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Morphology and crystal structure control of α -Fe₂O₃ films by hydrothermal-electrochemical deposition in the presence of Ce³⁺ and/or acetate, F[−] ions

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Hydrothermal-electrochemical growth of Hematite (α -Fe₂O₃) thin films in the presence of Ce³⁺ and/or CH₃COO[−] and F[−] ions is reported. Primary attention is paid to understanding the synergistic effect of temperature and additive ions on the growth of Hematite particles. The literature describes the shape-controlled electrodeposition of iron oxide films, but these reports involve low-temperature depositions (<100 °C) that require a post-annealing step to obtain the Hematite phase. We studied size and shape control of Hematite crystals by introducing capping agents during hydrothermal-electrochemical deposition (HED) at 130 °C under autonomous pressure. When HED is used together with growth-modifying species such as CH₃COO[−] and/or Ce³⁺, Hematite thin films with various structures including spherical, rhombohedral and platelet-like particles were obtained which were crystallized directly in the α -Fe₂O₃ phase without thermal annealing. In contrast, either Lepidocrocite or an amorphous phase forms with low-temperature electrodeposition under otherwise identical conditions. Addition of F[−] into the deposition solution induces formation of bundles that are composed of square planar Akaganeite particles even during HED. The aspect ratio of the Akaganeite particles is controlled with co-addition of Ce³⁺ ions. This variety of nanostructures gives us the opportunity to evaluate the photoelectrochemical performance of the α -Fe₂O₃ films based on particle size and shape. It was demonstrated that porous, square planar α -Fe₂O₃ with a high aspect ratio shows the highest performance.

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Introduction

There is a great interest in obtaining advanced materials with altered morphologies, since often shape and size are as crucial as crystal structure in determining the performance.^{1–3} Particularly, controlling the shape-guiding process during electrodeposition attracts interest since uniform and distinct morphologies in large scales with remarkable reliability and ease can be produced by a cheap and eco-friendly process. Furthermore, various semiconductor metal oxides and metallic crystals can be deposited directly on a conducting substrate which can be integrated into opto-electrical devices easily.^{4–6}

Hematite (α -Fe₂O₃), an *n*-type semiconductor ($E_g \sim 2.2$ eV), is the most thermodynamically stable phase of iron oxide. It has been extensively investigated for its use in medicine, catalysts, magnetic recording media, pigments, anticorrosive agents, gas sensors, electrochemical capacitors, and photoelectrochemical

cells; owing to its nontoxicity, low processing costs, high resistance to corrosion and absorption range which includes a considerable portion of solar energy.^{7,8} To date, well-defined nanostructures of iron oxides with different morphologies such as nanoparticles, nanorods, nanowires, nanotubes, nanorings, nanoflowers, nanocubes, as well as hollow and porous nanostructures have been obtained in an effort to study and understand how size and shape effect their performances in a wide range of applications such as gas sensors, electrode materials in lithium secondary batteries, catalysts, magnetic recording media, photocatalysis and water splitting.^{1,9–14} Mostly, solution based techniques including hydrothermal approach, sol-gel and forced hydrolysis are preferred for the controlled nanostructure growth.^{1,9,10,14–17}

Electrodeposition, on the other hand, offers a high degree of freedom in manipulating and monitoring the crystal growth processes *via* deposition potential, current, temperature, precursor concentration and additives. Both cathodic or anodic electrodepositions of α -Fe₂O₃ from aqueous solutions are reported to date and they require post-annealing process to produce Hematite from an iron oxyhydroxide phase.^{18–21} Mostly, cathodic electrodeposition route introduced by Schrebler *et al.* which is based on electrochemical generation of OH[−] ions by

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reduction of H_2O_2 in a solution containing Fe^{3+} ions, is used to electrochemically produce Hematite films.¹⁸ The resulting pH increase in the close proximity of the working electrode causes iron oxyhydroxide precipitation. Produced $\beta\text{-FeOOH}$ is then converted to Hematite phase and generally oval, round, globular particles are produced.^{18,22–25} It has been reported that well-faceted polyhedral Magnetite (Fe_3O_4) crystallites, Goethite ($\alpha\text{-FeOOH}$) layers composed of rhombohedral columns and lath-like Lepidocrocite ($\gamma\text{-FeOOH}$) crystals can be obtained by increasing the potential from -0.4 V to 1.0 V (vs. Ag/AgCl) from aqueous solutions containing $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and CH_3COOK ($\text{pH} = 6$) at 90°C .²⁶ In addition, nano-crystalline Hematite ($\alpha\text{-Fe}_2\text{O}_3$) film with nano-petal morphology was prepared using pulse reverse electrodeposition including cathodic and anodic pulses.²⁷ Shape-controlled preparation of $\alpha\text{-FeOOH}$ films through an anodic electrodeposition route is also reported with CH_3COO^- , NH_4F , and pyridine as capping agent.²⁸ After heat treatment Hematite particles of various morphologies were obtained including platelets, rhombohedral rods, square rods, six-fold snowflakes, and hexagonal particles.

It is known that the oxidation rate, concentration of the reagents, pH, temperature and other additives (anions or cations) present in the system, are the essential factors in determining the phase and shape of the Fe-oxide/hydroxide during the oxidation of aqueous ferrous systems.⁷ Therefore understanding the effect of these factors on the phase and shape control is required. Although literature describes shape-controlled electrodeposition of iron oxide films, the reported temperatures for electrochemical deposition range between 60 and 90°C below 100°C which is the limit for aqueous reactions. Recently, we have shown that a combination of hydrothermal and electrochemical methods (130°C , ~ 2 bar) enables the production of crystalline $\alpha\text{-Fe}_2\text{O}_3$ phase without thermal annealing as opposed to electrodepositions reported at ambient conditions.²⁹ Morphology control during hydrothermal-electrochemical deposition (HED) of iron oxide films have not been investigated so far.

Usually effect of organic additives and inorganic anions on the shape of $\alpha\text{-Fe}_2\text{O}_3$ have been studied while there are relatively few reports about controlling the morphology of nanostructures with cations. Recently, cation-assisted hydrothermal synthesis of $\alpha\text{-Fe}_2\text{O}_3$ crystals has been reported. Presence of Al^{3+} ions in the growth solution induced formation of Hematite nanoplates.³⁰ Quasi-cubic and hexagonal bipyramid $\alpha\text{-Fe}_2\text{O}_3$ polyhedrons were synthesized by applying metal ions Zn^{2+} , alkali earth metals or Cu^{2+} as growth modifying ions.^{14,31} Diverse adsorption properties of different metal ions on the different planes of Hematite would lead to the formation of various $\alpha\text{-Fe}_2\text{O}_3$ morphologies.

In this report, we investigated the influence of the Ce^{3+} cation, CH_3COO^- and F^- ions on crystal structure, particle shape and size of the end product during iron oxide/hydroxide HED and electrodeposition under ambient conditions. It is shown that temperature is a key parameter in determining crystalline phase of iron oxides. HED (except F^- -assisted growth) directly produced Hematite crystals, whereas morphology and particle size of these crystals are determined

with a synergistic effect of growth-modifying ions present in the deposition solution and temperature. Shape dependent photo-electrochemical properties of the Hematite particles were also evaluated. All of the nanostructures are photoactive. It was found that porous, square planar Hematite particles with high aspect ratio show higher performances than nanoplatelets and rhombohedral particles. Hence, HED provides a facile, low-cost synthesis for $\alpha\text{-Fe}_2\text{O}_3$ nanostructures as potential advanced materials for photoelectrochemical catalysis.

Experimental

Materials

Iron(II) chloride hexahydrate ($\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, 99% purity) was purchased from Sigma-Aldrich. Sodium acetate (NaCH_3COO , NaAc) was obtained from Merck. Indium tin oxide (ITO) ($\Omega < 5.0 \times 10^{-4}$ ohm cm, $R_s < 100$ ohm sq^{-1}) was purchased from Teknoma Ltd. Izmir, Turkey. Double distilled, high purity water was used from Milli-Q water (Millipore) system.

Synthesis and characterization

Potentiostatic electrodepositions were carried out at 75°C with a conventional 3-electrode cell system where ITO (indium tin oxide) coated glass was the working electrode, Ag/AgCl saturated with KCl was reference electrode and Pt was the counter electrode. The depositions at higher temperature (130°C) were performed in a modified glass reactor (Büchiglasuster, pico-clave; where pressure autonomously increases to $2.0\text{--}2.5$ bar at 130°C) at constant potential. The reference electrode was Ag/AgCl saturated with KCl (Corr Instruments, S/N P11092) whereas Pt wire served as counter electrode. Both acidic and neutral plating solutions were used for the anodic depositions at 1.2 V (vs. Ag/AgCl (satd)).³² Acidic plating solution contained 0.02 M FeCl_2 ($\text{pH} = 3.8$) and neutral plating solution consisted of 0.02 M FeCl_2 and 0.08 M NaCH_3COO or 0.08 M NaF ($\text{pH} = 6.2\text{--}6.8$) with different amount of cerium salt. Calcinations were performed at 520°C for 30 minutes when required to obtain the desired crystallinity or phase. Reaction parameters are summarized in Table 1. The crystal structure and crystallinity of the thin films were analyzed by Bruker D8 Discover with DaVinci X-ray diffractometer (XRD). ZEISS Ultraplus Field Emission Scanning Electron Microscope (FE-SEM) was used to study the surface morphology of the samples. Film composition was examined by X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha). Raman scattering experiments were carried out using a Renishaw Raman Microscope system at room temperature. A 633 nm laser beam was focused on the samples. Phase transformations from FeO to Fe_3O_4 , from Fe_3O_4 directly to $\alpha\text{-Fe}_2\text{O}_3$ (martitization)³³ and from Fe_3O_4 first to $\gamma\text{-Fe}_2\text{O}_3$ then to $\alpha\text{-Fe}_2\text{O}_3$ (ref. 34) are reported for iron oxide films during Raman scattering at high laser powers. Hence sacrificial films were first excited at different laser powers to determine a threshold power so that no phase transformations take place and high enough power is supplied for reasonable signal-to-noise ratio. Laser power of 1.2 mW was determined to be a safe limit. Spectra were taken over a range from wavenumbers 200 cm^{-1} to 1500 cm^{-1} .

Table 1 Reaction variables for hydrothermal-electrochemical deposition at 1.2 V vs. Ag/AgCl (satd) for 8 min

Film	[Fe ²⁺]	[NaAc]	[Ce ³⁺]	[NaF]	Deposition temperature	Phase	Morphology
H1	0.02 M	—	—	—	75 °C	Amorphous	No particular shape
H2	0.02 M	—	0.002 M	—	75 °C	Amorphous	No particular shape
H3 ^a	0.02 M	—	—	—	130 °C	Hematite	Monodisperse polyhedra
H4	0.02 M	—	0.002 M	—	130 °C	Hematite	Polydisperse polyhedra (<i>d</i> ~ μm range)
H5	0.02 M	—	0.01 M	—	130 °C	Hematite	Polydisperse polyhedra (<i>d</i> ~ nm range)
H6	0.02 M	0.08 M	—	—	75 °C	Lepidocrocite	No particular shape
H7	0.02 M	0.08 M	0.002 M	—	75 °C	Lepidocrocite	Platelets
H8 ^a	0.02 M	0.08 M	—	—	130 °C	Hematite	Polyhedra
H9	0.02 M	0.08 M	0.002 M	—	130 °C	Hematite	Platelets
H10	0.02 M	—	—	0.08 M	130 °C	Akaganeite	Square planar particles (<i>a</i> ~ 1 μm)
H11	0.02 M	—	0.002 M	0.08 M	130 °C	Akaganeite	Square planar particles (<i>a</i> ~ 800 nm)
H12	0.02 M	—	0.01 M	0.08 M	130 °C	Akaganeite	Square planar particles (<i>a</i> ~ 400 nm)

^a Data retrieved from previous work.²⁹ Details of preparation and characteristics of the films are available in ref. 29.

The acquisition time was 10 s to 30 s. X-ray fluorescence (XRF) measurements were carried out with a Bruker S8 Tiger XRF spectrometer under helium atmosphere (a 4 kW, Rh anode X-ray tube was used to generate X-rays.). The solutions were measured in liquid sample cups and Prolene (4 μm) film was used as the sample support window material. For the calculation of Ce amounts, a calibration curve was created from known concentrations of Ce solutions. Photoelectrochemical analyses were performed with Bio-Logic VSP model Potentiostat/Galvanostat system. The current–voltage (*I*–*V*) characteristics of the electrodes were measured under amplitude modulated-light illumination with a 200 W xenon arc lamp (Oriel, Stratford, CT) with the 3 electrode cell system in an aqueous solution of 0.1 M NaOH. Power density of the light struck on the films was measured to be 250 mW cm^{−2}.

Results and discussion

We have investigated the effect of electrodeposition temperature, pH (adjusted with CH₃COO[−] or F[−]) and presence of Ce³⁺ ions in the deposition bath on the structure and morphology of iron oxide films. Depositions were carried out both under ambient conditions at 75 °C and under hydrothermal conditions at 130 °C, ~2 bar.

Effect of cerium ions in electrodepositions from acidic solution

When electrodeposition was carried out from a bath containing only 0.02 M Fe²⁺ ions (pH = 3.8), at 75 °C, the film, H1, was composed of particles with no particular shapes as reported by Spray and Choi (Fig. 1a).³² Ce(NO₃)₂ was introduced into the electrodeposition bath so that [Ce³⁺]/[Fe²⁺] ratio was 0.1 or 0.5. The pristine film prepared from an aqueous bath containing Ce³⁺ ions, H2, were very similar with particles of no particular shapes (Fig. 1c). Upon annealing oval-round particles with diameters ranging between 10 and 50 nm were formed both in H1 and H2 (Fig. 1b–d).

Electrodeposition at higher temperature (130 °C) and pressure from an aqueous bath containing 0.02 M FeCl₂, H3, was

previously reported to result in the formation of monodisperse, almost-spherical polyhedra of around 300–400 nm which preserved their size and morphology after annealing.²⁹ Similarly electrodeposition at 130 °C with 10% Ce³⁺ ions resulted in formation of polyhedral particles, H4, (Fig. 1e). However, the film was very polydisperse; growth of smaller polyhedra on the faces of the larger crystals can be observed. Upon annealing at 520 °C, polyhedral particle shape was transformed into rhombohedral nanosized particles (Fig. 1f). When Ce³⁺ amount was increased to 50% of Fe²⁺ ions, H5, size of the polyhedra formed decreased significantly from μm to nm range and only some of the particles were transformed into rhombohedra after annealing (Fig. 1g–h).

The anodic deposition condition used promotes oxidation of Fe²⁺ ions to Fe³⁺ ions (eqn (1)), which is followed by precipitation of Fe³⁺ ions as amorphous ferric oxyhydroxide due to the limited solubility of Fe³⁺ ions in the plating solution ([Fe³⁺] ≈ 1 × 10^{−7} at pH 4.1) (eqn (2));^{20,26}

Hence, it is expected that as-deposited films contain amorphous ferric oxyhydroxide which is converted to crystalline α-Fe₂O₃ upon annealing as reported before.^{19,20} To identify the structure and phases of the obtained films, XRD and Raman spectroscopy were employed. As expected, H1 and H2 were amorphous with only substrate peaks present (data not shown) but converted to crystalline form upon annealing at 520 °C (Fig. 2). XRD patterns revealed very weak peaks at 24°, 33°, and 35° which can be indexed to (012), (104) and (110) reflections of rhombohedral α-Fe₂O₃, Hematite, structure {JCPDS card no. 86-0550} for the annealed films, with no other phase being detected. On the other hand, the as-synthesized films deposited at 130 °C (H3 and H4) showed crystalline structure that can be indexed to pure rhombohedral Hematite even before the annealing step (Fig. 2), in line with our previous report.²⁹ The presence of higher-order reflections implies higher crystallinity for the pristine films

Fig. 1 FE-SEM images of Hematite films obtained with electrodeposition at 1.2 V (vs. Ag/AgCl) from solutions containing 0.02 M Fe^{2+} (a) H1, at 75 °C, as-deposited (b) H1, annealed (c) H2, at 75 °C, 10% Ce^{3+} , as-deposited (d) H2, annealed (e) H4, at 130 °C, 10% Ce^{3+} , as-deposited (f) H4, annealed (g) H5, at 130 °C, 50% Ce^{3+} , as-deposited (h) H5, annealed.

Fig. 2 XRD diagrams of Hematite films obtained with electrodeposition at 1.2 V (vs. Ag/AgCl) from acidic solution.

deposited under hydrothermal conditions. No phase related to ceria could be observed in any of the films.

To further evaluate phase purity of Hematite, Raman spectroscopy was used. Raman spectrum of the annealed film deposited at 75 °C from only Fe^{2+} containing solution, H1, exhibits major peaks at 226, 247, 296, 411, and 615 cm^{-1} all correspond to well-known $\alpha\text{-Fe}_2\text{O}_3$ modes at 225, 247, 293, 299, 412, 613 and 498 cm^{-1} (Fig. 3) like the previously reported, the as-synthesized film at 130 °C, H3.^{29,33} In addition to these peaks, modes around $\sim 660\text{ cm}^{-1}$ and $\sim 1320\text{ cm}^{-1}$ were present in all Hematite Raman spectra obtained in the whole study. The 660 cm^{-1} mode is present in several published Hematite spectra and it is either assigned to Magnetite (Fe_3O_4)/wustite (FeO) impurity or considered as characteristics of Hematite and assigned to a disorder phase.^{35,36} There is no evidence of any other iron oxide phase in the XRD diagrams (Fig. 2). In addition,

no trace of iron in (+2) state could be found in XPS analysis (discussed below). Lack of evidence for presence of impurity phase suggests 660 cm^{-1} peak is related to Hematite phase which has been ascribed to disorder in the crystal lattice and the breaking of symmetry upon crystallization.^{29,35} The mode around 1320 cm^{-1} has been suggested to be an overtone of the peak at 660 cm^{-1} .³⁵ It was also ascribed to a two-magnon scattering including magnon–magnon interactions.³³ There are also additional peaks around 820 and 1050–1100 cm^{-1} . They are reported to exist in the xx polarized spectra.³⁷

Chemical bonding state of iron in the films was analyzed by XPS spectroscopy and representative Fe 2p spectra (since the peak positions were same for all of the films) of iron oxide films prepared by hydrothermal-electrodeposition in the presence of

Fig. 3 Raman spectra of Hematite films obtained with electrodeposition at 1.2 V (vs. Ag/AgCl) from acidic solution.

Ce^{3+} and/or NaAc, NaF are shown in Fig. 4a. The films display peaks located around 710.4–711 ($\text{Fe } 2p_{3/2}$) and ~ 724 ($\text{Fe } 2p_{1/2}$) eV which can be attributed to Fe^{3+} 2p spectrum rather than Fe^{2+} ($\text{Fe } 2p_{3/2}$ at ~ 709 eV).^{10,38,39} The $\text{Fe } 2p_{3/2}$ peak of Fe^{3+} has also a distinct, clearly distinguishable satellite peak at approximately 8 eV above the main peak which is present in all of the films (~ 718 eV, indicated by the arrows in Fig. 4a). The satellite binding energy of $\text{Fe } 2p_{3/2}$ is located at 715 eV for Fe^{2+} in FeO and Fe_3O_4 does not have a satellite peak.³⁹ There appears to be a weak and broad peak around 730 eV which can be assigned to be a satellite peak for $\text{Fe } 2p_{1/2}$ as suggested by Yamashita and Hayes.³⁹ Hence, appearance of $\text{Fe } 2p_{3/2} \sim 710$ –711 eV with a satellite peak ~ 718 eV indicates absence of Magnetite (Fe_3O_4)/wustite (FeO) impurities in the films in line with Raman analysis. Raman spectroscopy data of H2, H4 and H5 similarly indicates Hematite phase for as-deposited film at 130 °C and annealed sample synthesized at 75 °C (Fig. 3). Raman spectra of the films were analyzed also to evaluate presence of secondary ceria phase. Cerium dioxide fluorite phase has a single allowed

triply degenerate Raman active mode of F_{2g} symmetry which represents the symmetrical stretching vibration of CeO_8 vibrational unit.⁴⁰ In addition to F_{2g} mode, CeO_2 also exhibit weak bands at 258, 595, and 1179 cm^{-1} , due to second-order transverse acoustic (2 TA) mode, defect-induced (D) mode, and second-order longitudinal optical (2LO) mode, respectively.⁴¹ Absence of strongest F_{2g} peak at 462 cm^{-1} in Raman spectra of the films suggests there is no CeO_2 related phase in any of the films. Furthermore, no clear XPS peaks associated with cerium could be detected in Ce 3d spectra (Fig. 4b). For comparison, an iron oxide film, H13, prepared by modified-cathodic electrodeposition route as described by Schreiber *et al.*¹⁸ was subjected to XPS analysis under identical measurement conditions. H13 was grown by a potential cycling procedure at a potential sweep rate of 0.02 V s^{-1} , from -0.51 to 0.39 V (vs. Ag/AgCl (satd)), for 25 cycles at 50 °C from a deposition bath containing 0.005 M FeCl_3 + 0.0005 M Ce^{3+} + 0.005 M NaF + 1 M H_2O_2 + 0.1 M NaCl. The characteristic complex XPS spectrum of cerium is clearly displayed by H13 (Fig. 4b).⁴² On the other hand, Ce atoms could not be detected on the films grown by hydrothermal-electrochemical deposition. XRF analysis also supports absence of Ce atoms in the films (Fig. 5). Absence of Ce-related secondary phase in XRD and Ce signal in XPS or XRF spectra suggests Ce ions are excluded from Hematite crystal lattice. XRF analysis of the deposition solutions before and after hydrothermal-electrodeposition confirmed that Ce^{3+} ions are retained in the electrolyte solution after deposition.

Fig. 4 XPS spectra of H4, H9 and H11 (a) Fe 2p spectra (arrows indicate the satellites of the main peaks) (b) Ce 3d spectra (*H13: Ce 3d spectrum of iron oxide film prepared by Schreiber method¹ in the presence of 10% Ce^{3+}).

Effect of cerium ions in electrodepositions from neutral solution

Anodic deposition of FeOOH films which were converted to Hematite phase by annealing, from a neutral aqueous medium (pH 6.6–8.0) was reported before by Cohen and Leibenguth¹⁹ and Spray and Choi.³² To stabilize Fe^{2+} ions in neutral solution

Fig. 5 Wavelength dispersive X-ray spectra of H4, H9 and H11 films.

ammonium sulfate/ammonium or boric acid/sodium borate was used as complexing agents by Cohen and Leibenguth.¹⁹ Spray and Choi used NH_4Cl for the same purpose. We added NaCH_3COO or NaF into the deposition solution for stabilization of Fe^{2+} ions and carried out electrodeposition similarly at 75 and 130 °C.

NaCH_3COO case. Particles with no particular shapes were observed for the as-synthesized films prepared at low temperature from a bath containing 0.2 M Fe^{2+} and 0.8 M NaCH_3COO , H6, (Fig. 6a). The annealed film was composed of ~ 30 nm nanostructures (Fig. 6b). The film prepared by electrodeposition from neutral solution at high temperature, 130 °C, was reported to be composed of aggregated polyhedra which were clustered together to form larger spheres after annealing.²⁹ We have investigated the effect of Ce^{3+} ions on the morphology of Hematite films electrodeposited from neutral bath. $\text{Ce}(\text{NO}_3)_3$ amount in the solution was adjusted so that $[\text{Ce}^{3+}]/[\text{Fe}^{2+}]$ was 0.1. When Ce^{3+} ions were present in the deposition solution, platelets formed with both low and high temperature electrodeposition (Fig. 6c and e). The platelets were elongated in the c -direction, with each individual plate grown almost normal to the substrate surface. The particles grown by hydrothermal-electrochemical deposition were larger, ~ 50 nm thick and ~ 200 nm wide in the pristine films. Particle shape did not change but particle size increased after annealing (Fig. 6d and f).

Raman spectrum of the as-synthesized film deposited at 75 °C from neutral Fe^{2+} containing solution, H6, exhibits major peaks at 251, 377 cm^{-1} and some weak features at 528, 652, 733 and 1292 cm^{-1} which can be ascribed to orthorhombic Lepidocrocite ($\gamma\text{-FeOOH}$) structure (Fig. 7)^{32,33} which is consistent with literature. It has been demonstrated that under anodic

Fig. 7 Raman spectra of Hematite films obtained with electrodeposition at 1.2 V (vs. Ag/AgCl) from solutions containing 0.02 M Fe^{2+} and 0.08 M NaCH_3COO (and 10% Ce^{3+} for H7 and H9).

potentials from 200 to 1000 mV vs. Ag/AgCl, $\gamma\text{-FeOOH}$ is the only single phase deposited from electrolyte containing $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and CH_3COOK at 90 °C.²⁶ After annealing, Lepidocrocite phase is converted to Hematite (Fig. 7). Similarly to the films prepared in acidic conditions, Hematite phase is reported to be directly formed by hydrothermal-electrodeposition²⁹ but Lepidocrocite forms at low temperature from

Fig. 6 FE-SEM images of Hematite films obtained with electrodeposition at 1.2 V (vs. Ag/AgCl), from solutions containing 0.02 M Fe^{2+} and 0.08 M NaCH_3COO (a) H6, at 75 °C, as-deposited (b) H6, annealed (c) H7, at 75 °C, 10% Ce^{3+} , as-deposited (d) H7, annealed (e) H9, at 130 °C, 10% Ce^{3+} , as-deposited (f) H9, annealed.

neutral deposition baths (Fig. 7). Addition of Ce^{3+} ions into the deposition solution did not induce formation of different iron oxide/hydroxide phases (Fig. 7). Hence, it can be concluded that obtained crystal structure on contrary to morphology depends on the temperature under present circumstances and Ce^{3+} is a significant factor in determining the morphology of the products. Raman spectroscopy data also verifies Hematite phase for the as-synthesized film deposited at 130 °C, H9, and annealed film deposited at 75 °C, H7, in the presence of Ce^{3+} from neutral bath and there is no evidence of cerium-related phases in the films. Similarly to the acidic deposition Raman spectroscopy, XPS and XRF studies showed that Ce^{3+} ion is excluded from Hematite crystal lattice, although it directed the growth process. Hence, Hematite platelets can be produced in the presence of Ce^{3+} ions with hydrothermal-electrochemical deposition from a solution containing NaCH_3COO .

With no Ce^{3+} ions present in the neutral deposition solution, nanostructures at 75 °C, H6, and spheres of aggregated polyhedra at 130 °C, H8,²⁹ were obtained. In the presence of Ce^{3+} ions, on the other hand, lath-like platelets elongated perpendicular to the substrate surface, were formed. Spray and Choi produced round, oval Lepidocrocite particles with anodic electrodeposition from acidic FeCl_2 solution and plate-like particles from neutral deposition solution.³² They discussed this anisotropic columnar structure occurs when the growth process is more favored than the nucleation process. In addition, Sudakar *et al.* observed formation of lath/lamellar shaped particles in the presence of Pt^{4+} , Pd^{2+} , or Rh^{3+} cations whereas aggregates of small particles precipitated without these cationic additives due to preferential adsorption on (001) planes of Lepidocrocite.⁴³ Hence, it can be concluded that Ce^{3+} additive in the initial

deposition solution act as growth regulating agent by being adsorbed on specific crystallographic planes in the neutral electrodeposition solution prepared with NaCH_3COO .

NaF case. For stabilization of Fe^{2+} ions at pH ~ 6.0–6.4, F^- ions were also used and electrodepositions were carried out at 130 °C. The film prepared with 0.02 M FeCl_2 and 0.08 M NaF, H10, consists of spheres composed of square planar particles with edges around 1 μm (Fig. 8a). Particles seemed to be aggregated and a porous structure was observed after annealing (Fig. 8b). When Ce^{3+} ions were introduced into the deposition solution so that $[\text{Ce}^{3+}]/[\text{Fe}^{2+}]$ was 0.1, H11, square planar particles with slightly smaller sizes (edges around 800 nm) were obtained (Fig. 8c). Square plate structure (almost cubic) with higher aspect ratio was more apparent for the film prepared with $[\text{Ce}^{3+}]/[\text{Fe}^{2+}]$ ratio of 0.5, H12, and square planar particles had smaller edges (~400 nm) (Fig. 8e). In addition, it can be observed from FE-SEM images that the aspect ratios of the particles tend to increase with increasing $[\text{Ce}^{3+}]$ in the deposition solution. Particles seemed to be aggregated and a porous structure was observed for all of the films after annealing (Fig. 8b, d and f).

Raman spectra of the as-prepared films in the presence of NaF exhibit strong bands at around 307, 400–409, and weaker bands around 548–550, 620 and 730 cm^{-1} (Fig. 9). These bands can be attributed to Akaganeite ($\beta\text{-FeOOH}$) structure with reported band positions at 310, 385, 535, 615, and 725 cm^{-1} .⁴⁴ Upon annealing at 520 °C Akaganeite structure is transformed to Hematite for all of the films (Fig. 9). Absence of 462 cm^{-1} peak in Raman spectra suggests there is no CeO_2 phase in any of the films. Similarly to the acidic deposition Raman, XPS and XRF studies showed that Ce^{3+} ion is excluded from Akaganeite and Hematite crystal lattices.

Fig. 8 FE-SEM of Hematite films obtained with electrodeposition at 1.2 V (vs. Ag/AgCl) from solutions containing 0.02 M Fe^{2+} and 0.8 M NaF at 130 °C (a) H10, as-deposited (b) H10, annealed (c) H11, 10% Ce^{3+} as-deposited, (d) H11, annealed (e) H12, 50% Ce^{3+} , as-deposited, (f) H12, annealed.

Fig. 9 Raman spectra of Hematite films obtained with electrodeposition at 1.2 V (vs. Ag/AgCl) from solutions containing 0.02 M Fe^{2+} and 0.8 M NaF at 130 °C (and 10% Ce^{3+} for H11, 50% Ce^{3+} for H12).

It was reported before that the shape and size of the iron oxyhydroxides and oxides depended on the anion(s) of the Fe(III) salts used for the synthesis.⁴⁵ K. Hu *et al.*, have investigated effect of ions on the morphology of iron oxyhydroxides and demonstrated formation of platelets, rhombohedral rods, square rods, six-fold snowflakes, and hexagonal particles with different capping agents.²⁸ They obtained platelets in the presence of CH_3COO^- and rhombohedral rods were formed when NH_4F was added into the deposition solution. The synthesis of $\beta\text{-FeOOH}$ nanorods was also shown to be highly influenced by the presence of salt ions (e.g., NO_3^- , SO_4^{2-} , F^- , Cl^- , and Br^-); depending on the nature of their interaction with Fe^{3+} ions they can influence greatly the morphology, size, porosity, and crystalline structure of $\beta\text{-FeOOH}$ particles.⁴⁶

X. Jiang and their group have reported that FeCl_3 favors tetragonal phase of Akaganeite, whereas the $\text{Fe}(\text{NO}_3)_3$ and $\text{Fe}_2(\text{SO}_4)_3$ salt leads to the formation of nitrate and an amorphous mixture of Goethite and Schwertmannite, respectively.⁴⁶ They discuss some of the Cl^- ions are incorporated into the lattice of Akaganeite tunnel structure and help to stabilize the tunnel structure along the *c*-axis favoring nanorod formation. However, larger ions destabilize Akaganeite structure and favor formation of Goethite. They also compared ability of F^- and Cl^- to stabilize Akaganeite tunnel. They discussed that due to its high electronegativity, F^- can form strong interactions with Fe^{3+} ions. However F^- ion would lead to a deformed Akaganeite structure due to its smaller size. Hence, changing stabilizing anion from CH_3COO^- to F^- resulted in formation of square planar particles of $\beta\text{-FeOOH}$ rather than Lepidocrocite platelets which were transformed into Hematite particles upon annealing. Porous, square planar Hematite particles were obtained after transformation. It has been demonstrated that potential microporosity of Akaganeite due to the tunnel structure

develops into slit shaped micropores which coalesce into mesopores and phase transformation take place as temperature is increased.⁴⁷

It has been discussed that side planes of Akaganeite rod *i.e.*; $(100) \equiv (-100) \equiv (010) \equiv (0-10)$; $(110) \equiv (-110) \equiv (1-10) \equiv (-1-10)$ and the parallel planes in the growth direction $(001) \equiv (00-1)$ are equivalent in surface energy due to their mirror symmetry in the tetragonal lattice.⁴⁶ However, anisotropic growth still takes place since diffusion constants of anions vary according to the crystal plane they interact. It has been shown with molecular dynamics simulation that the $\beta\text{-FeOOH}$ (100) and (110) surfaces have a minimal interaction with the anions whereas F^- is highly adsorbed on the (001) surface.⁴⁶ Hence the growth along the [001] direction is faster to form a nanorod. The aspect ratio of the nanorods can be controlled by $[\text{Fe}^{3+}]$. It has been demonstrated that length of the rods decrease with decreasing concentration and even spherical particles can be obtained with dilute solutions.⁴⁶ In this study, Fe^{2+} concentration is under critical value which might be responsible for square planar particles (Fig. 8). As $[\text{Ce}(\text{NO}_3)_3]$ in the deposition solution is increased, size of the square planar particles decrease whereas thickness of the particles increase which suggests growth in lateral direction is repressed. Since it has been shown that NO_3^- ions does not interact strongly with any of the Akaganeite planes,⁴⁶ Ce^{3+} ions are responsible for the morphology change. It is most likely that the Ce^{3+} ions in the deposition solution are adsorbed onto the side surfaces of $\beta\text{-FeOOH}$ parallel to the *c*-axis and hence preventing the growth in the lateral direction.

Photoelectrochemical properties

Hematite nanoparticles are useful for various applications such as the anode of photoelectrochemical cells, detection electrode for gas sensors, the positive electrode for Li-ion batteries and photodegradation of dyes. Particle morphology has been recognized as a key factor influencing material performances.^{1,9-14} Hence, we have performed photoelectrochemical analysis on the produced films to investigate shape-property relationship. Photoelectrochemical (PEC) performances of annealed $\alpha\text{-Fe}_2\text{O}_3$ electrodes were measured under 250 mW cm^{-2} light illumination at 1.5 V vs. Ag/AgCl in 1 M NaOH. The transient photocurrent responses of the films are shown in Fig. 10. All of the electrodes are photoactive and the anodic nature of the photocurrent produced suggests n-type behavior for all of the films and the responses are quite stable with no sign of photocorrosion. The net photocurrent densities ($I_{\text{photocurrent}} - I_{\text{dark current}}$) of the films are 9.1, 29.2, 8.9, 20.1, 28.8, 35.5, 21.11 and 43.7 $\mu\text{A cm}^{-2}$, respectively for H1, H2, H4, H6, H7, H9, H10 and H12. The maximum photocurrent density, of 43.7 μA is achieved for the film prepared from the solution containing 0.02 M Fe^{2+} , 0.08 M F^- , 0.01 M Ce^{3+} . The difference in photoresponse of the electrodes can be explained, at least partially, by varying particle size, shape and amount of photoactive material.

Although Hematite possesses an ideal band-gap energy enabling a high proportion of solar light and high chemical

Fig. 10 The photocurrent responses of the Hematite films at 1.5 V (vs. Ag/AgCl) in 0.1 M NaOH under amplitude modulated illumination with 250 mW cm^{-2} light.

stability, it suffers from short lifetime of its photogenerated charge carriers (hence high recombination rate) and short hole diffusion length resulting in low PEC performances. Nano-sized structures are designed in an attempt to decrease the distance that holes would travel to reach the Fe_2O_3 /electrolyte interface for photocatalytic reaction. Hematite nanorod arrays have been shown to display much higher PEC performances than nanoparticulate Hematite, although nanoparticles have higher surface area than nanorods.⁴⁸ Higher performance of nanorod is mainly attributed to the channelized electron transport which enhances charge separation and lowers the electron-hole (e^- - h^+) recombination rate.⁴⁸

The photo-sensitivity of the electrodes follow the sequence H12, cubic particles > H9, lath-like rectangular platelets > H2, oval-round nanoparticles > H7, smaller lath-like rectangular platelets > H10, square platelets of lower aspect ratio > H6, nanostructures > H1, oval-round nanoparticles > H4, rhombohedral particles. H1-H2 and H6-H7 were prepared by anodic electrodeposition at 75°C using electrolytes of very similar compositions (*i.e.*, identical Fe^{2+} source, identical Fe^{2+} concentration, identical types of anions in the plating solution except Ce^{3+}) and were thermally treated using identical conditions. In addition, H1 and H2 display very similar morphology, oval-round particles with diameters ranging between 10 and 50 nm. The films prepared in the presence of Ce^{3+} ions showed higher photo-activity than their counterparts prepared with identical conditions (except Ce). The difference in the produced photocurrent between H6 and H7 is higher than the difference between that of H1 and H2 which indicates contribution of the particle shape effect; nanoplatelets (H7) *vs.* nanostructures (H6). This increase can be attributed to enhancement of the directional electron transport due to the vertical alignment⁴⁹ of two dimensional nanoplatelets. The photoelectrochemical performance of H9 is enhanced compared to H7 which were

deposited from identical solutions at different temperatures. Even though, H7 consists of smaller sized particles (Fig. 6), which provide higher surface area and thereby beneficial to decrease recombination losses, H9 generates higher photocurrent than H7. The difference in photoresponses of H9 and H7 might stem from higher Fe_2O_3 loading on H9. We have shown that electrodeposition rate of iron oxides increases with temperature considerably, previously.²⁹ Hence, higher amount of Hematite should have been deposited at 130°C compared to 75°C while all other parameters are kept constant which would result in increased number of generated electron-hole pairs that can contribute to photocurrent generation for H9. The photoresponse of H12 is higher than that of H9 and $\sim$ twice of the response of the H10. The discrepancy in the performances of H10 and 12 can be explained by the differences in the aspect ratio of the square platelet and cubic particles since increase in the aspect ratio is expected to enhance the separation of photogenerated carriers.⁵⁰ However, even though, aspect ratio of the nanoplatelets in H9 is higher than aspect ratio of the cubic particles in H12, H12 generates higher photocurrent than H9. Annealed films deposited from F^- containing solutions display porous structures since tunnelled Akaganeite structure grows into mesopores with thermal treatment. Mesoporous nature of H12 would provide larger interfacial area in contact with the electrolyte thereby a shorter distance for the photogenerated holes to reach the electrolyte.⁴⁸ Hence, decreased recombination losses would allow enhanced photocatalytic performance.

Conclusions

$\alpha\text{-Fe}_2\text{O}_3$ crystals with different morphologies, including spherical, rhombohedral, and platelets were obtained by using hydrothermal-electrodeposition (HED) together with growth-modifying ions such as CH_3COO^- , Ce^{3+} and F^- . It is remarkable that ion identity and temperature (and autonomous pressure) are key parameters to control both the crystalline phase and morphology of iron oxide particles.

When Ce^{3+} ions present in the acidic deposition solution, worm-like, amorphous particles and Hematite polyhedra can be obtained at 75°C and 130°C , respectively. Anodic deposition of FeOOH /Hematite films from $\sim$ neutral aqueous medium (pH 6.6–6.8) by adding NaCH_3COO into the deposition solution for stabilization of Fe^{2+} ions was also performed. Lepidocrocite phase is favored with electrodeposition from this solution under ambient conditions. Nanostructured Lepidocrocite, $\gamma\text{-FeOOH}$, particles and rhombohedral Hematite particles were formed at 75°C and 130°C , respectively. Electrodepositions from neutral solutions containing Ce^{3+} ions resulted in platelets both for low and high temperature synthesis. Here, Ce^{3+} ions act as shape-dictating additive due to preferential adsorption on (001) planes of Lepidocrocite and result in anisotropic columnar structures. Addition of F^- into the deposition solution induces Akaganeite, $\beta\text{-FeOOH}$, formation composed of bundles of square planar particles even under hydrothermal-electrochemical deposition. When Ce^{3+} ions are introduced into the deposition solution together with F^- , they act as growth-regulating agent *via* specific absorption rather than inducing formation of a different

phase. The aspect ratio of the particles tends to increase with increasing Ce^{3+} concentration in the deposition solution due to restriction of lateral growth. Annealing promotes a mesoporous structure in these square planar particles. The porous, high aspect ratio square planar particles display highest photo-electrochemical performances.

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Notes and references

- 1 J. Zhang, A. Thurber, C. Hanna and A. Punnoose, *Langmuir*, 2010, **26**, 5273–5278.
- 2 Y.-T. Kim, J. Park, S. Kim, D. W. Park and J. Choi, *Electrochim. Acta*, 2012, **78**, 417–421.
- 3 S. A. Vanalakar, S. S. Mali, R. C. Pawar, N. L. Tarwal, a. V. Moholkar, J. H. Kim and P. S. Patil, *J. Appl. Phys.*, 2012, **112**, 044302.
- 4 G. Li, X. Lu, W.-X. Zhao, C.-Y. Su and Y.-X. Tong, *Cryst. Growth Des.*, 2008, **8**, 1276–1281.
- 5 B. Xue, Y. Liang, L. Donglai, N. Eryong, S. Congli, F. Huanhuan, X. Jingjing, J. Yong, J. Zhifeng and S. Xiaosong, *Appl. Surf. Sci.*, 2011, **257**, 10317–10321.
- 6 B. E. Prasad, P. V. Kamath and S. Ranganath, *J. Solid State Electrochem.*, 2012, **16**, 3715–3722.
- 7 M. Mohapatra and S. Anand, *Int. J. Eng. Sci. Technol.*, 2010, **2**, 127–146.
- 8 D. K. Bora, A. Braun and E. C. Constable, *Energy Environ. Sci.*, 2013, **6**, 407.
- 9 Y. Yang, H. Ma, J. Zhuang and X. Wang, *Inorg. Chem.*, 2011, **50**, 10143–10151.
- 10 X. Hu, J. C. Yu, J. Gong, Q. Li and G. Li, *Adv. Mater.*, 2007, **19**, 2324–2329.
- 11 S. B. Wang, Y. L. Min and S. H. Yu, *J. Phys. Chem. C*, 2007, **111**, 3551–3554.
- 12 S. Zeng, K. Tang, T. Li, Z. Liang, D. Wang, Y. Wang, Y. Qi and W. Zhou, *J. Phys. Chem. C*, 2008, **112**, 4836–4843.
- 13 Q. Xiang, G. Chen and T. C. Lau, *RSC Adv.*, 2015, **5**, 52210–52216.
- 14 J. Zhao, H. S. Chen, K. Matras-Postolek and P. Yang, *CrystEngComm*, 2015, **17**, 7175.
- 15 H. Liang, X. Xu, W. Chen, B. Xu and Z. Wang, *CrystEngComm*, 2014, **16**, 959.
- 16 W. Dong and C. Zhu, *J. Mater. Chem.*, 2002, **12**, 1676–1683.
- 17 J. Wang, L. Xu, Z. Zhang, P. P. Sun, M. Fang and H. K. Liu, *RSC Adv.*, 2015, **5**, 49696–49702.
- 18 R. Schrebler, K. Bello, F. Vera, P. Cury, E. Muñoz, R. del Río, H. Gómez Meier, R. Córdova and E. A. Dalchiele, *Electrochem. Solid-State Lett.*, 2006, **9**, C110.
- 19 J.-L. Leibenguth and M. Cohen, *J. Electrochem. Soc.*, 1972, **119**, 987.
- 20 R. L. Spray and K.-S. Choi, *Chem. Mater.*, 2009, **21**, 3701–3709.
- 21 S. Jiao, L. Xu, K. Hu, J. Li, S. Gao and D. Xu, *J. Phys. Chem. C*, 2010, **114**, 269–273.
- 22 A. Bak, W. Choi and H. Park, *Appl. Catal., B*, 2011, **110**, 207–215.
- 23 A. Kleiman-Shwarscstein, M. N. Huda, A. Walsh, Y. Yan, G. D. Stucky, Y.-S. Hu, M. M. Al-Jassim and E. W. McFarland, *Chem. Mater.*, 2010, **22**, 510–517.
- 24 A. Kleiman-shwarscstein, Y. Hu, A. J. Forman, G. D. Stucky and E. W. Mcfarland, *J. Phys. Chem. C*, 2008, **112**, 15900–15907.
- 25 P. Kumar, P. Sharma, R. Shrivastav, S. Dass and V. R. Satsangi, *Int. J. Hydrogen Energy*, 2011, **36**, 2777–2784.
- 26 L. Martinez, D. Leinen, F. Martin, M. Gabas, J. R. Ramos-Barrado, E. Quagliata and E. A. Dalchiele, *J. Electrochem. Soc.*, 2007, **154**, D126.
- 27 P. S. Shinde, G. H. Go and W. J. Lee, *J. Mater. Chem.*, 2012, **22**, 10469.
- 28 S. Jiao, L. Xu, K. Hu, J. Li, S. Gao and D. Xu, *J. Phys. Chem. C*, 2010, **114**, 269–273.
- 29 C. Yilmaz and U. Unal, *RSC Adv.*, 2015, **5**, 16082–16088.
- 30 R. Liu, Y. Jiang, Q. Lu, W. Du and F. Gao, *CrystEngComm*, 2013, **15**, 443–446.
- 31 R. Liu, Y. Jiang, H. Fan, Q. Lu, W. Du and F. Gao, *Chem.–Eur. J.*, 2012, **18**, 8957–8963.
- 32 R. L. Spray and K.-S. Choi, *Chem. Mater.*, 2009, **21**, 3701–3709.
- 33 D. L. Faria, S. V. Silva and M. T. Oliveria, *J. Raman Spectrosc.*, 1997, **28**, 873–878.
- 34 Y.-S. Li, J. S. Church and A. L. Woodhead, *J. Magn. Magn. Mater.*, 2012, **324**, 1543–1550.
- 35 B. M. Klahr, A. B. F. Martinson and T. W. Hamann, *Langmuir*, 2011, **27**, 461–468.
- 36 J. A. Glasscock, P. R. F. Barnes, I. C. Plumb, A. Bendavid and P. J. Martin, *Thin Solid Films*, 2008, **516**, 1716–1724.
- 37 D. Bersani, P. P. Lottici and A. Montenero, *J. Raman Spectrosc.*, 1999, **30**, 355–360.
- 38 L. Liu, H. Kou, W. Mo, H. Liu and Y. Wang, *J. Phys. Chem. B*, 2006, **110**, 15218–15223.
- 39 T. Yamashita and P. Hayes, *Appl. Surf. Sci.*, 2008, **254**, 2441–2449.
- 40 M. Santamaria, L. Asaro, P. Bocchetta, B. Megna and F. Di Quarto, *J. Electrochem. Soc.*, 2013, **160**, D212–D217.
- 41 Z. Wu, M. Li, J. Howe, H. M. Meyer and S. H. Overbury, *Langmuir*, 2010, **26**, 16595–16606.
- 42 F. Zhang, P. Wang, J. Koberstein, S. Khalid and S. W. Chan, *Surf. Sci.*, 2004, **563**, 74–82.
- 43 C. Sudakar, G. N. Subbanna and T. R. N. Kutty, *J. Phys. Chem. Solids*, 2003, **64**, 2337–2349.
- 44 S. Das and M. J. Hendry, *Chem. Geol.*, 2011, **290**, 101–108.
- 45 S. Music, A. Vertes, G. Simmons, I. CzakoNagy and H. Leidheiser, *J. Colloid Interface Sci.*, 1982, **85**, 256–266.

- 46 J. Yue, X. Jiang and A. Yu, *J. Nanopart. Res.*, 2011, **13**, 3961–3974.
- 47 R. M. Cornell and U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*, Wiley, 2nd edn., 2006.
- 48 S. Shen, *J. Mater. Res.*, 2014, **29**, 29–46.
- 49 M. Chirita and I. Grozescu, *Chem. Bull. "Politeh." Univ. Timisoara*, 2009, **54**, 1–8.
- 50 X. Zhang, J. Qin, Y. Xue, P. Yu, B. Zhang, L. Wang and R. Liu, *Sci. Rep.*, 2014, **4**, 4596.