**RESEARCH PAPER** 

# Hydrothermal synthesis, characterization, and growth mechanism of hematite nanoparticles

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Abstract Polyhedron-shaped hematite  $(\alpha - Fe_2O_3)$ nanoparticles have been successfully synthesized via a facile hydrothermal method by mixing FeCl<sub>3</sub> and NH<sub>4</sub>OH at high temperature. In this work, the influences of experimental conditions such as the effects of the concentration of iron's ion, NH<sub>4</sub>OH concentration, and reaction temperature on the hematite's particle size, dispersity, and growth rate were investigated. Results show that hematite nanoparticles with good crystallinity with the particle size of 100 nm could be obtained when the hydrothermal reaction was carried out with concentration of  $Fe^{3+} = 16 \text{ mM}$ ,  $NH_4OH = 40 \text{ mM}$ , reaction temperature = 120 °C, and reaction time = 24 h. In addition, this study investigates the hematite nanoparticle-formation mechanism with reaction time. It is observed that the formation of hematite nanoparticles are initiated by the formation of intermediate phase of goethite nanorods in the early stage of hydrothermal reaction, which further transform into hematite crystal as the reaction is progressed.

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#### Introduction

In acknowledgment of its vast and remarkable potential for many applications, research on the synthesis of different types of iron oxide nanoparticles is growing tremendously. Different polymorphic types of iron oxide are already being used in various applications such as magnetic liquids in photocatalysis, diagnostic imaging, drug delivery, electrodes in non-aqueous batteries, and as catalysts (Kulkarni and Lokhande 2003; Sha et al. 2004; Lee et al. 2009; Hassanjani-Roshan et al. 2011; Caudron et al. 2011; Lu et al. 2012). Among the various polymorphic forms of iron oxide,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) is widely used in catalysts, pigments, and gas sensors owing to its low cost, high resistance to corrosion, environmental friendliness, and nontoxicity (Pu et al. 2006; Tadić et al. 2011; Xu et al. 2011; Yang et al. 2012; Sarkar et al. 2012; Navale et al. 2013; Khan et al. 2013).

Due to its excellent properties and good application prospects, various techniques have been reported for the synthesis of hematite nanoparticles. For example, Itoh and Sugimoto have prepared and systematically controlled uniform hematite nanoparticles with controlled size and shapes by a sol–gel method (Itoh and Sugimoto 2003). Cherian et al. (2012) synthesized hematite nanorods by electrospinning polyvinylpyrrolidone/

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ferric acetyl acetonate composite precursors and then annealing at 500 °C for 5 h. The particle sizes of the hematite nanorods were found to be 150 nm. By calcining y-Fe<sub>2</sub>O<sub>3</sub> at 500 °C for 1 h, Darezereshki (2011) obtained hematite nanocrystals with a particle size of  $18 \pm 2$  nm. However, compared with the above methods, hydrothermal synthesis was considered as the most promising method because it not only offers an effective control over the size and shape of the particles at relatively low temperatures and short reaction times, but also provides well-crystallized nanostructures with high degree of homogeneity and definite composition (Byrappa and Adschiri 2007; Almeida et al. 2010). With the hydrothermal process, Zhu et al. (2012) synthesized hematite nanostructures with narrow size distribution using poly(vinylpyrrolidone) as surfactant and NaAc as precipitation agent. Fan et al. (2009) also reported the synthesis of hematite nanoparticles by hydrothermal treatment of FeCl<sub>3</sub> with sulfate and phosphate additives. They obtained hematite nanoparticles with various morphologies including hollow nanoparticles, nanocapsules, nanotubes, and nanospindles.

Although hematite nanocrystals have been synthesized using the above methods, precise controls in terms of their size, shape, and dispersity are still challenging. In addition, the production of large quantities of uniform-sized nanocrystals will become critical for the realization of high-quality nanoscale devices and many nanotechnological applications. This paper reports a facile hydrothermal method to fabricate hematite nanoparticles. FeCl<sub>3</sub> and NH<sub>4</sub>OH were used to prepare hematite nanocrystals without any surfactant additives. The effects of Fe<sup>3+</sup> concentration, NH<sub>4</sub>OH concentration, and reaction temperature on the particle size, morphology, dispersity, and growth rate were systematically studied. Finally, hematite nanocrystals' development with reaction times was also investigated and characterized in detail in order to provide better insight into the hematite nanoparticles growth mechanism.

#### **Experimental method**

## Materials

#### Hydrothermal synthesis of hematite nanoparticles

Hematite nanoparticles were synthesized by stirring an aqueous solution of iron source and ammonium hydroxide at room temperature. Then, the mixture was transferred into a 120 mL Teflon-lined stainless-steel autoclave and reacted at different temperatures and reaction times. After the reaction, the autoclave was cooled to room temperature naturally, and the red solid precipitates were collected by centrifugation and washed with distillated water and ethanol three times. Finally, this reaction product which was in the form of red solid precipitate was dried under vacuum at 70 °C for 12 h. The quality of the hematite nanoparticles can be controlled by adjusting the amount of FeCl<sub>3</sub>·6H<sub>2</sub>O, NH<sub>4</sub>OH, reaction time, and temperature.

#### Characterization

An X-ray diffraction study of the synthesized hematite nanoparticles was carried out using a PANalytical X'Pert Pro diffractometer equipped with PIXcel detector (PANalytical B.V., Almelo, Netherlands). The measurements were performed on zero-background silicon plates with the diffraction angle from  $6^{\circ}$  to  $70^{\circ}$  using Cu K $\alpha$  radiation. Data were collected using X'Pert Data Collector software and processed using X'Pert HighScore Plus (PANalytical B.V.). Raman active bands for the final products were performed using a LabRAM ARAMIS Raman microspectrometer (Horiba Jobin Yvon, Lille, France). The excitation laser source was a Ventus 532 nm mpc6000 laser (Laser Quantum, England). The spectral region was recorded and investigated in the range of  $200-2,500 \text{ cm}^{-1}$ . Spectral acquisition and data processing were carried out with Labspec5 Software (Horiba Jobin Yvon, Lille, France). Transmission electron microscopy (TEM) images were collected using a JEOL 2010 EX high-resolution transmission electron microscope. The hydrodynamic particle size was determined using Microtrac Zetatrac (Model NPA152-31A)-a dynamic light scattering (DLS) analyzer.

## **Results and discussion**

Characterization of hematite nanoparticles

XRD, Raman spectroscopy, and TEM were used to characterize the morphology and crystal structure of



Fig. 1 a XRD pattern and b Raman spectra of the reaction products synthesized with 16 mM of FeCl<sub>3</sub>·6H<sub>2</sub>O; 40 mM NH<sub>4</sub>OH at 120 °C

the synthesized hematite nanoparticles. The phase purity and crystal structure of the prepared hematite nanocrystals were examined by XRD and Raman spectroscopy. Figure 1 shows the results of XRD pattern and Raman spectra of the prepared particles. All the diffraction peaks observed on the XRD pattern can be unambiguously indexed as the rhombohedral phase of hematite. Furthermore, no diffraction peaks for any other impurities were detected, indicating that high purity and good crystallinity of the prepared hematite were obtained. This result is also supported by Raman spectroscopy since the spectra for the reaction products indicate all active bands for hematite crystal; i.e., two  $A_{1g}$  modes (observed at 227.2 and 496.96 cm<sup>-1</sup>), four  $E_g$  modes (observed at 246.4, 295.84, 412, and  $614.08 \text{ cm}^{-1}$ ), and a magnon scattering band at 1327.56  $\text{cm}^{-1}$  with an additional line at 661.12  $\text{cm}^{-1}$  attributed to the Raman-forbidden longitudinal optical (LO)  $E_{\rm u}$  mode (de Faria et al. 1997; Chernyshova et al. 2007; Froment et al. 2008). In addition, TEM images of the synthesized hematite nanoparticles, as shown in Fig. 2, show that the hematite nanocrystals are of mostly polyhedronal morphology. The hematite nanocrystals, as prepared, have a uniform particle size of around 100 nm.

## Effect of concentration of iron ions

In this study, different experimental conditions were examined in order to investigate the effects of those experimental parameters on the size and growing rate of hematite nanoparticles. First, the effect of concentration of iron ions was investigated. Figure 3 presents the TEM images of hematite nanoparticles synthesized with different concentrations of iron ions. Based on Fig. 3, it is clear that concentration of iron ions has a significant effect on the shape and particle size of hematite nanoparticles. At very low iron ion's concentration, small and monodisperse hematite nanoparticles are obtained. In Fig. 3a, it is shown that the average hematite nanoparticle's diameter was 88 nm and had a polyhedral shape. When higher amounts of iron source are used, bigger particles with a pseudo-cubical particle shape are obtained. Figure 3b and c show that particles with average size of 294 and 406 nm are obtained when the reaction is carried out with 40 and 64 mM of iron source, respectively. In addition, some needle-shaped nanorods were observed at high iron concentrations (Fig. 3b, c). Further insight on these nanorods using high-resolution electron microscopy revealed that the crystal structure of the nanorods belongs to goethite ( $\alpha$ -FeOOH). Through calculation, the lattice fringes of 0.4178 and 0.2540 nm (Fig. 3d) in the observed nanocrystallites agree well with the (110) and (021) lattice planes of  $\alpha$ -FeOOH, respectively. In addition, the crystal phase of  $\alpha$ -FeOOH is also confirmed by the SAED analysis. On the inset of Fig. 3d, the diffraction pattern shows two ring features for goethite, i.e., (111) and (140), in addition to several ring features for hematite as the main product of the reaction. These results support and refine the concept developed earlier on the formation of goethite and hematite from ferrihydrate via two different and competitive



Fig. 2 TEM of synthesized hematite nanoparticles at different magnifications (reaction conditions: 16 mM FeCl<sub>3</sub>·6H<sub>2</sub>O; 40 mM NH<sub>4</sub>OH at 120 °C for 24 h)

processes at the beginning of the hydrothermal reaction, i.e., goethite is formed in solution from dissolved Fe<sup>3+</sup> ion produced by dissolution of ferrihydrate, while hematite forms through an internal dehydration and rearrangement within the ferrihydrate aggregate (Fischer and Schwertmann 1975; Schwertmann et al. 1999). Therefore, goethite formation is favorable at high concentration of Fe<sup>3+</sup> ions, and hematite should be favored as the concentration decreases (Schwertmann et al. 1999). In addition, it is also known that goethite nanocrystals were transformed into hematite by dehydration in the successive hydrothermal treatment (Jia and Gao 2008). Therefore, larger amounts of goethite may also lead to the formation of larger hematite crystals.

Figure 4 displays changes in hematite particle size at different concentrations of  $Fe^{3+}$  with reaction time. At low Fe<sup>3+</sup> concentrations, the particle growth rate (the slope of the plot in Fig. 4) was lower than that at high concentrations of Fe<sup>3+</sup>. The reason for this phenomenon can be explained by Von Weimarn's precipitation theory. It is well known that the process for the formation of nanoparticles in liquid phase is divided into two steps: nucleation of primary nanocrystals, and growth of the nanocrystals (Barlow et al. 2004; Zhu et al. 2012). The nucleation process normally occurs within a very short time span. The second step, growth of the nanocrystals, concerns the growth of the nuclei as a result of diffusion, precipitation, or agglomeration. At a high concentration of iron source, the diffusion rate (the amount of substance that diffuse per unit area per unit time) is expected to be higher than that at a low concentration of iron source, which results in a faster growth rate and greater particle size. Figure 4 also shows that, with a high concentration of  $Fe^{3+}$ , the hematite nanocrystals have a wider particle size distribution than those grown at a low concentration of  $Fe^{3+}$ . This can be explained by particle agglomeration during the nanocrystal growth process. When the  $Fe^{3+}$  concentration is high, many nuclei are formed from the solution, leading to some aggregation of the resultant hematite particles (Itoh and Sugimoto 2003).

#### Effect of precipitation agent's concentration

Another important reaction parameter that influences the quality of the synthesized hematite nanoparticles is the concentration of precipitation agent. Figure 5 presents TEM images of the synthesized hematite nanoparticles with different amounts of NH<sub>4</sub>OH. The results show that bigger hematite particles can be obtained at lower precipitation agent's concentrations. As shown in Fig. 5, hematite crystals with average particle sizes of  $\sim 140$  nm,  $\sim 100$  nm, and  $\sim 70$  nm are obtained when concentrations of NH<sub>4</sub>OH are 8, 40, and 56 mM;, respectively. Similar results were also reported by Zhu and co-workers when NaAc was used as the precipitation agent (Zhu et al. 2012). At low concentrations of NH<sub>4</sub>OH, limited hematite nuclei were generated from the solution. Therefore, the growth of nanocrystals with NH<sub>4</sub>OH is preferable since there are enough precursors for it, leading to larger hematite particles. When NH<sub>4</sub>OH concentration increases, the amount of the precursor consumed in the nucleation process also increases. Then, lower number



Fig. 3 TEM images of nanoparticles synthesized at different concentrations of iron source: **a** 16 mM, **b** 40 mM, and **c** 64 mM. Other conditions: 40 mM of NH<sub>4</sub>OH; reaction temperature and time, respectively, of 120 °C and 24 h.

of precursors are available for crystal growth, and the size of the hematite crystal is smaller. In addition, Fig. 5 also displays that the dispersion of the synthesized hematite particles is poor when  $NH_4OH$  concentration is high. It is clearly shown in Fig. 5c that larger amounts of hematite particles were aggregated when  $NH_4OH$  concentration was 56 mM. This can be easily explained because, in the high concentration of  $NH_4OH$ , larger amounts of hematite nuclei are

**d** High-resolution TEM image of nanorods synthesized at 40 mM iron source concentration with corresponding SAED pattern (*inset*)

precipitated from the solution, and these nuclei can easily contact and aggregate during the growth step.

Figure 6 shows the changes in the hematite particle size with reaction time at different concentrations of  $NH_4OH$ . The results indicate that, at certain concentration of  $NH_4OH$ , hematite particle growth rate decreases as  $NH_4OH$  concentration increases. For example, the particle growth rate at  $NH_4OH$  concentration of 8 mM is greater than that with  $NH_4OH$ 



**Fig. 4** Hydrodynamic particle size of hematite nanoparticles synthesized at different concentration of  $\text{Fe}^{3+}$ : 16, 40, and 64 mM. Other conditions: 40 mM of NH<sub>4</sub>OH; reaction temperature and time, respectively, of 120 °C and 24 h

concentration of 40 mM. However, when  $NH_4OH$  concentration is too high, hematite nanocrystal aggregation occurs causing an increase in the particle growth rate. Figure 6 also shows that, at high concentrations of  $NH_4OH$  such as 56 mM, the particles have a broad particle size distribution, indicating that particle aggregation occurred during the growth process.

## Effect of reaction temperature

Besides the concentrations of the precursor and precipitation agent, the effect of reaction temperature was also investigated in this work. Herein, hematite nanoparticle samples were synthesized at three different temperatures while keeping the concentrations of both concentrations of iron source (16 mM) and precipitation agent (40 mM) constant. Figure 7 presents TEM images of hematite nanoparticles synthesized at different reaction temperatures: 120, 160, and 180 °C. Based on these results, it appears that temperature has little effect on the size of the synthesized hematite particles. Little change in particle size was observed as the reaction temperature increased from 120 to 180 °C. However, the effect of temperature on hematite nanocrystal dispersion is clearly observed. As shown in Fig. 7a, a good dispersion of hematite nanoparticles is obtained when the reaction is carried out at 120 °C. However, when temperature is increased to 180 °C, severe particle aggregation occurs. This result is also observed in the particle size measurement as shown in Fig. 8. The prepared hematite particles have broader particle size distribution at 180 °C than that at 120 °C.

#### Hematite particles developed with reaction time

To further understand the phase transformation of hematite crystal from iron precursors during hydrothermal reaction, the synthesized nanocrystals samples were collected and analyzed at every interval of the hydrothermal reaction. Even though extensive studies have been done in the past few decades to investigate the growth mechanism of the hematite from different iron precursors, the fundamental understanding on the nanoparticles growth and the occurrence different types of intermediate phases are still not yet clear. In general, in the early stage of hydrolysis of Fe<sup>3+</sup>, the reaction produces an intermediate form of iron oxyhydroxy-salt which further transform into ferrihydrate through a dissolution– reprecipitation process (Lin et al. 2013). Depending on



Fig. 5 TEM images of reaction product synthesized at different NH<sub>4</sub>OH concentration: **a** 8 mM, **b** 40 mM, and **c** 56 mM. Other conditions: 16 mM of FeCl<sub>3</sub>·6H<sub>2</sub>O; reaction temperature and time, respectively, of 120 °C and 24 h



**Fig. 6** Hydrodynamic particle size of reaction product synthesized at different precipitation agent's concentrations: 8, 40, and 56 mM. Other conditions: 16 mM of FeCl<sub>3</sub>·6H<sub>2</sub>O; reaction temperature and time, respectively, of 20 °C and 24 h

the reaction conditions, such as pH and temperature, these ferrihydrates could then be transformed into different types of iron oxide products such as hematite, maghemite, goethite, akaganeite, lepidocrocite (Cornell and Schwertmann 2003). In a study by Almeida and co-workers on the hydrothermal growth of hematite nanorods from aqueous solution of iron(III) chloride, needle-shape of  $\beta$ -FeOOH (akaganeite) nanoparticles are known to form as an intermediate which then undergo dissolution–reprecipitation to form hematite (Almeida et al. 2010). However, the formation of hematite via dehydration of  $\alpha$ -FeOOH (goethite) as an intermediate is also possible (Jia and Gao 2008; Fan et al. 2009).

Therefore, to investigate the effect of reaction time on hematite formation, XRD analysis was carried out at every interval of the hydrothermal reaction. However, since nanocrystals from the first 3 h of the reaction were too small to centrifugally separate from the solution, analysis could only be done from 8.5 h of hydrothermal reaction. Figure 9 shows the XRD patterns of products at different reaction times. It is apparent that the formation of hematite nanoparticles occurs as early as 8.5 h of hydrothermal treatment since major XRD peaks for hematite were observed. As the reaction progresses, the intensity of peaks increases indicating more hematite with high crystallinity were produced. In addition, to monitor the crystal growth and phase transformation of reaction product, electron microscopy were also carried out at every interval of reaction time. Figure 10 presents the TEM images of nanoparticles collected after different reaction times. As shown in Fig. 10a and b, nanorods (20–30 nm in length and 5–8 nm in width) are formed during the first 3 h of the reaction. Based on selected area diffraction pattern and lattice fringe analysis on the high-resolution images of the nanorods in Fig. 10f, it is known that the nanorods can be identified as  $\alpha$ -FeOOH (goethite) since the characteristic lattice fringe of 0.2450 nm corresponds to (111) planes of goethite, which also very close to the standard XRD data of d spacing of goethite (0.2446 nm). According to literatures, it has been reported that ferrihydrate, a metastable phase, would be generated first in hydrolysis of iron precursor and then transformed to goethite or hematite depending on the pH of the system (Schwertmann et al. 2004; Cudennec and Lecerf 2006). It is suggested that goethite is strongly favored where the concentration of monovalent Fe(III) ions, either  $Fe(OH)_2^+$  or  $Fe(OH)_2^-$ , is at its maximum with pH  $\sim$  4 or pH  $\sim$  12, respectively (Schwertmann



Fig. 7 TEM images of reaction product synthesized at different temperature concentrations: a 120 °C, b 160 °C, and c 180 °C. Other conditions: 16 mM of FeCl<sub>3</sub>·6H<sub>2</sub>O, 40 mM of NH<sub>4</sub>OH, and reaction time of 24 h



Fig. 8 Hydrodynamic particle size of reaction product synthesized at different temperatures; other conditions: 16 mM of  $FeCl_3$ ·6H<sub>2</sub>O, 40 mM of NH<sub>4</sub>OH, and reaction time of 24 h

et al. 1999). Meanwhile, hematite is preferred where the concentrations of these monovalent ions are at minimum, i.e., with ~pH 8, which is also the ZPC of ferrihydride. In addition, hematite is also formed at pH below 4 as the concentration of monovalent ions of  $Fe(OH)_2^+$  is overridden by divalent  $Fe(OH)^{2+}$  ions which appear to be less favorable for goethite crystal formation (Schwertmann et al. 1999). Since the pH in this work is around 4, the generation of goethite in the early stage of hydrothermal reaction is rational.

As the reaction progressed, the sequential transformation of goethite to form hematite crystal can be realized as the hydrothermal reaction is prolonged further to 15 and 24 h. From the TEM images on Fig. 10c-e, goethite nanorods transformed and grew into polyhedronal hematite nanoparticles. The generation of hematite nanoparticles is confirmed by SAED, and the characteristic lattice fringe of 0.3684 nm agrees with (012) lattice plane of hematite crystal (Fig. 10g). The formation of hematite is also proven by XRD analysis in Fig. 9. Therefore, it can be concluded that the formation of hematite is preceded by generation of goethite nanorods as intermediates, which undergo dehydration in the successive treatment. The phase transformation of amorphous ferric hydroxide to goethite and then to hematite have also been reported in many publications (Beruto 1983; Bbusca and Rossi 1983). A solid-phase transformation of goethite to hematite at high temperature (200 and 300 °C) in terms of reaction isotherms, rate constant, and activation energy have also been reported (Diamandescu et al. 1997). Recent study by Burleson and Penn showed that





Fig. 9 XRD pattern of reaction product synthesized at **a** 8.5 h, **b** 15 h, and **c** 24 h; other conditions: 16 mM of FeCl<sub>3</sub>·6H<sub>2</sub>O, 40 mM of NH<sub>4</sub>OH, and reaction temperature of 120 °C (*filled square* peaks correspond to hematite)

the transformation of ferrihydrate to goethite occurs in two steps via oriented-aggregation growth, which is similar to the result reported by Jia and co-workers (Burleson and Penn 2006; Jia et al. 2007). Unlike the formation of hematite from dissolution/recrystallization of akaganeite as intermediate, the crystal structures of goethite and hematite share great analogy, and it is not likely that goethite would transform to hematite with great structural modification (Jia et al. 2007). It is known that the gentle structural modification occurs via topotactic transformation which allows hematite to retain the morphology and the single-crystal characteristic of goethite as reported by Cudennec and Lecerf (2006). Further development of hematite crystal followed then by Ostwald's ripening mechanism-as hydrothermal reaction progresses in the solutionresults in polyhedronal hematite nanoparticles, since no organic or surfactant additives were used to control the crystal growth in certain plane. It is rational to



**Fig. 10** TEM images of nanoparticles collected from reaction product that is synthesized at different reaction times: **a** 1, **b** 3, **c** 8.5, **d** 15, and **e** 24 h; other reaction conditions are 16 mM of

assume that the particles would grow randomly without restriction in the absence of additives and result in isotropic products.

## Conclusion

A facile, one-step hydrothermal method for hematite nanoparticles synthesis has been presented in this work. Polyhedron-shaped hematite nanocrystals were successfully synthesized with FeCl<sub>3</sub> and NH<sub>4</sub>OH. In summary, the size, dispersity, and growth rate of hematite crystals are found to be dependent on experimental conditions, such as Fe<sup>3+</sup> concentration, precipitation agent concentration, and reaction

FeCl<sub>3</sub>·6H<sub>2</sub>O, and 40 mM of NH<sub>4</sub>OH at 120 °C. High-resolution TEM image of nanorods and nanocrystals collected at **f** 3 h and **g** 15 h with corresponding FFT pattern (*inset*)

temperature. Result shows that the hematite nanoparticles, as prepared, are around 100 nm in size (concentration of Fe<sup>3+</sup> = 16 mM, NH<sub>4</sub>OH = 40 mM, temperature = 120 °C, and reaction time = 24 h). The study of hematite nanocrystals formed with reaction time revealed that hematite nanoparticle growth was initiated by the generation of goethite from ferrihydrate in the early stage of hydrothermal reaction, in which they undergo dehydration in the successive treatment to form hematite crystal.

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