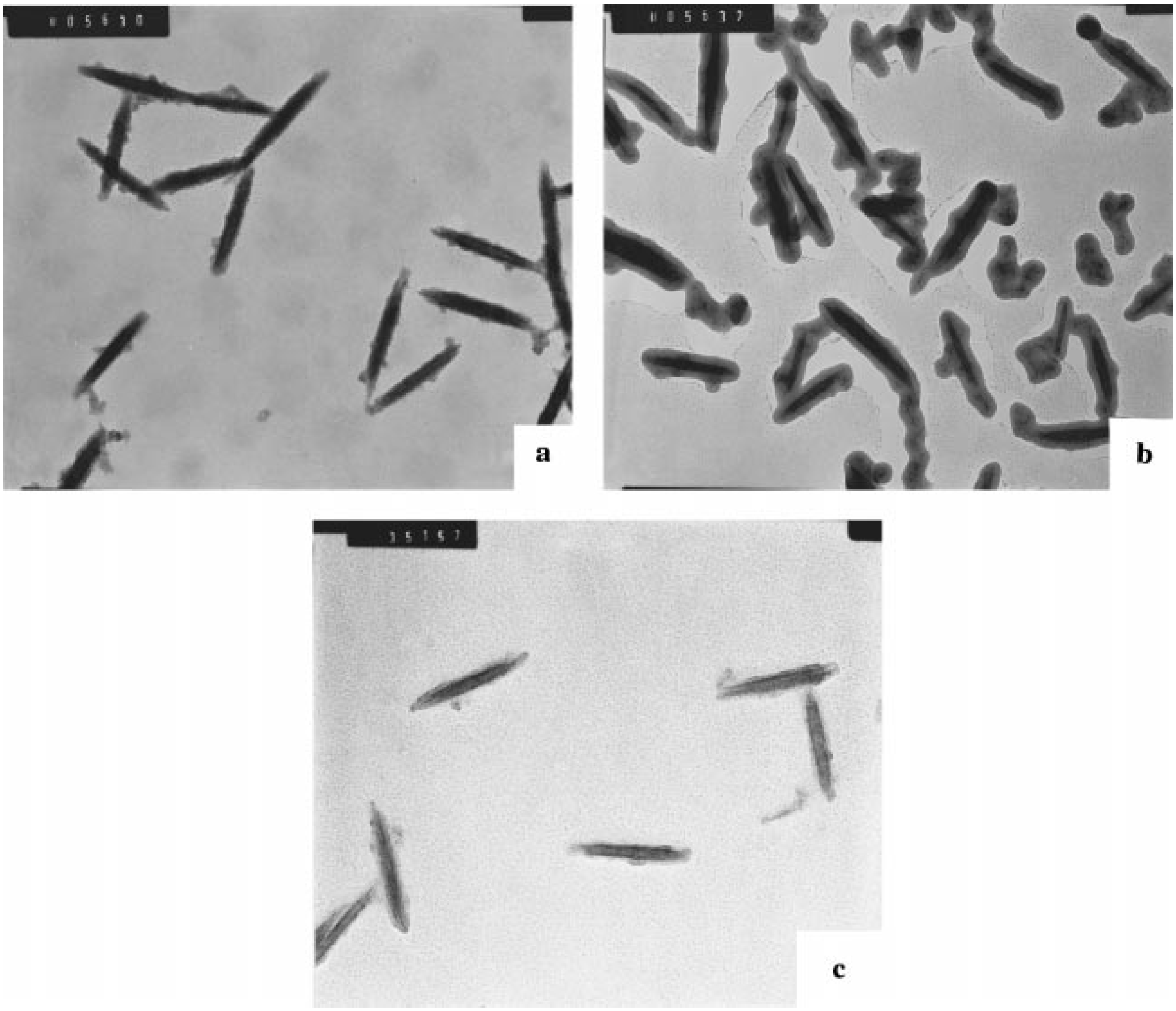
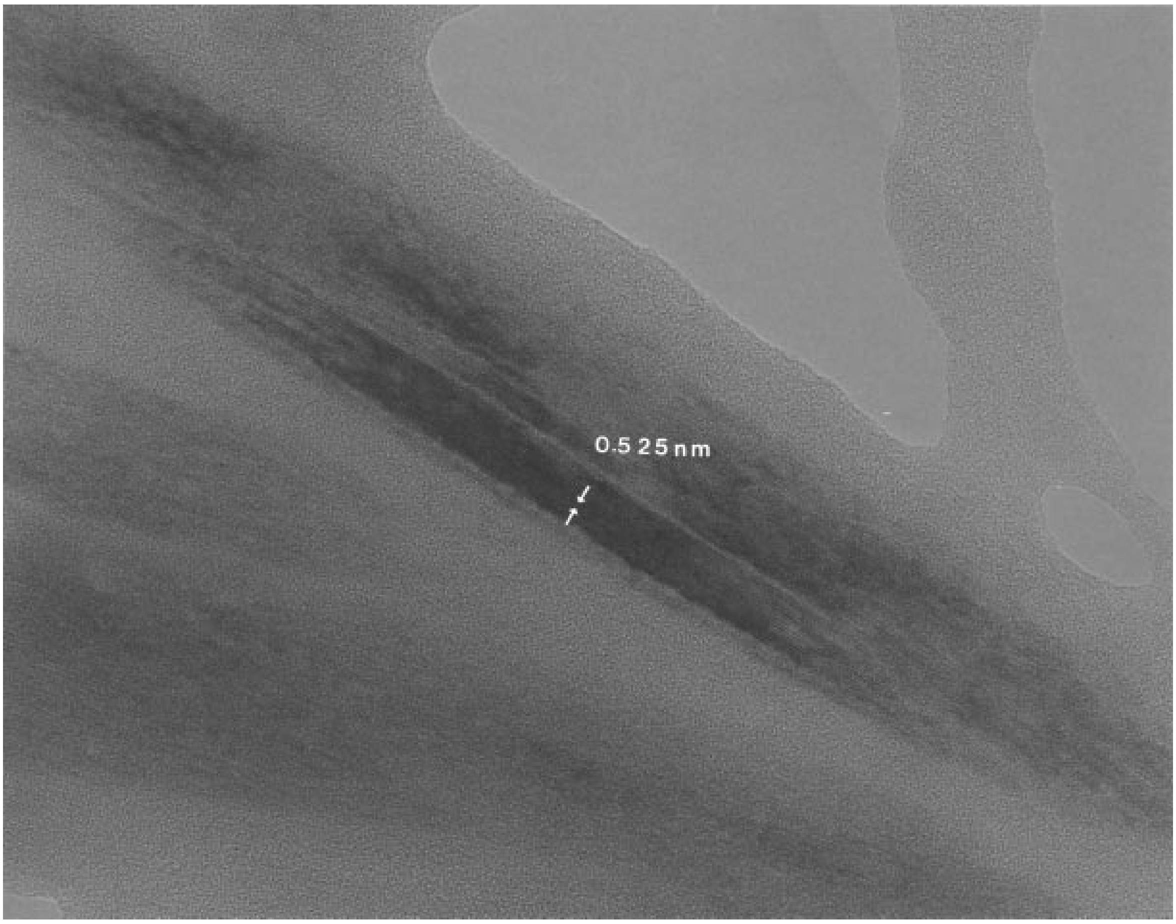
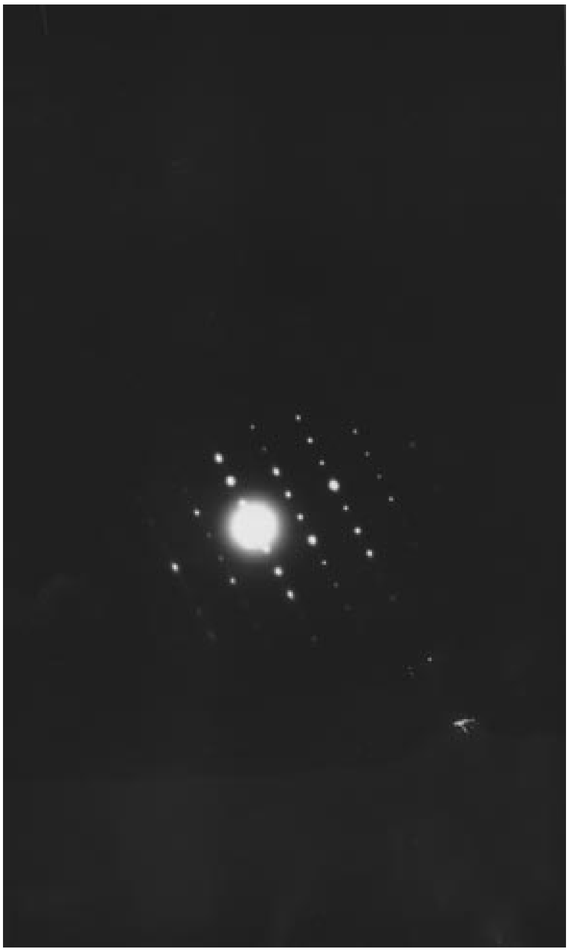


Figure 5 The SiO_2 thin layer coating onto β-FeOOH nanoparticles. (a) 0.15 ml TEOS added at once. (b) 0.5 ml TEOS added at once. (c) 0.3 ml TEOS added at three aliquots.



(a)



(b)

Figure 6 (a) HRTEM of β-FeOOH nanorod coated with SiO_2. (b) The corresponding NBDP.

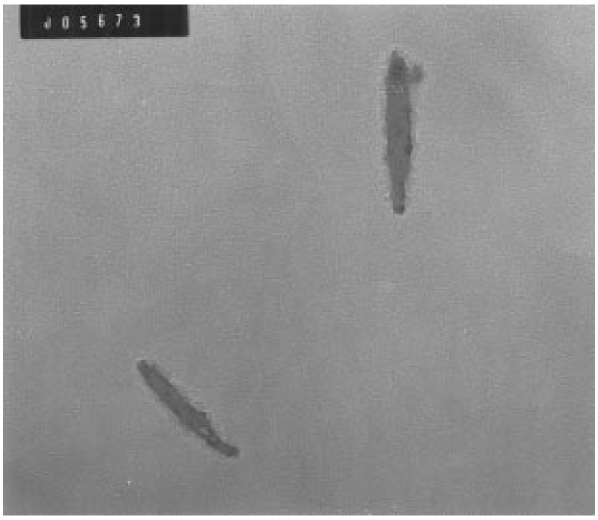


Figure 7 TEM image of magnetic SiO_2 coated γ-Fe_2O_3 nanoparticles converted from the β-FeOOH of 24 hour hydrolysis, magnification number = 125,000.

$$\gamma\text{-}Fe_2O_3\text{-}\overset{|}{\underset{|}{Si}}\text{-}OH + HOCH_2CH_2OCH_2CH_2OH$$

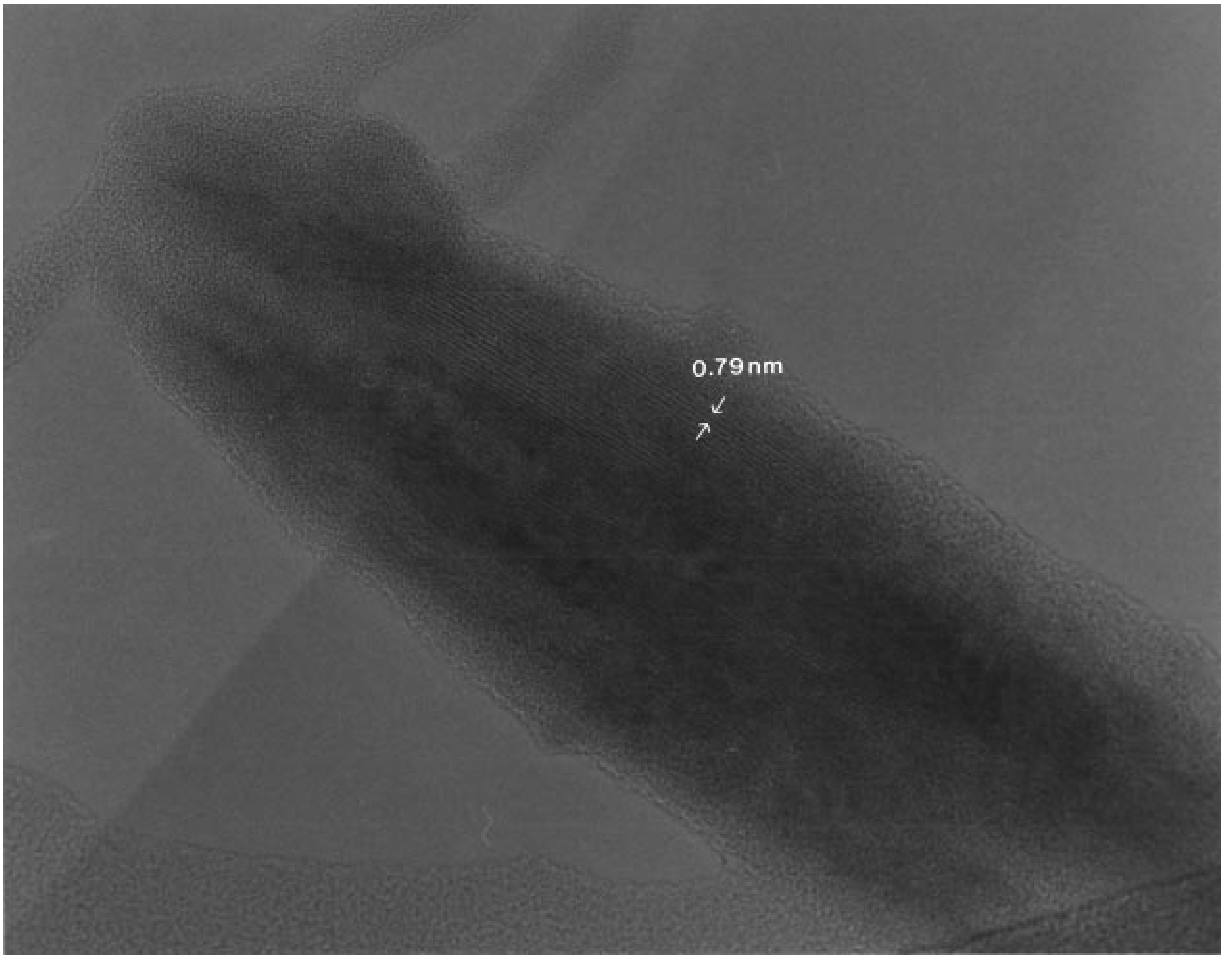
$$\rightarrow \gamma\text{-}Fe_2O_3\text{-}\overset{|}{\underset{|}{Si}}\text{-}OCH_2CH_2OCH_2CH_2OH$$

After the temperature treatment, β-FeOOH nanorods underwent a phase change transformation into γ-Fe_2O_3 nanorods. This was confirmed by electron diffraction studies. Fig. 8a is a high resolution view of a γ-Fe_2O_3 nanorod and 8b corresponds to a [101] reflection reported for the γ-Fe_2O_3 phase. This agrees with the corresponding diffraction pattern.

Fig. 9 shows another view of the γ-Fe_2O_3 nanorods. It is possible to see that the γ-Fe_2O_3 nanorods tend to bend during the phase transformation and the porosity of the silica increases but maintains the rod shape during the process. The bending is attributed to thermal stresses induced by the differing coefficients of thermal expansion of the constituent phases of the nanorods. Futhermore, a longer period of heat treatment was not favorable for the formation of γ-Fe_2O_3 nanorods, even with a thicker silica coating. This is shown in Fig. 10. In this case the nanorods were very unstable under the electron beam.

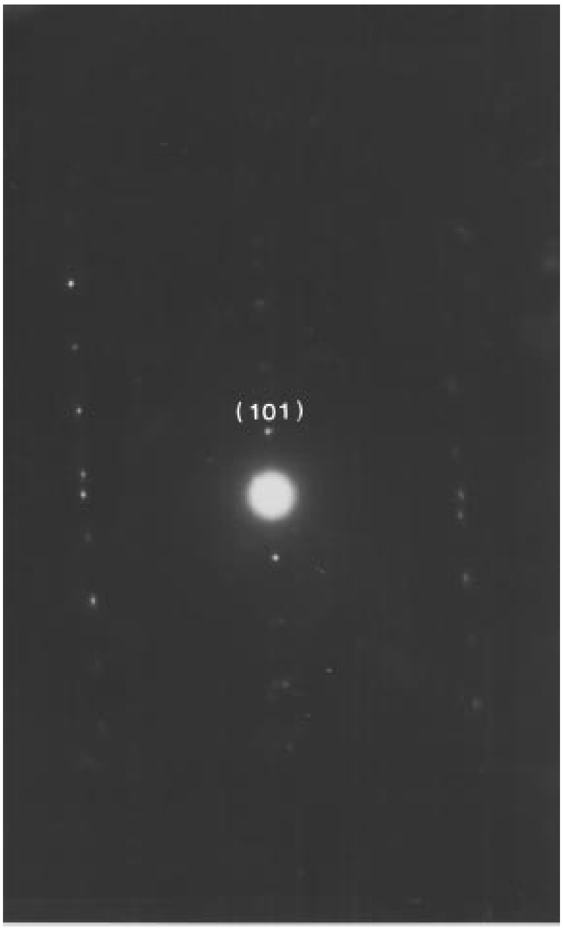
The DRIFTS spectra of the magnetic nanorods indicate the grafting of 2-hydroxyethyl ether molecules onto the surface of β-FeOOH particles (Fig. 11). The XPS analysis of the magnetic nanorods showed a strong increment of the carbon peak corresponding to the C-O-C, and -C-OH groups in comparison to the silica coated nanorods prior to the conversion (Fig. 12).

The silica coated γ-Fe_2O_3 nanorods could be well dispersed in a solution of PMMA in MEK/MIBK (3 : 1). Fig. 13a and b shows these dispersions without and with the presence of a magnetic field. Further studies



(a)

Figure 8 (a) HRTEM of a γ-Fe_2O_3 nanorod (b) NBED of the γ-Fe_2O_3. (*Continued*).



(b)

Figure 8 (*Continued*).

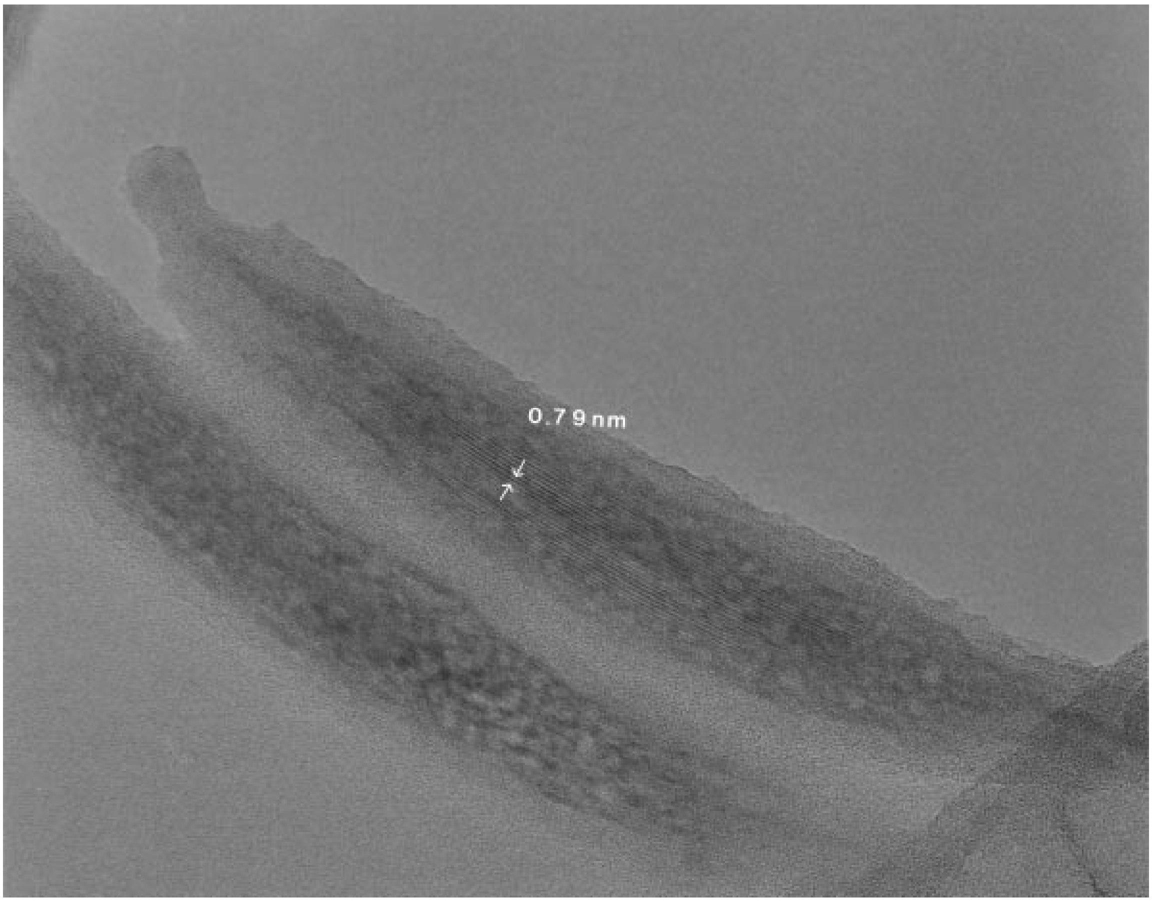


Figure 9 γ-Fe_2O_3 nanorods tend to bend after annealing treatment. The high temperature treatment also increases the porosity of the silica coating.

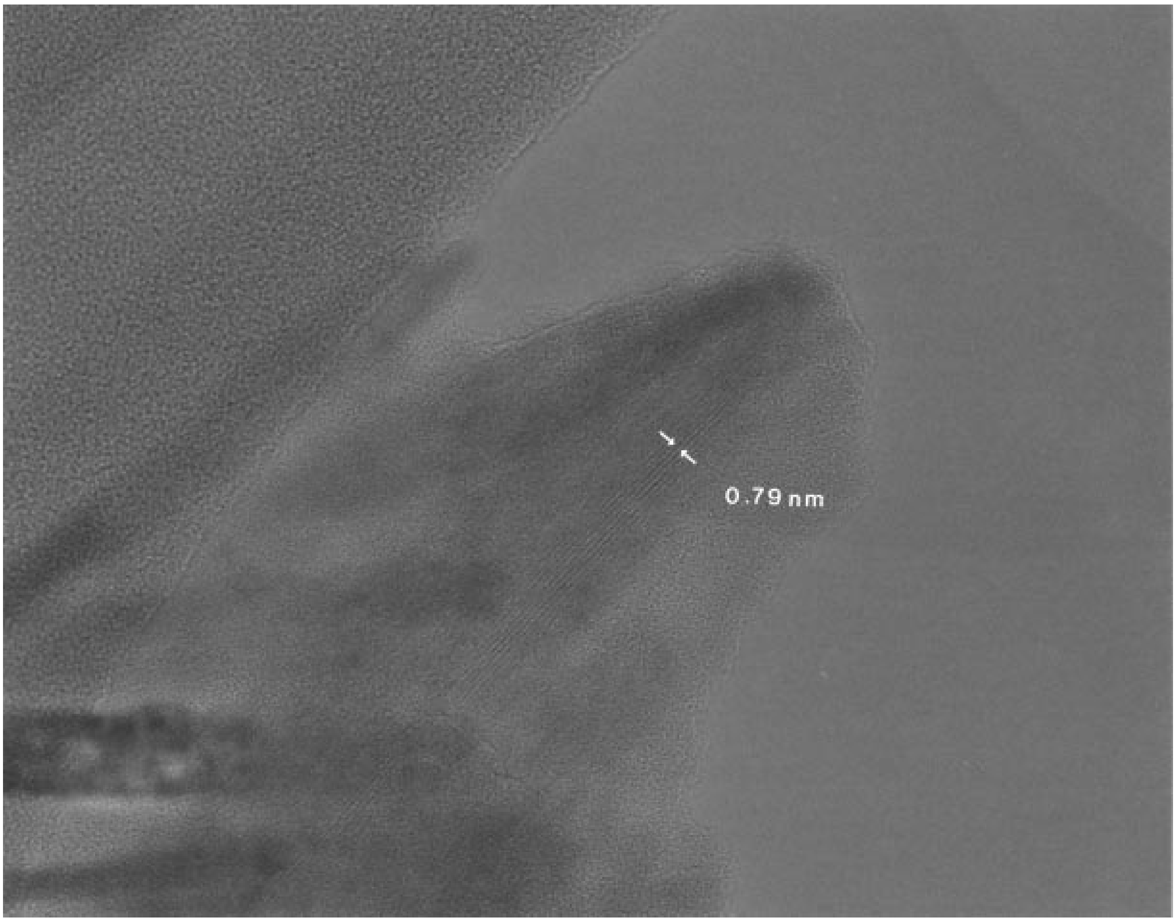


Figure 10 γ-Fe$_2$O$_3$ nanrod from a sample with a longer annealing time and thicker silica coating. Most of the γ-Fe$_2$O$_3$ nanorods were amorphous and highly unstable under the electron beam.

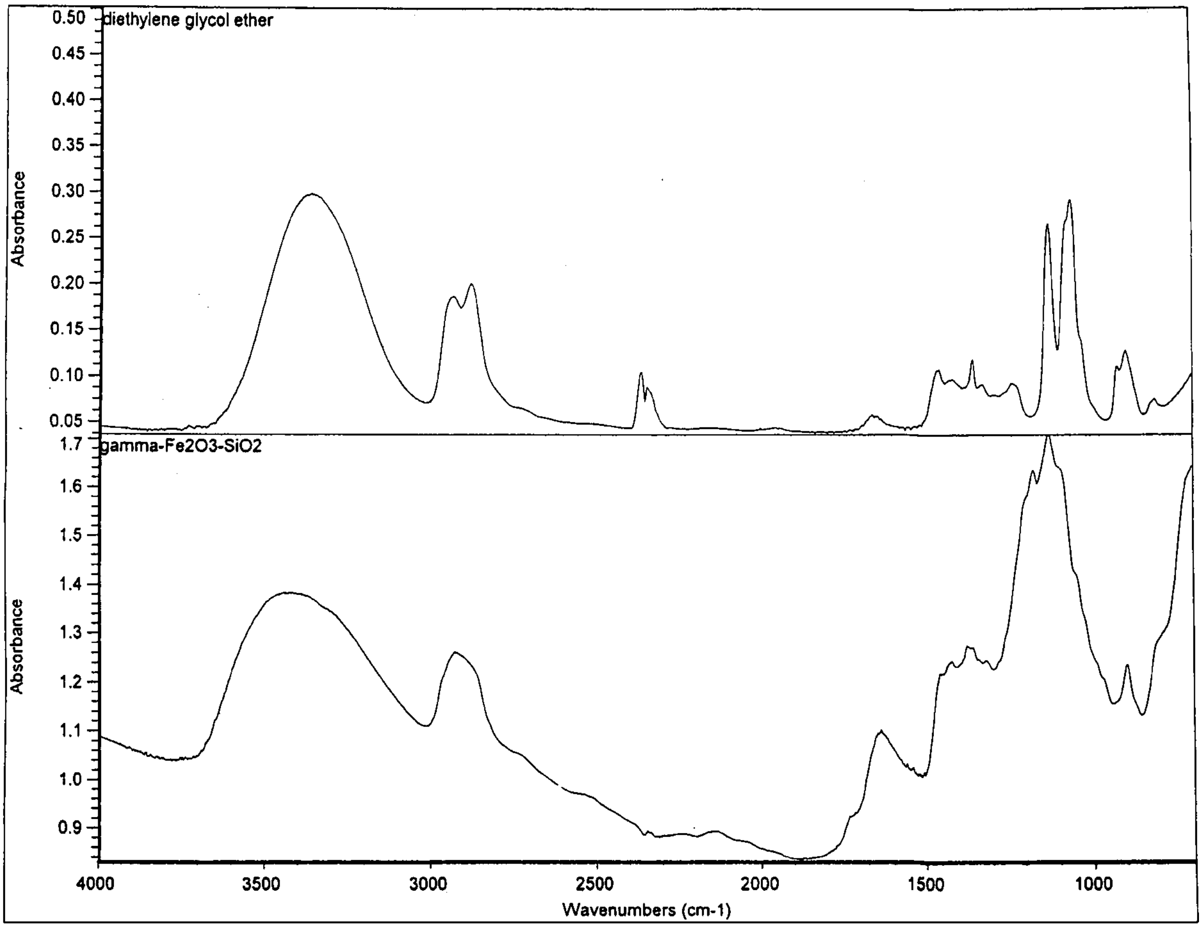


Figure 11 The comparison of DRIFTS spectra between pure 2-hydroxyethyl ether (top) and magnetic SiO$_2$ coated γ-Fe$_2$O$_3$ nanoparticles (bottom).

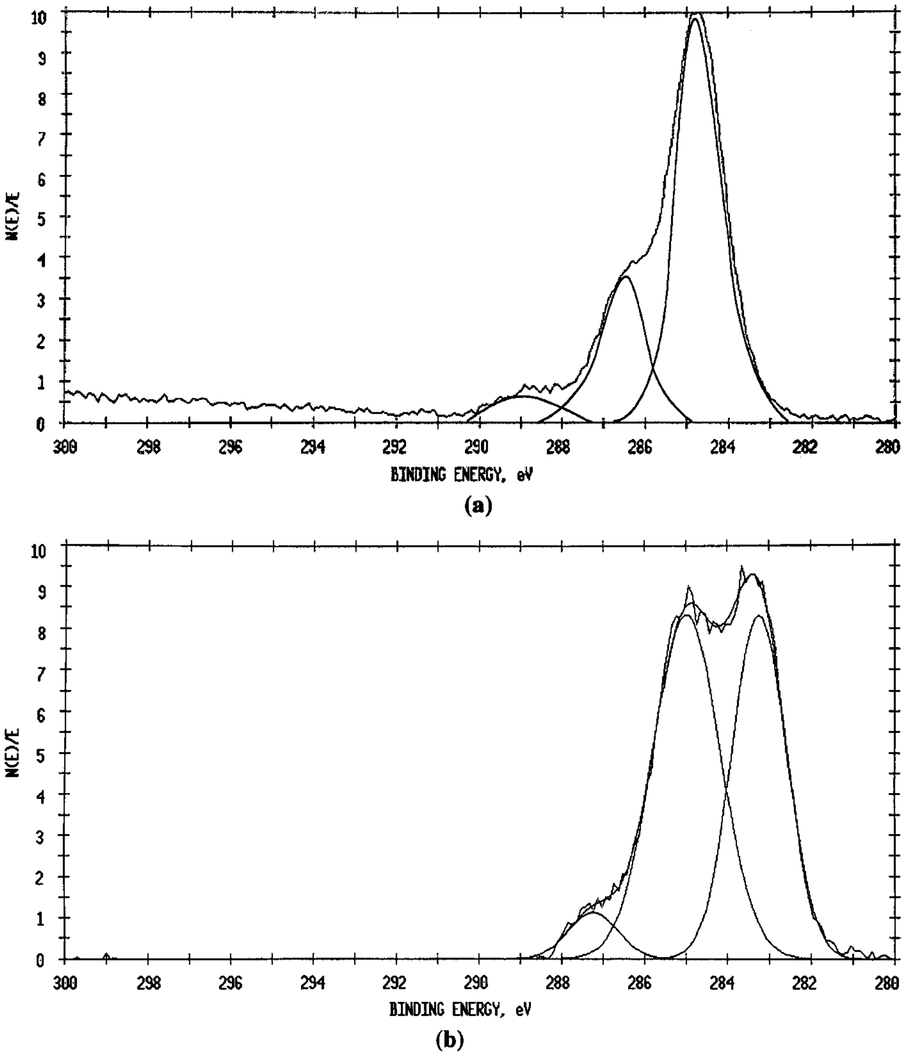
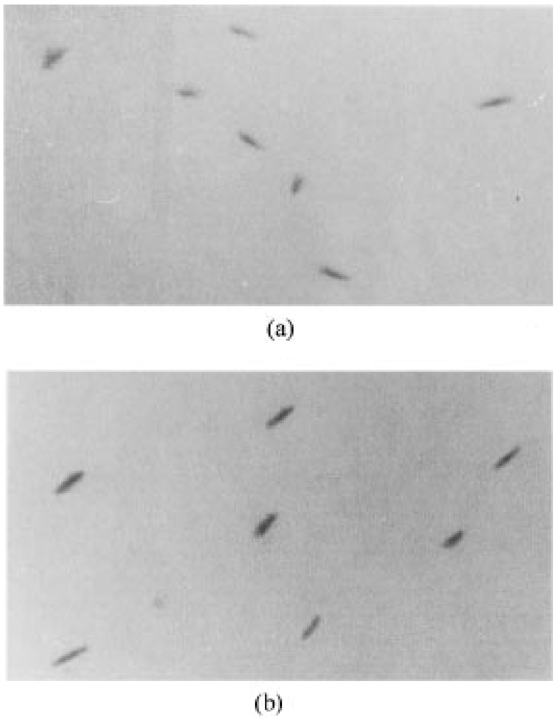


Figure 12 The comparison of XPS spectra between SiO_2 coated β-FeOOH nanoparticles and magnetic SiO_2 coated γ-Fe_2O_3 nanoparticles. The conversion process resulted in significant increment of the middle peak corresponding to C-O-C and C-OH groups.


(a)

(b)

Figure 13 TEM images (X25,000) of dispersions of magnetic SiO_2 coated γ-Fe_2O_3 nanoparticles prepared from β-FeOOH of 5 hours hydrolysis (a) without a magnetic field, and (b) in a magnetic field (2–12 kOe).

regarding the alignment of these nanorods will be reported later.

4. Conclusion

Acicular β-FeOOH nanoparticles of various dimensions, as small as 70 nm and aspect ratio of 7, have been synthesized by forced hydrolysis. The particle size of β-FeOOH can be controlled by the hydrolysis time. An aqueous dispersion of β-FeOOH was successfully transformed into an alcohol dispersion by dialysis, and by the Stöber method, a thin layer of SiO_2 was coated onto β-FeOOH particles. The SiO_2 coated β-FeOOH particles were converted into magnetic γ-Fe_2O_3 by a colloidal process, which avoids agglomeration of nanoparticles. The γ-Fe_2O_3 nanorods were readily dispersed into an organic solvent, as well as in PMMA resulting in a polymer nanocomposite.

The magnetic characterization of the nanorods is under investigation, as well as the instability of the higher temperature treated nanorods under the electron beam.

Acknowledgments

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