Structural- and optical-properties analysis of single crystalline hematite (\(\alpha\)-Fe\(_2\)O\(_3\)) nanocubes prepared by one-pot hydrothermal approach

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High quality single crystal hematite (\(\alpha\)-Fe\(_2\)O\(_3\)) nanocubes with average dimensions of 40 nm were successfully synthesized by a facile one-pot hydrothermal method. Systematic analyses were performed to investigate the morphological-, structural- and optical-properties of the as-synthesized \(\alpha\)-Fe\(_2\)O\(_3\) nanocubes. Continuous formation and hourly monitoring towards proper arrangement of single crystal \(\alpha\)-Fe\(_2\)O\(_3\) nanocubes was observed throughout the hydrothermal heating process of 180 \(^\circ\)C from 4 h to 12 h. The probable growth mechanism on the formation of cubic nanostructures is also proposed. Electron micrographs show the cubic \(\alpha\)-Fe\(_2\)O\(_3\) synthesized at the most optimum 8 h hydrothermal heating duration are indeed produced in high-yield with a well-defined cubical shape. The typical rhombohedral structure of cubic \(\alpha\)-Fe\(_2\)O\(_3\) was evident from the XRD pattern. The SAED pattern indicates that the \(\alpha\)-Fe\(_2\)O\(_3\) nanocubes are single-crystalline in nature, with lattice-fringes and a \(d\)-spacing value of 3.6 Å. The optical characterization reveals that \(\alpha\)-Fe\(_2\)O\(_3\) nanocubes show strong visible-light absorption with a band gap energy of \(\sim 2.1\) eV while the photoluminescence emission spectra depicts a mono-peak centered at \(\sim 590\) nm. Both the SAED pattern and UV-vis spectra show a strong correlation with the standard \(\alpha\)-Fe\(_2\)O\(_3\). The as-synthesized \(\alpha\)-Fe\(_2\)O\(_3\) single crystal is of high quality that potentially could be used as a visible-light active nanomaterial in renewable energy device applications.

1.0 Introduction

Rational design and synthesis of metal oxide nanocrystals with tunable shape and properties have attracted enormous research interest for their unique size and shape-dependent intrinsic physicochemical properties. In particular, metal oxide semiconductor nanocrystals have been identified as important materials with potential applications in a wide range of fields (optical, electrical, magnetic, catalytic, chemical, etc.).\(^{1-5}\) Hematite (\(\alpha\)-Fe\(_2\)O\(_3\)) is among one of the most interesting n-type metal oxide semiconductors with an optical bandgap of 2.1 eV.\(^{6,7}\) Due to its prevalence, hardness, chemical- and thermal-stability, and environmentally benignity, it has become an attractive material in a spectrum of semiconducting applications. In addition, its ability to absorb light makes it a particularly attractive material for use in solar energy conversion.\(^{8,9}\) \(\alpha\)-Fe\(_2\)O\(_3\) is isostructural with corundum, Al\(_2\)O\(_3\), which is trigonal (hexagonal scalenohedral, symbol 32/m) with space group \(R3c\) and lattice parameters \(a = 5.0356\) Å, \(c = 13.7489\) Å, having Fe\(^{3+}\) ions occupy 2/3 of its octahedral sites that are confined by the nearly ideal hexagonal closed-pack \(O\) lattice.\(^{10}\) The dense hexagonal close packing of oxygen combined with the interstitially positioned iron yields a very dense structure (5.26 g cm\(^{-3}\)) exhibiting a high polarizability and high refractive index (3.15).\(^{11}\) Attributed to its layered structure also generates complex behaviour when interacting with photons and electrons, it is of interest among researchers to exploit \(\alpha\)-Fe\(_2\)O\(_3\) nanocrystals in numerous promising applications, such as gas sensors,\(^{12}\) catalysts/photocatalysts,\(^{13}\) electrode materials in lithium secondary batteries,\(^{14}\) magnetic recording media,\(^{15}\) photo-assisted electrolysis of water,\(^{16}\) and optical and electromagnetic devices as well as environmental remediation in wastewater treatment.\(^{17-19}\)

It is noted that the morphology and size of \(\alpha\)-Fe\(_2\)O\(_3\) have a great impact on its intrinsic physicochemical properties and thus determine its application.\(^{20}\) Therefore, much effort has been made in the design of \(\alpha\)-Fe\(_2\)O\(_3\) materials with a desired structure and morphology such as zero-dimensional (0D) nanoparticles,\(^{21}\) one-dimensional (1D) nanowires,\(^{22}\) nanobelts,\(^{23}\) nanorods,\(^{24}\) nanotubes,\(^{25}\) two-dimensional (2D)
nanorings, three-dimensional (3D) nanocubes, urchin-like nanostructures, nanoflowers, and etc. In particular, well-defined single crystalline $\alpha$-Fe$_2$O$_3$ nanocubes exposing specific facets are demonstrated to be extremely notable due to the highly reactive surfaces and excellent electron mobility. In terms of crystallinity nature, a single crystalline $\alpha$-Fe$_2$O$_3$ has a continuous crystal lattice for its entire nanostructure. The crystal lattice arrangement is endless until the edge of the atomic arrays, with no grain boundaries observed. Such a continuous atomic array indeed renders several advantages especially the aspect of its congruent electronic properties. For instance, the absence of grain boundaries in the crystal structure are found to be able to accelerate the movement of electric charges in a circuit especially in solar cells and PEC cells. Additionally, single crystallinity also allows a longer lifetime of electron–hole pairs which could enhance the efficiency in the aforementioned applications. As in the case of gas sensor application, a single crystalline $\alpha$-Fe$_2$O$_3$ nanostructure is found to be able to reduce instability problems associated with grain coalescence and drift in electrical properties, which alternatively improve its sensitivity and stability. Therefore, it is worth noting that the advantageous characteristics can be harnessed through such a structure that would enhance and diversify its performance.

To date, a myriad of chemical and physical methods have been developed for the synthesis of single crystalline $\alpha$-Fe$_2$O$_3$ nanocubes. These methods include a sonochemical route, thermal decomposition of inorganic precursors, forced hydrolysis, electrospinning, and a hydrothermal approach. Compared with other fabrication techniques, hydrothermal synthesis is considered as the most robust method and has attracted a rapidly increasing interest for the preparation of single crystalline $\alpha$-Fe$_2$O$_3$ nanocubes due to several merits: the products have a high purity and excellent crystallinity, morphologies can be easily tuned, a relatively low reaction temperature and readily available for scale-up production. For example, Pu and co-workers have successfully synthesized $\alpha$-Fe$_2$O$_3$ nanocubes by a templating method, in which they employed the cationic capping agent/surfactant cetyl trimethylammonium bromide (CTAB) and showed that concentration variation of the precursor could lead to different sizes and shapes of $\alpha$-Fe$_2$O$_3$. In this study, the rod-like $\beta$-FeOOH precursors were firstly obtained by varying FeCl$_3$ concentration ranging from 0.01 to 0.05 M at 120 °C, and then the precursors aggregated into raft-like particles and thereby transformed to $\alpha$-Fe$_2$O$_3$ cubic particles. Mitra et al. have reported the controlled synthesis of $\alpha$-Fe$_2$O$_3$ microporous particles by pH-controlled hydrolysis of Fe(NO$_3$)$_3$·9H$_2$O with the use of ethylenediamine as the basic ligand to facilitate the formation of cubic samples, whereas Su et al. used ammonium acetate in FeCl$_3$·6H$_2$O aqueous solution as the capping agent to produce $\alpha$-Fe$_2$O$_3$ at 160 °C for 24 h. In addition to this, Ma and colleagues synthesized single-crystal $\alpha$-Fe$_2$O$_3$ nanocubes by the use of diethylene glycol (DEG) at 200 °C for 10 h in Li ion battery applications. Very recently, Patra and his group used a proportional amount of sodium salicylate and NaOH/water to prepare single crystalline $\alpha$-Fe$_2$O$_3$ nanocubic particles via a hydrothermal route for 36 h at 423 K and investigated the facet-dependent photoredox catalytic activity. However, most of the aforementioned synthetic routes tend to involve the use of organic surfactants, which means a much more complicated process including complete template removal at elevated temperature is needed. Furthermore, solvents used are either potentially hazardous or a rather complicated protocol is involved, and some synthesis methods are often time-consuming (>24 h). It is therefore necessary to investigate further the growth of single crystalline $\alpha$-Fe$_2$O$_3$ nanocubes and conveniently sort the particle size and desired morphology through a facile, simple, economic, and straightforward strategy in a hydrothermal method.

In the experiment reported herein, driven by the demand for one pot facile hydrothermal synthesis of single crystalline $\alpha$-Fe$_2$O$_3$ nanocubes with well-defined morphology and scrutinizing its size- and morphology-dependent properties, we employed the chloride-based cation Fe$^{3+}$ that was reacted with the oleate functional group in the presence of oleylamine (OAm). In the present work, it is noteworthy that: (i) the current synthetic method is very simple and straightforward. The synthetic scheme involved only a one-step process that does not require high temperature or high pressure. (ii) It is particularly interesting to highlight that only the reaction time was varied in the range of 4 h to 12 h at a constant temperature, in contrast to other typical hydrothermal synthesis of 24 h or a few days. The morphological evolution of the nanostructures and their corresponding growth processes were able to be elucidated. Thereafter, detailed discussion based on the insightful analysis of the shape and structure was also presented. (iii) We report on the shape- and size-selective synthesis of single crystalline $\alpha$-Fe$_2$O$_3$ nanocubes with good reproducibility without the use of additional capping agents or surfactants. Instead, we have used a mixture of solvents with OAm as one of the key elements to determine the final shape of single crystalline $\alpha$-Fe$_2$O$_3$ nanocubes.

Previously, many experimental and theoretical studies primarily focused on the size and morphology of the $\alpha$-Fe$_2$O$_3$ nanostructures. Since $\alpha$-Fe$_2$O$_3$ is well-known for its various applications. Hence, one of the most important aims of this paper was to present a study of the time-dependent morphological evolution of $\alpha$-Fe$_2$O$_3$ and its transformation from 0D to 3D (cubic shape). Finally, the high quality single crystalline $\alpha$-Fe$_2$O$_3$ nanocubes are characterized by using various analytical tools to investigate the structural- and optical-properties of $\alpha$-Fe$_2$O$_3$ nanocubes in a much more detailed manner. The as-obtained information is compared with that of commercial $\alpha$-Fe$_2$O$_3$ nanoparticles to show the novelty of the as-synthesized product. In addition, the possible transformation mechanism of the $\alpha$-Fe$_2$O$_3$ through a “1D → 3D” mode was also proposed in the following sections. The detailed crystallographic-, structural- and optical-properties of...
the as-prepared α-Fe2O3 nanocubes presented are of fundamental importance to comprehend the shape and growth of single crystallinity of α-Fe2O3 nanocubes and thus provide direct correlation between the shape and exposed facet-controlled properties to its applications in a future study.

2.0 Experimental

All the chemicals used in the experiments were of analytical grade and no further purification was required. Potassium oleate (C38H72K2O12, Sigma Aldrich, ≥87%), ferric chloride hexahydrate (FeCl3·6H2O, Merck), Oleylamine (C38H72N2O3, Sigma Aldrich, 70%) and absolute ethanol (C2H5OH, HmbG Chemicals) were obtained. In this study, all the chemical reactions were carried out in deionized water.

2.1 Synthesis of α-Fe2O3 nanocubes

Hematite (α-Fe2O3) cubic nanocrystals were synthesized using a hydrothermal method. This experimental method of synthesis was carried out at different durations and the samples were collected every 2 h. The remaining factors were kept constant while synthesizing the nanocrystals. Typically, a mixture consisting of 3.33 mmol of potassium oleate was dissolved in 5.34 mL ethanol with the addition of 1 mL oleylamine (OAm). Subsequently, the mixture was transferred into a Teflon-lined stainless steel autoclave that has been pre-loaded with 10.67 mL deionized water and 1.11 mmol of FeCl3·6H2O aqueous solution. The resultant reagents were stirred continuously at room temperature for 2 hours until a reddish solution was formed. Then, the autoclave was sealed and hydrothermally treated at 180 °C for different heating times (4 h, 6 h, 8 h, 10 h and 12 h). After the finite induction period, the autoclave was left to cool down naturally. The resulting dark red precipitate was collected by centrifugation and washed several times with ethanol. Finally, this synthesized material was dried in an oven at 55 °C for 24 h.

2.2 Characterizations

The size, shape, morphology, chemical composition, structural features and optical properties of the nanocrystals were investigated by using different analytical characterization techniques. We systematically observed the time-dependent morphological transformation of α-Fe2O3 nanocrystal structure via TEM images and SAED patterns with a JEOL JEM-2100F instrument operated at 200 kV. In order to observe the yield of α-Fe2O3 nanocubes in large quantities, a field-emission scanning electron microscope (FESEM, Hitachi SU8000 with the operation voltage of 2 kV) was employed. Information relating to the elemental mapping and elemental composition was studied by using energy dispersive X-ray analysis (EDXA, Oxford Instrument). The bulk-crystallinity and phase identification of the samples were characterized by X-ray powder diffractometer (XRD, PANalytical EMPYREAN, 40 kV/35 mA with Cu Kα irradiation at λ = 1.5406 Å). The scanning process covered an angular range from 10° to 80° with a scanning rate of 0.02° per minute. In addition, a study of phonon vibration mode was conducted by means of a Renishaw inVia Raman Microscope equipped with a Leica DMLM microscope (objective lens of 50× (UV)). A 514 nm HeCd laser source was subjected onto the samples for 30 s at 50 mW of laser power. The spectra were collected within the range of 150 to 800 cm⁻¹ by subjecting the samples to the beam source at room temperature. The X-ray photoelectron spectroscopy (XPS) measurement was performed by using synchrotron radiation from photoemission spectroscopy (PES) beamline no. 3.2a at the Synchrotron Light Research Institute, Thailand in order to further study the chemical elements and bonding of the single crystalline α-Fe2O3 nanocubes. The PES system was employed with a Thermo VG Scientific CLAM2 electron spectrometer and functioned in the conditions of maximum photon energy of 600 eV with a kinetic energy step of 1 eV for a wide scan and 0.1 eV for a narrow scan. Optical absorption spectra were analyzed by an ultra violet-near infrared spectrophotometer (UV-vis-NIR, Perkin Elmer Lambda 950). The photoluminescence (PL) spectra were obtained by using Ar⁺ laser as the excitation source operated at a wavelength of 325 nm.

3.0 Results and discussion

To acquire insight into the details of morphological evolutionary growth events and the formation of single crystalline α-Fe2O3 nanocubes, we have performed a time-dependent observation of the crystal growth in FeCl₃ solution under hydrothermal conditions at 180 °C. We have withdrawn samples from the reaction solution at various intervals (4 h, 6 h, 8 h, 10 h, and 12 h). A series of TEM images of the as-prepared samples are presented in Fig. 1a–e. Continuous formation towards the proper arrangement of α-Fe2O3 nanocubes from 0-D quantum dots to 3-D cubic shapes was observed throughout the heating process starting from the 4th hour until the 8th hour at a constant temperature of 180 °C. At the 4th hour, it was clear that a large number of quantum dots with a particle size ranging from 2 to 5 nm were synthesized (Fig. 1a). Many tiny spots with a clear contrast difference in each spherical particle were acquired. A closer inspection of a selected particle reveals that the interplanar distance of 2.05 Å belongs to the (202) plane of α-Fe2O3, as depicted in Fig. 1f. The corresponding selected area electron diffraction (SAED) ring patterns together with the intensity profile (Fig. 1k) of the spherical α-Fe2O₃ particle also reveal a set of diffraction spots of (104), (110), (006), (024), (116) and (300) planes. As the SAED pattern can provide the internal crystal information of the whole particle, it can thus be concluded that the quantum dots are of α-Fe2O₃ primary particles while no detectable amounts of impurity were produced. After 6 h, these individual particles started to undergo coalescence and spontaneously aggregated into a larger size of particle to form a cluster. The corresponding d-spacing values of (012) planes obtained from different individual particles (Fig. 1g) reveal that the cluster is indeed composed of α-Fe2O₃ primary...
nanoparticles by attaching intimately with each other. Thus, these interconnected particles can serve as building blocks for the transformation of nanocrystals into various shapes and sizes during the later development. When the hydrothermal heating duration is further prolonged to 8 h, a distinctive cubic crystal with an edge length of \( \sim 40 \) nm was obtained and is represented by TEM microscopy in Fig. 1c. Each individual crystal appears to be a well-defined cubical shape and it is found to be attached at the flat edges to its adjacent crystal. This preferential arrangement minimizes the total surface energy as well as surface area of the as-synthesis single crystal \( \alpha{-}\text{Fe}_{2}\text{O}_{3} \) nanocubes.\(^{50,51} \) The HRTEM image (Fig. 1h) and SAED pattern (Fig. 1m) of the selected region, respectively, confirms the presence of \( \alpha{-}\text{Fe}_{2}\text{O}_{3} \). It is noteworthy that the diffraction pattern of this sample displays many individual spots indicating the as-synthesized nanocubes are of highly crystalline \( \alpha{-}\text{Fe}_{2}\text{O}_{3} \). Intriguingly, with the increase of reaction time up to 10 h, the cubical shape of \( \alpha{-}\text{Fe}_{2}\text{O}_{3} \) is no longer observed and a lot of particles with sizes ranging from \( 7{-}15 \) nm start to form and the irregularity of their structure can be seen in Fig. 1d. The HRTEM image (Fig. 1i) and the SAED pattern (Fig. 1n) display the mixture of different phases that can be found in this sample. The calculated \( d \)-spacing values of 4.78 \( \text{Å} \) and 3.78 \( \text{Å} \) can be ascribed to (111) and (210) planes of maghemite (\( \gamma{-}\text{Fe}_{2}\text{O}_{3} \)). Further increments of the reaction time (up to 12 h) cause the particles to undergo dissolution whereby the bigger crystals begin to deform and a smaller size of nanocrystals with an irregular shape are seen such as in Fig. 1e. Similarly, we found the presence of a \( \gamma{-}\text{Fe}_{2}\text{O}_{3} \) phase traceable through the \( d \)-spacing calculation of the selected particle in Fig. 1j and the indexed SAED pattern (Fig. 1o). The above results indicate that the morphology of \( \alpha{-}\text{Fe}_{2}\text{O}_{3} \) nanocrystals can be easily tuned and the nanocubic crystal structure is obtainable by simply adjusting the reaction time at fixed temperature in this facile one-pot procedure.

The composition and phase purity of the as-prepared samples were further elucidated by powder XRD technique. Fig. 2 shows the evolution of the iron oxide phase and crystallinity changes by analyzing the \( \alpha{-}\text{Fe}_{2}\text{O}_{3} \) nanostructures that were hydrothermally treated from 4 h to 12 h (Fig. 2a–e). Crystalline \( \alpha{-}\text{Fe}_{2}\text{O}_{3} \) rhombohedral structures were observed at the early stage of the hydrothermal heating process from 4 h to 8 h. (JCPDS: 33-0664). It can be seen that all of the peaks can be indexed as rhombohedral \( \alpha{-}\text{Fe}_{2}\text{O}_{3} \) (\( a = 5.035 \text{Å} \) and \( c = 13.747 \text{Å} \)) with JCPDS: 33-0664. Distinctively, the \( \alpha{-}\text{Fe}_{2}\text{O}_{3} \) nanocubes produced at 8 h show the strongest diffraction peaks at \( \sim 24.11^\circ \), \( 33.16^\circ \) and \( 35.62^\circ \) indicating excellent crystallinity of the \( \alpha{-}\text{Fe}_{2}\text{O}_{3} \) phase produced in the nanocubes. In particular, we have performed a crystallographic calculation and the formula is given in eqn (1) as below. The lattice constants obtained mainly for \( \alpha{-}\text{Fe}_{2}\text{O}_{3} \) nanocubes are \( a = 5.0240 \)
Å and $c = 13.7180$ Å, which agrees well with the rhombohedral $\alpha$-Fe$_2$O$_3$.

$$d^2 = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right)$$  \(1\)

where $d$ is the $d$-spacing of the hexagonal crystal structure, $a$ and $c$ are the lattice constants, and $(hkl)$ is the crystal plane of $(012)$ and $(104)$. Furthermore, if the reaction duration is increased to $10$ h and $12$ h (Fig. 2d and e, respectively), the phase of the products changes from $\alpha$-Fe$_2$O$_3$ to $\gamma$-Fe$_2$O$_3$, which is evidenced from the appearance of peaks at $\sim 30.24^\circ$ and $\sim 57.19^\circ$ (marked with grey dotted lines) and are consistent with JCPDS: 39-1346 of $\gamma$-Fe$_2$O$_3$. These results are also in agreement with the TEM microscopic images shown in Fig. 1d and e, in which the shape of the product turns irregular (at $10$ h and $12$ h).

A possible formation mechanism of the as-prepared $\alpha$-Fe$_2$O$_3$ nanocubes and their morphological evolution is tentatively proposed, as shown in Fig. 3. Initially, FeCl$_3$ precursor in the reactant mixture was first hydrolyzed in the presence of water and undergoes dissolution with ethanol, producing a large number of Fe$^{3+}$ ions (Fig. 3a). During the first $4$ h, these ions nucleate into primary $\alpha$-Fe$_2$O$_3$ quantum dots (Fig. 3b) attributed to the dissolution–recrystallization process and continuous growth via Ostwald ripening. The crystal growth is caused by effective coarsening at which the nucleation of the particle has taken place. The chemical reactions involved in this stage can be referred to as follows:

$$\text{Fe}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \quad (2)$$

$$2\text{Fe(OH)}_3 \leftrightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (3)$$

The OH$^-$ anions serve as a bridging agent facilitating the formation of the Fe–O–Fe skeleton. These tiny 0-D $\alpha$-Fe$_2$O$_3$ quantum dots could be temporarily stabilized by oleate ions and form coordination complexes with oleylamine (OAm). As time goes on (6th hour), the OAm coordinated $\alpha$-Fe$_2$O$_3$ quantum dots will subsequently grow at the expense of Fe$^{3+}$ ions.

Fig. 2 XRD patterns of as-synthesized $\alpha$-Fe$_2$O$_3$ nanocrystal prepared at 180 °C for (a) $4$ h, (b) $6$ h, (c) $8$ h, (d) $10$ h, (e) $12$ h.

Fig. 3 Growth mechanism of $\alpha$-Fe$_2$O$_3$ nanocubes and time-dependent shape evolutionary process under hydrothermal conditions at 180 °C from (a–e) 4–12 h.
from the solution and aggregation is thus promoted. The non-aggregated quantum dots, on the other hand, will grow independently of each other, slowly consuming the smaller \( \alpha{-}\text{Fe}_2\text{O}_3 \) particles. With the increase of reaction time, the size of aggregated particles will become a cluster (Fig. 3c). During this stage, it is believed that the \( \alpha{-}\text{Fe}_2\text{O}_3 \) nanocrystals collide with each other and attach together by sharing a common crystallographic orientation in the initial product. This so-called topotaxial replacement\(^{24}\) is the key transformation of \( \alpha{-}\text{Fe}_2\text{O}_3 \) clusters into a nanocuboid shape through localized conversion of single crystals into one or more nanocrystals with definite axes of symmetry. It is noteworthy that during the occurrence of this event, the fusion of \( \alpha{-}\text{Fe}_2\text{O}_3 \) nanocrystals into clusters may be rationalized by lowering the surface energy along the [001] direction and thus promote the growth along the [001] plane. The following growth process from 6 h to 8 h is indeed quite interesting. In contrast, the growth of crystals into a nanocuboid system is a complicated process, for the sake of understanding the growth mechanism of nanocubes, we have performed sample withdrawal taken from the oven at every two hours for post-reaction characterization via TEM technique. In the growth of nanocrystals, different facets grow at different rates. It is believed that the high-energy facets grow to a greater extent than the low-energy facets causing the nanocrystals to be terminated with low-energy facets. One can say that the final crystal shape is strongly dependent by the slow-growing facets and the shapes of the energy minima.\(^{55-57}\) In the present study, OAm and potassium oleate were used as the capping agents to inhibit the formation of Fe–O–Fe bonds owing to the strong covalent interaction between the oleate anions and positively charged Fe\(^{3+}\) centers with some atomic configuration occurring on the nanocrystal surfaces. In our case, crystal growth takes place along \{102\}, \{112\} and \{012\} surfaces and its equivalent direction.\(^{58-60}\) This means that the OAm moiety controls growth on these three facets (Fig. 3d). At this hour, the \{012\} facet and its equivalent surface grew to become exposed. As the duration of the reaction was further prolonged to 10 h, nanocrystals of irregular shape started to form due to a greater number of high energy surfaces being exposed (Fig. 3e). As a result, there is a competing crystal growth from different facets at different rates causing this irregularity. We believed that some OAm by now are selectively bonded to certain crystal facets leaving the exposed facets continuous to grow. On the basis of the results shown in Fig. 3i and j, it is also important to note that starting from 10 h to 12 h (Fig. 3e and f), one can observe the presence of \( \gamma{-}\text{Fe}_2\text{O}_3 \) in the samples indicating there is also a phase transformation event taking place. The transformation from \( \alpha{-}\text{Fe}_2\text{O}_3 \) to \( \gamma{-}\text{Fe}_2\text{O}_3 \) has been well-studied and is governed by the nature of the precursor concentration, pH, temperature, and other synthetic conditions. Phase transformation from \( \alpha{-}\text{Fe}_2\text{O}_3 \) to \( \gamma{-}\text{Fe}_2\text{O}_3 \) is favoured when \( \alpha{-}\text{Fe}_2\text{O}_3 \) reaches a critical size at which the combined bulk particles and surface Gibbs free energy of the \( \gamma{-}\text{Fe}_2\text{O}_3 \) is greater than that of \( \alpha{-}\text{Fe}_2\text{O}_3 \) particles.\(^{61}\)

In order to clarify the construction of \( \alpha{-}\text{Fe}_2\text{O}_3 \) nanocubes, the nanocrystals obtained at 8 h of the reaction process were collected and characterized in detail by electron microscopy. The representative FESEM image that was projected from the top view in order to obtain the three-dimensional nature of the \( \alpha{-}\text{Fe}_2\text{O}_3 \) crystals is shown in Fig. 4a. Inset of Fig. 4a depicts only a single crystalline \( \alpha{-}\text{Fe}_2\text{O}_3 \) nanocube with the edge length of \( \sim 40 \text{ nm} \). In addition, Fig. 4b and c represent the TEM images of the \( \alpha{-}\text{Fe}_2\text{O}_3 \) nanocubes demonstrating that the products are all cubic in shape with no other morphology observed. The typical nanocubes of uniform size are seen throughout the specimen indicating high monodispersity. Each nanocube has a distinct flat-edge with an average edge-length of 40 nm and the surfaces that are viewed perpendicular to the direction of incident electron beam appear to be faceted. The statistical edge length distribution is illustrated in Fig. 4b. The tendency for the formation of well-faceted nanostructures that are consistent in shape is attributed to the surface energy minimization.\(^{57}\) The HRTEM image shown in Fig. 4d with the lattice spacing is measured to be 0.37 nm, corresponding to the (012) plane. It could be seen that these nanocubes have an interfacial dihedral angle of 86\(^\circ\). Fig. 4e shows a fast Fourier transformation (FFT) pattern, which is obtained from the region in Fig. 4d. By examining Fig. 4e, we can also observe from the FFT that the diffraction spots are attributed to (006), (112), (202) and (012) lattice spots, along the \( [421\bar{1}] \) zone axis which is representative of the area marked with a yellow square.\(^{45}\) The analysis reveals the single crystalline nature of the \( \alpha{-}\text{Fe}_2\text{O}_3 \) nanocrystals, being nanocuboidal in shape.\(^{62,63}\) Based on the above analysis, the 3D geometrical structure of the nanocube is drawn in Fig. 4f. The nanocube is enclosed by two \{102\}, two \{012\}, and two \{112\} exposed facets.

SEM coupled with EDXA was employed to highlight the different chemical elements present in the synthesized powder of \( \alpha{-}\text{Fe}_2\text{O}_3 \) nanocuboid structures and the results are depicted in Fig. 4g–j. The wt% and at% of the constituents of the sample, respectively, are shown in the table enclosed in the EDX spectrum. The presence of Fe and O components in EDXA confirms the formation of the desired material. EDX analysis has also shown the presence of C and Cu peaks in addition to Fe and O peaks. The existence of a C peak at \( \sim 0.2 \text{ keV} \) in the EDX spectrum is primarily due to the carbon tape that was used for holding the sample during the SEM and EDXA measurements. The average at% formation of Fe and O in \( \alpha{-}\text{Fe}_2\text{O}_3 \) nanocubic structures is 38.08% and 61.92%, respectively. This result confirms that the O/Fe at% ratio of the \( \alpha{-}\text{Fe}_2\text{O}_3 \) nanocubes analyzed is calculated to be 1.63, which is relatively consistent with the theoretical O/Fe atomic ratio of 1.50 for the \( \alpha{-}\text{Fe}_2\text{O}_3 \). On the other hand, the elemental mapping images clearly depict that the distribution for both Fe and O is highly uniform throughout the sample.

In addition to FESEM and TEM analyses, Raman spectroscopy has been performed to give further insight into the quality and crystal phase of \( \alpha{-}\text{Fe}_2\text{O}_3 \) nanocubes. It is an
established, simple and most direct tool to distinguish iron oxide polymorphs, which consist of α-Fe₂O₃, β-Fe₂O₃, γ-Fe₂O₃ and ε-Fe₂O₃; as well as other impurities. A representative Raman spectrum of the as-synthesized single crystalline α-Fe₂O₃ nanocubes and commercial α-Fe₂O₃ is presented in Fig. 5. No peaks associated with any impurities can be observed. By adopting the spectral signature band of typical α-Fe₂O₃ in Table 1 to the present study, it is perceptible that the value of Raman peaks obtained for both commercial and single crystal α-Fe₂O₃ nanocubes are shifted towards lower wavenumbers. However, on the whole, one can see that the spectrum is correlated with the commercial α-Fe₂O₃ nanoparticles reference spectrum. Typical α-Fe₂O₃ signature bands can be observed in the region of 150 to 800 cm⁻¹. Typically,
there are two classes of Raman-active vibrational modes (A\textsubscript{1g} modes and E\textsubscript{g} modes) which can be observed at 200 to 700 cm\textsuperscript{-1}, attributed to the appearance of the major α-Fe\textsubscript{2}O\textsubscript{3} characteristic within these bands.\textsuperscript{67} The values of the spectral signature peaks deemed to be characteristic of typical α-Fe\textsubscript{2}O\textsubscript{3} are presented in Table 1. Significant points of the apparent spectra are as follows: due to the fact that Fe atoms are much heavier than O atoms, peak lines between 200 and 300 cm\textsuperscript{-1} are Fe atom vibrations. Meanwhile, bands between 350 to 600 cm\textsuperscript{-1} are due to O atom vibrations. Further elucidation describes the A\textsubscript{1g} band at 212 cm\textsuperscript{-1} to be assigned to movements of ion cations along the c-axis while the E\textsubscript{g} mode at 384 cm\textsuperscript{-1} is assigned to the symmetric breathing mode of the O atoms relative to each cation in the plane perpendicular to the crystallographic c-axis.\textsuperscript{68} The red shift of the Raman lines for both commercial and single crystal α-Fe\textsubscript{2}O\textsubscript{3} nanocubes was reported to be due to heating during the Raman scanning process.\textsuperscript{69} A laser source of 514 nm was used; higher laser energy that highly focused on the surface of the samples could induce an increase in temperature. The high activation energy projected on to the surface of the particles could cause dehydration that consequently increases the interfacial energy of commercial and single crystalline α-Fe\textsubscript{2}O\textsubscript{3} nanocubes.

XPS analysis was then conducted to precisely identify the chemical purity, estimated binding energy (BE) and chemical structure of single crystalline α-Fe\textsubscript{2}O\textsubscript{3}. Fig. 6a depicts a wide scan spectrum recorded in the BE ranged from 0 to 550 eV. The C1s spectra contain peaks originating from various oxygen species (–COH, –COOH, CO\textsubscript{3}\textsuperscript{2–}) in addition to aliphatic hydrocarbons.\textsuperscript{70} Specifically, distinct peaks allocated as Fe3p and O1s have been observed in the range of 46 to 64 eV and 521 to 541 eV, respectively. The spectra obtained are shown in Fig. 6b and c. The peak position corresponding to Fe3p is located at 55.2 eV. On the other hand, there are three peaks fitted in the O1s spectra. The peaks are positioned at 530.0, 531.4 and 533.3 eV. The peak at 530.0 eV is due to the α-Fe\textsubscript{2}O\textsubscript{3}. The peak at 531.4 eV is in accordance to OH surface groups of the iron oxide and the peak at 533.3 eV is assigned to be carbon-based ligands.\textsuperscript{71} Therefore, it is worth noting that no impurities were detected except for carbon-based compounds that are inevitably present due to the amine capping ligand used for the synthesis of single crystalline α-Fe\textsubscript{2}O\textsubscript{3} nanocubes.

UV-vis spectrophotometry was used to study the optical absorption properties of single crystal α-Fe\textsubscript{2}O\textsubscript{3} nanocubes at room temperature. Fig. 7a shows an absorption spectrum of single crystal α-Fe\textsubscript{2}O\textsubscript{3} nanocubes within the near UV and visible region from 250–1100 nm. Noticeably, three peaks have been identified, which fall within the range of far UV (250–300 nm) and the visible region (425–500 nm and 520–650 nm). In order to explain both of these absorption phenomena, a molecular orbital theory called the ligand field model that describes the bonding, orbital arrangement and other characteristics of coordination complex was employed.\textsuperscript{72} In general, the band assignments of these absorption spectra can be made using this ligand field theory. According to Sherman et al. (1985), it is well-established that there are three types of electronic transition inclusive of Fe\textsuperscript{3+} ligand field or d–d transitions, pair excitation or double exciton processes and ligand-to-metal charge transitions (LMCT).\textsuperscript{73} In general, the ligand field transition parameter is the orbital energy separation between two sets of Fe (3d) orbitals or the crystal field splitting.

As shown in Fig. 7b, the region including 250–300 nm can be mainly assigned to LMCT since the energy of the transition during the photoexcitation process is greater than 4.59 eV (λ = 270 nm). At this transition energy, charge transfer may occur from the non-bonding ligand molecular orbitals (O2p) to the antibonding partially filled metal d-orbitals (Fe3d).\textsuperscript{74} On the other hand, the second absorption region (Fig. 7c) that lies in the range of 425–500 nm can be ascribed to ligand field transitions of Fe\textsuperscript{3+}, which can be assigned to A\textsubscript{1g} → E\textsubscript{i}, A\textsubscript{1g} (E\textsubscript{g}).\textsuperscript{73} The transition of the ground state (A\textsubscript{1g}) within the crystal structure can take place with only two conditions. Firstly, the Fe\textsuperscript{3+} ions species must be present. Secondly, there must be formation of binuclear inorganic

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**Table 1** Band positions, corresponding intensities and assignments in the Raman spectra of typical hematite, commercial α-Fe\textsubscript{2}O\textsubscript{3} and as-synthesized single crystal α-Fe\textsubscript{2}O\textsubscript{3} nanocubes

<table>
<thead>
<tr>
<th>Typical Raman shift (cm\textsuperscript{-1})</th>
<th>Raman shift of commercial α-Fe\textsubscript{2}O\textsubscript{3} (cm\textsuperscript{-1})</th>
<th>Raman shift of as-synthesized α-Fe\textsubscript{2}O\textsubscript{3} (cm\textsuperscript{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>225</td>
<td>195</td>
<td>212</td>
<td>A\textsubscript{1g}</td>
</tr>
<tr>
<td>247</td>
<td>274</td>
<td>274</td>
<td>E\textsubscript{g}</td>
</tr>
<tr>
<td>412</td>
<td>388</td>
<td>384</td>
<td>E\textsubscript{g}</td>
</tr>
<tr>
<td>498</td>
<td>486</td>
<td>472</td>
<td>A\textsubscript{1g}</td>
</tr>
<tr>
<td>613</td>
<td>591</td>
<td>589</td>
<td>E\textsubscript{g}</td>
</tr>
<tr>
<td>824</td>
<td>804</td>
<td>800</td>
<td>Hematite</td>
</tr>
</tbody>
</table>
complexes through the magnetic coupling of electronic spins of the next-nearest neighbour Fe$^{3+}$ cations. With respect to the region between 520–650 nm, the transitions are caused by ‘double exciton processes’ that involves strongly coupled Fe$^{3+}$ cations rather than single Fe$^{3+}$ cations as stated by the spectroscopic selection rule.\textsuperscript{75} The excitations of Fe$^{3+}$–Fe$^{3+}$ pairs are attributed to the sum of two single ion Fe$^{3+}$ ligand field transitions that can be assigned to $^6A_1 + ^6A_1 \rightarrow ^4T_1 (^4G) + ^4T_1 (^4G)$.\textsuperscript{73} Regarding the trend of the absorbance characteristics, the ‘double exciton processes’ triggers the progressively-steep onset absorption from the wavelength of 770 nm and results in the strongest absorption in the region of 520–650 nm. The peak (571 nm) within this region is highest among the three interband transitions observed. Such a steep absorption edge in the visible range of 580–770 nm is responsible for the reddish colour of the as-synthesized single crystal $\alpha$-Fe$_2$O$_3$ nanocubes (inset of Fig. 7a), which is consistent with literature reports.\textsuperscript{73–76} The determination of the bandgap for $\alpha$-Fe$_2$O$_3$ nanocubes from spectroscopic absorbance measurements ($\alpha h\nu$)$^{1/2}$ is plotted against the photon energy as represented in Fig. 7d. Typically, the bandgap energy was calculated from the absorbance ($\alpha h\nu$) data of $\alpha$-Fe$_2$O$_3$ recorded in the wavelength range of 250–1100 nm using the Tauc relation;

$$\alpha h\nu = A_0(h\nu - E_g)^n$$

where,

$$A_0 = \left[\frac{e^2}{n\hbar^2m_e}\right](2m_e)^{3/2}$$

Here, $\alpha$ is the measured absorption coefficient (cm$^{-1}$) near the absorption edge, $A_0$ is a constant, $h\nu$ is the photon energy (eV), $E_g$ is the optical band (eV), $n$ is a constant. The value of $n$ is determined from the nature of the optical transition $n = 1/2$ or 2 for direct allowed and indirect allowed transitions, respectively. $m_e^*$ and $m_e$ are the effective and reduced masses of the charge carriers, respectively. The indirect bandgap energy was determined by extra-plotting the linear fit to the experimental data to zero absorbance. Hematite has an indirect bandgap and thus we have determined its indirect bandgap energies by plotting ($\alpha h\nu$)$^{1/2}$ versus the photon energy for $\alpha$-Fe$_2$O$_3$, respectively. The size of the bandgap is calculated to be $\sim 2.1$ eV, which is correlated to the literature reported value.\textsuperscript{77,78} Fig. 7e explains the indirect transition in the parabolic nature of the bands close to the band edges of $\alpha$-Fe$_2$O$_3$ pictorially. Briefly, the incoming photons (visible light) with energy in excess of the bandgap are readily absorbed, as they are likely to have enough energy to excite electrons from the band edges. For an allowed indirect bandgap semiconductor, the valence band energy peak and conduction band energy minimum occur at two different momentums. Thus, the electrons must undergo a change in momentum in addition to photon absorption in order to be fully excited into the conduction band and subsequently fall back to the valence band via a dissipation of energy in the form of a photon.
Fig. 8 depicts the photoluminescence (PL) spectra of the nanocubes and commercial \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticles as standard reference for comparison. Intriguingly, the nanocubes only exhibit a single photoemission peak centered at around 590 nm, whereas the commercial sample displays 6 peaks (434, 468, 591, 722, 844 and 892 nm). Basically, for the small \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticles with dimensions less than 20 nm only the PL phenomenon is observable due to the quantum confinement effect.\(^{79}\) In contrast, bulk \( \alpha \)-Fe\(_2\)O\(_3\) with dimensions greater than 70 nm do not exhibit prominent PL since the optical transition is forbidden.\(^{80}\) In a current study, the nanocubes appear to have dimensions of 40 nm that lies between the small and bulk sizes, where the effect of size still needs to be considered. According to Fu et al. (2004), the sub-nanometer geometry of our nanocubes also possibly increases the Fe–O bonding separation, resulting in an enhancement of the magnetic coupling of the neighbouring Fe\(^{3+}\), which is responsible for the PL of \( \alpha \)-Fe\(_2\)O\(_3\) nanoparticle.\(^{81}\) In other words, nanocubes with dimensions greater than that of the smaller nanoparticles give smaller Racah parameters which weaken the neighboring covalency more than those of smaller particles.\(^{82}\) This finally leads to the red shift of the emission band. The single broad PL peak emitted by the as-synthesized nanocubes suggests that the sample has
single crystalline properties, having no grain boundaries compared to commercial $\alpha$-$\text{Fe}_2\text{O}_3$ nanostructures.

4.0 Conclusion

Single crystal nanometer-sized rhombohedral $\alpha$-$\text{Fe}_2\text{O}_3$ cubic particles were successfully synthesized by a facile one-pot hydrothermal method at 180 °C for several hours to study the morphological, structural and optical properties of the as-synthesized sample in details. By varying the hydrothermal heating duration from 4 h to 12 h, it was concluded that the 8 h hydrothermal heating duration is the optimum for formation of a high quality single crystal $\alpha$-$\text{Fe}_2\text{O}_3$ cubic structure. For the 8th hour of hydrothermal treatment, the as-prepared $\alpha$-$\text{Fe}_2\text{O}_3$ comprises numerous cubes with an average edge length of 40 nm and shows characteristics of a single crystal structure. The cubic formation was interpreted along the diagonal [421] zone axis. The cubes were enclosed by a (012), (112) and (102) planes with an angle of 86°. The existence of $\text{Fe}^{3+}$-oxo complexes in single crystal $\alpha$-$\text{Fe}_2\text{O}_3$ nanocubes as observed by Raman spectroscopy, was not present in commercial $\alpha$-$\text{Fe}_2\text{O}_3$. The PL emission of single crystal $\alpha$-$\text{Fe}_2\text{O}_3$ nanocubes confirms the single crystal characteristics with no grain boundaries. PL emission spectrum also supports the fact that cubic single crystal $\alpha$-$\text{Fe}_2\text{O}_3$ contains $\text{Fe}^{3+}$ ions and binuclear inorganic complexes which allowed the optical indirect transitions to occur with the existence of magnetic coupling of electronic spins of next-nearest neighbour $\text{Fe}^{3+}$ cations in the crystal structure. The transition is thus supported by UV-vis spectrophotometry.

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References