Fe–EBT Chelate Complex: A Novel Mean for Growth of α -FeOOH and γ -Fe₂O₃ Nanostructures

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Abstract Acicular goethite (α -FeOOH) and worm-like maghamite (γ -Fe₂O₃) nanostructures have been prepared adopting a novel route, using Na₂[Fe(HL)₂(H₂O)₂] chelate complex in alkaline medium. It is found that concentration of hydrated Fe(III) ions increased with increasing temperature, which later play a key role in generation of different phases of iron oxide. Phase and morphology of the products are investigated using XRD, FTIR, SEM, and TEM analysis. Using UV–Vis spectra, various electronic transitions of goethite and maghamite particles are examined. Maghamite nanostructures exhibit superparamagnetic property at room temperature. On the basis of experimental observations and analytical data, growth mechanism of the nanostructures is discussed.

KEY WORDS: Iron oxide; Nanostructures; Chemical synthesis; Growth mechanism; Magnetic properties

1 Introduction

Magnetic iron oxide nanostructures have drawn enough attention in the recent years because of their tremendous properties and potential applications in the field of magnetic recording, catalysis, sorption, lithium-ion batteries and sensors [1–5]. Among the four important crystalline polymorphs of ferric oxides, such as α , β , γ and ϵ -Fe₂O₃, the cubic, spinel-structured γ -Fe₂O₃ (maghamite) has paid special interest in biomedical field, and it has successfully been used in magnetic resonance imaging, drug delivery and therapy [6, 7]. The nontoxic, chemically stable and physiologically acceptable γ -Fe₂O₃ nanoparticles, having compatible size with biomolecules, like protein, antibody, biotin and DNA, have tremendous applications in diagnosis and target drug delivery [8, 9]. Typically in the size range

of <20 nm, due to finite-size effect and high surface/volume ratio [10], each maghamite nanoparticle behaves as a single magnetic entity and shows superparamagnetic behaviour. The nanoparticle as single magnetic entity behaves as a giant paramagnetic atom having a large magnetic moment, and thus has a great ability to absorb energy from the magnetic fields [11, 12]. Goethite (α -FeOOH) is thermodynamically stable iron oxide material, which is commonly found in soils [13]. It is used as electrode material [14] and for removing both organic dyes and heavy metal ions from the effluent water [15, 16].

Most commonly, iron oxide nanostructures have been prepared by precipitation of Fe²⁺/Fe³⁺ salts in aqueous medium. The morphology and phase of the products have been controlled by solution pH, precursor's concentration, temperature, stabilizers and counter ions. In order to improve size distribution and quality of the products, organic-phase synthetic routes have also been claimed and developed [17]. However, in view of toxicity concern of the organic-phase synthesis, aqueous-phase synthetic processes are preferable, especially for biomedical applications.

On hydrolysing Fe²⁺/Fe³⁺ ions, generally goethite (α -FeOOH), alkegenite (β -FeOOH), lepidocrocite (γ -FeOOH)

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or ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$) precipitated initially, which converted to magnetite (Fe_3O_4) and ferric oxides (usually α and γ) upon heat treatment [18–21]. Recently Maiti et al. [22] reported the formation of rod-shaped α - FeOOH and spherical γ - Fe_2O_3 by controlled addition of hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$).

It is generally observed that, during hydrolysis of the iron salts, the rate of reaction is too rapid to control the crystal growth, because then the metal ions are readily available, therefore it is difficult to monitor the phase evolution of the products. In this sense, the use of metal complex as metal source may be beneficial, since it provides $\text{Fe}^{2+}/\text{Fe}^{3+}$ in controlled manner during the course of reaction. Oaki et al. [18] reported the chelation-mediated synthesis of iron oxyhydroxide nanostructures using EDTA as chelating ligand. Xiong et al. [23], prepared aligned β - FeOOH nanowires using $[\text{Fe}(\text{phen})_3]^{2+}$, wherein the orientation of chelate complex governed the evolution of nanowires.

Herein, in the present study, α - FeOOH and γ - Fe_2O_3 nanostructures have been prepared using Fe–EBT chelate complex as metal source in alkaline medium, and the effect of chelation and temperature on phase and morphology of the products have been investigated.

2 Experimental

2.1 Materials

All the chemicals used in this investigation were analytical grade. Ferrous sulphate pentahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), sodium hydroxide (NaOH), and eriochrome black T (NaH_2L) were purchased from Fischer Scientific. Double distilled water and ethanol were used as solvents. Ethanol was purified by distillation while eriochrome black T was purified by a method described in an earlier report [24].

2.2 Synthesis

In a typical process, iron oxide nanostructures were prepared adopting a novel synthetic route. Firstly, water soluble $\text{Fe}(\text{II})$ –EBT complex, with structural formula $\text{Na}_2[\text{Fe}(\text{HL})_2(\text{H}_2\text{O})_2]$ has been synthesised according to our previously reported method [25]. In the second step, iron oxide nanostructures were prepared using alkaline $\text{Fe}(\text{II})$ –EBT complex as $\text{Fe}(\text{II})$ source. An aqueous solution of metal complex (4 mmol; 4.06 g of $\text{Na}_2[\text{Fe}(\text{HL})_2(\text{H}_2\text{O})_2]$, dissolved in 40 mL double distilled water) was prepared, and it was made alkaline (pH 10) by adding an appropriate amount of 10^{-3} mol/L NaOH solution. The reaction mixture was refluxed for 1 h, in continuous supply of water cooling, to maintain temperature at 80 °C. During heating, the colour of the reaction mixture turned blue, indicating

Fig. 1 XRD patterns of as-prepared α - FeOOH **a** and γ - Fe_2O_3 **b** nanostructures

release of HL^{2-} in the reaction mixture. After 1 h, the solution was cooled naturally to room temperature, ultra-centrifuged, washed initially three times with double distilled water to remove water-soluble ions, and finally with ethanol to remove the organic impurities. Orange-brown product, so produced, was dried at 60 °C.

In order to observe the effect of reaction temperature on the phase and morphology of the products, the above reaction was performed at 120 °C while keeping other reaction parameters the same. Except for the colour of the end product (which is reddish-brown), the other observations of the reaction (at 120 °C) were the same, as were at 80 °C.

2.3 Characterization

X-ray powder diffraction (XRD) pattern of the products were recorded with Panalytical's X'Pert Pro X-ray diffractometer in 2θ range from 20° to 80° using $\text{CuK}\alpha$ radiation in step sizes of 0.02° ($d = 0.1541$ nm). Size and morphologies of the samples were observed by TEM (H-7500, Hitachi) and SEM (Quanta 400 ESEM from FEI Company) instruments. The FTIR spectra were recorded on Perkin-Elmer Spectrum RXI. UV–Vis spectral analysis was carried out using UV-2450 (Shimadzu) spectrophotometer. Magnetic property of maghemite sample was studied at room temperature using a physical property measurement system (PPMS, Quantum Design, USA).

3 Results and Discussion

Crystal structure and phase of the above-prepared samples were observed by XRD measurement. All the lines in the XRD pattern of orange-brown material, synthesised at 80 °C for 1 h of reaction time (Fig. 1a), are consistent with

Fig. 2 FTIR spectra of **a** α -FeOOH and γ -Fe₂O₃ materials; **b** magnified view of FTIR spectra

Fig. 3 **a, b** SEM images of as-prepared α -FeOOH; **c–e** TEM images of as-prepared α -FeOOH nanostructures

those of bulk α -FeOOH (JCPDS card No. 29-0713). No other peaks could be detected in the XRD pattern, indicating that the above material is pure orthorhombic goethite phase, with lattice constants $a = 0.4607$ nm, $b = 0.0954$ nm and $c = 0.3022$ nm. Furthermore, the

product is well crystalline, as evidenced by sharp and intense peaks.

The diffraction pattern of the as-synthesised reddish-brown material obtained at 120 °C is shown in Fig. 1b. All the diffraction peaks of the above sample match very well

Fig. 4 **a** SEM image of as-prepared $\gamma\text{-Fe}_2\text{O}_3$; **b–d** TEM images of as-prepared $\gamma\text{-Fe}_2\text{O}_3$ nanostructures

with those of maghemite (JCPDS card No. 39-1346), suggesting that the above sample is pure crystalline cubic $\gamma\text{-Fe}_2\text{O}_3$ with lattice parameter $a = 0.836$ nm. The sizes of crystallites formed in the above two reactions were calculated using Scherrer's formula [26], which is found to be 8 and 17 nm for $\alpha\text{-FeOOH}$ and $\gamma\text{-Fe}_2\text{O}_3$, respectively.

Since maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4) have the similar diffraction patterns, it is difficult to predict the formation of maghemite merely by XRD patterns. The claim for the formation of maghemite has been verified by experimental conditions and FTIR data. Since in the alkaline medium, Fe^{2+} is unstable, therefore the formation of magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$) is ruled out. FTIR spectra of the above-prepared $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ nanostructures are shown in Fig. 2a. Three low frequency bands at 580, 610 and 651 cm^{-1} have been observed in the FTIR (Fig. 2a). It is known that only one peak is observed in the FTIR spectra of Fe_3O_4 between 500 and 700 cm^{-1} , while in case of $\gamma\text{-Fe}_2\text{O}_3$, two to three peaks are observed in this region, suggesting the above product is $\gamma\text{-Fe}_2\text{O}_3$ [27]. In case of $\alpha\text{-FeOOH}$ (Fig. 2b), three characteristic bands appeared in the low frequency region, at 444, 578 and 646 cm^{-1} due to

Fe–O stretching [28]. Besides these, the bands at 790 and 895 cm^{-1} are attributed to δ_{OH} in-plane bending and δ_{OH} out-plane bending of $\alpha\text{-FeOOH}$ [29, 30]. The other peaks between 3,350–3,370 cm^{-1} , 1,630–1,644 cm^{-1} , 1,450–1,470 cm^{-1} and 1,100–1,150 cm^{-1} in the FTIR spectra of $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ may be due to –OH, CO, N=N and –SO_3^- groups [31] of some adsorbed EBT.

The morphology and size of the as-synthesised nanostructures were studied by SEM and TEM analysis. Figures 3a and b represent the SEM images of $\alpha\text{-FeOOH}$ nanostructures, formed by hydrolysing $\text{Na}_2[\text{Fe}(\text{HL})_2(\text{H}_2\text{O})_2]$ complex in alkaline medium (pH 10) at 80 °C for 1 h. In the SEM images, 9–15 nm wide, ~300 nm-long needle-like structures are observed. Although there is large variation in width and length, the tips of $\alpha\text{-FeOOH}$ nanostructures are uniformly sharp. Corresponding TEM images (Fig. 3c–e) reveal the formation of acicular $\alpha\text{-FeOOH}$ nanostructures. Keeping other reaction parameters same, when reaction was performed at higher temperature 120 °C, surprisingly 10–30 nm diameter, worm-like $\gamma\text{-Fe}_2\text{O}_3$ structures are observed in the SEM image (Fig. 4a); however, in the TEM images, (Fig. 4b–d), it is found that there is a large variation

Fig. 5 UV-Vis absorption spectra of as-synthesised α -FeOOH and γ -Fe₂O₃ materials

in diameter. The structures are terminated in the form of hexagonal/polygonal shapes. Further careful observation of TEM images revealed that the worm-like γ -Fe₂O₃ structures are composed of small nanocrystallites.

Three types of electronic transitions are possible for Fe³⁺ in condensed phase (e.g. iron oxides), first due to ligand field transition, second corresponds to ligand metal charge transfer (LMCT from O²⁻ → Fe³⁺) and third due to paired excitation of magnetically coupled Fe³⁺ ions occupying the adjacent sites in the crystals [32]. The UV-Vis absorption spectra of as-synthesised goethite and maghamite nanostructures are shown in Fig. 5. The bands at 484 nm (goethite) and 526 nm (maghamite) are assigned as $6A_1 + 6A_1 \rightarrow 4T_1 (^4G) + 4T_1 (^4G)$ pair excitation. The weak band at ~392 nm in both goethite and maghamite may be due to $6A_1 \rightarrow 4E (^4D)$ transition. The strong bands at 240 nm in case of goethite and 230 nm for maghamite are readily assigned as LMCT transitions [33].

The magnetic hysteresis loop of as-prepared worm-like γ -Fe₂O₃ structures (Fig. 6) was measured between the applied magnetic field −1,600 to 1,600 A/m at 300 K. The result shows that the worm-like γ -Fe₂O₃ exhibit superparamagnetic property at room temperature. On applying a large external field, the magnetization of the nanoparticles aligns with the field direction, which reaches its saturation value for maghamite nanoparticles. The saturation magnetization (M_s) value for maghamite sample was 52.5 A m²/kg, indicating that the sample has the strong magnetic response to the applied magnetic field.

EBT reacts with Fe(II) ions in 1:2 (M:L) ratio, forming water-soluble Na₂[Fe(HL)₂(H₂O)₂] chelate complex. Since the ligand EBT (NaH₂L) belongs to α -hydroxy-azo group,

Fig. 6 Room temperature magnetic hysteresis loops of γ -Fe₂O₃

when dissolved in water, fast intramolecular electron transfer takes place between enol-azo and keto-hydrazone forms (Fig. 7a–c), thus forming two active electron pair donor centres (O, N) along with $-\text{SO}_3^-$ and $-\text{NO}_2$, for complexation. Further, the keto-hydrazone form (c) is more stable than enol-azo form, due to the presence of two electron-withdrawing groups $-\text{SO}_3^-$ and $-\text{NO}_2$, which is involved in the Na₂[Fe(HL)₂(H₂O)₂] chelate complex formation in aqueous medium (Fig. 8).

When Na₂[Fe(HL)₂(H₂O)₂] is dissolved in water and solution is made alkaline (pH 10), OH[−] ions attack the naphtholic protons, eliminating HL^{2−} ions and forming [Fe_{II}(OH)₂(H₂O)₄], which is facilitated by high temperature used in the reaction (reaction 2).

This hypothesis is supported by observed colour of reaction mixture during reaction. In aqueous medium, the colour of ligand H₂L[−] is dependent on the degree of protonation. H₂L[−] form (red coloured) is stable in acidic medium while HL^{2−} (blue coloured) is stable in basic medium (reaction 3). The observed blue colour of reaction mixture during heating is due to the release of HL^{2−} form of the ligand, since the pH value of solution mixture is around 10.

Further, in alkaline medium, since Fe³⁺ ion is more stable than Fe²⁺ ion, it is readily converted to hydrated Fe(III) ion (reaction 4).

Fig. 7 Enol-azo and keto-hydrazone forms of the ligand H_2L^-

Fig. 8 Structure of $Na_2[Fe(HL)_2(H_2O)_2]$ chelate complex

It is supposed that $[Fe_{III}(OH)_3(H_2O)_3]$ solidifies as $Fe(OH)_{3(s)}$ (reaction 5) by poly-condensation or by dehydration, which acts as nucleation sites for α -FeOOH and γ -Fe₂O₃ nanostructures [29]. After nucleation, there are two probable routes for α -FeOOH and γ -Fe₂O₃ nanostructures growth. In the one possible way, condensation of Fe(III) ions, as $Fe(OH)_3$, takes place on the nucleates (Scheme I). Now, depending on the physical parameters, like Fe(III) ions concentration and temperature, the primary $Fe(OH)_3$ particles

grow in specific size, then they dehydrate slowly to transform their phase to form α -FeOOH or γ -Fe₂O₃ nanostructures. In the second mechanism (Scheme II), instead of phase transformation, goethite and maghemite phases may be evolved by the deposition of hydrated Fe(III) ions on $Fe(OH)_{3(s)}$ nucleate as surface selective manner, and the particular phase (goethite or maghemite) evolution takes place as the growth proceeds. The phase and morphology evolution, in this way (α -FeOOH and γ -Fe₂O₃), are dependent on surface energy of the growing crystals [34, 35]. Therefore, the phase and morphology will very much depend upon the concentration of Fe(III) ions and ionic strength of the solution.

In many earlier reports, α -FeOOH and γ -Fe₂O₃ have been synthesised using Fe^{2+}/Fe^{3+} salts. The reactions involving metal salts as Fe source are too rapid to control the crystal growth. In this sense, the use of $Na_2[Fe(HL)_2(H_2O)_2]$ complex is advantageous because it not only ensures the controlled release of the metal ions but also facilitates the adsorption of the metal ions onto the specific facets of growing crystals, evolving a particular shape α -FeOOH/ γ -Fe₂O₃ nanocrystals.

In the present investigation, it is likely that the α -FeOOH and γ -Fe₂O₃ nanostructures are formed according to Scheme II. When $Na_2[Fe(HL)_2(H_2O)_2]$ complex is dissolved in water, the amount of Fe(III) ions are very small.

On increasing the temperature, Fe–O and Fe–N bonds weakened, which completely broke at $\sim 80^\circ\text{C}$, releasing Fe(II), which readily converted to hydrated Fe(III). Now sufficient amount of Fe(III) species are available for the growth of goethite nanostructures via condensation of hydrated Fe(III) ions as $\alpha\text{-FeOOH}$ on the $\text{Fe}(\text{OH})_{3(s)}$ nucleates. In this way, performing reaction for 1 h at 80°C , 9–15 nm diameter and $\sim 300\text{-nm}$ long acicular $\alpha\text{-FeOOH}$ structures are evolved. At higher temperature 120°C , $\gamma\text{-Fe}_2\text{O}_3$ is formed because now largely available hydrated Fe(III) favours to condense as $\gamma\text{-Fe}_2\text{O}_3$, rather than as $\alpha\text{-FeOOH}$, at the nucleates.

4 Conclusions

In summary, acicular $\alpha\text{-FeOOH}$ and worm-like $\gamma\text{-Fe}_2\text{O}_3$ have successfully been synthesised using $\text{Na}_2[\text{Fe}(\text{HL})_2(\text{H}_2\text{O})_2]$ chelate complex in alkaline medium. XRD patterns indicate the formation of goethite and maghemite nanomaterials, which is further supported by FTIR and UV–Vis spectral data. Maghemite nanostructures exhibit superparamagnetic behaviour at room temperature and has saturation magnetisation $52.5\text{ A m}^2/\text{kg}$. Water-soluble $\text{Na}_2[\text{Fe}(\text{HL})_2(\text{H}_2\text{O})_2]$ chelate complex is decomposed to form $[\text{Fe}_{\text{II}}(\text{OH})_2(\text{H}_2\text{O})_4]$, which is readily converted to form $[\text{Fe}_{\text{III}}(\text{OH})_3(\text{H}_2\text{O})_3]$ in alkaline medium. This fact was supported by the observed blue colour of solution due to release of HL^{2-} form of the ligand at pH 10. $[\text{Fe}_{\text{III}}(\text{OH})_3(\text{H}_2\text{O})_3]_{(\text{aq})}$ solidifies by poly-condensation/dehydration, forming $\text{Fe}(\text{OH})_{3(s)}$ initially, which acts as nucleation sites. Goethite and maghemite nanostructures growth takes place by condensation of hydrated Fe(III) ions at the $\text{Fe}(\text{OH})_{3(s)}$ nucleates, generating the $\alpha\text{-FeOOH}$ and $\gamma\text{-Fe}_2\text{O}_3$ phases as growth proceeds. At lower temperature 80°C , $\alpha\text{-FeOOH}$ is formed because the concentration of hydrated Fe(III) is smaller, while higher temperature 120°C makes a suitable condition for $\gamma\text{-Fe}_2\text{O}_3$ growth, by providing larger amount of hydrated Fe(III) ions as well as high temperature, which are suitable for the formation of more stable $\gamma\text{-Fe}_2\text{O}_3$.

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