Accepted Manuscript

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PII: S0169-4332(16)30154-4
DOI: <http://dx.doi.org/doi:10.1016/j.apsusc.2016.02.007>
Reference: APSUSC 32525

To appear in: *APSUSC*

Received date: 19-11-2015
Revised date: 30-1-2016
Accepted date: 1-2-2016

Please cite this article as: Q. Meng, Z. Wang, X. Chai, Z. Weng, R. Ding, L. Dong, Fabrication of Hematite ($\alpha\text{-Fe}_2\text{O}_3$) Nanoparticles Using Electrochemical Deposition, *Applied Surface Science* (2016), <http://dx.doi.org/10.1016/j.apsusc.2016.02.007>

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- Cathodic electrochemical deposition proposed to fabricate hematite nanoparticles.
- Hematite nanoparticles were fabricated on indium-tin-oxide coated glass substrates.
- The size and shape of nanoparticles were determined by deposition conditions.
- The nanoparticles were well decentralized for different potential applications.
- Electrochemical deposition is a useful approach in fabricating nanoparticles.

Fabrication of Hematite ($\alpha\text{-Fe}_2\text{O}_3$) Nanoparticles Using Electrochemical Deposition

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Abstract—In this work, cathodic electrochemical deposition was proposed to fabricate reproducible and homogeneous hematite ($\alpha\text{-Fe}_2\text{O}_3$) nanoparticles on indium-tin-oxide (ITO) films. The $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles, which were quasi-hexagonally shaped, were deposited in an aqueous mixture of FeCl_2 and FeCl_3 at the temperatures 16.5 °C, 40 °C and 60 °C. The electrochemically deposited $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles showed excellent stability and good crystallinity. The $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were characterized by Raman spectroscopy and X-ray diffractometer (XRD). A scanning electron microscope (SEM) was used to measure the size and shape of the nanoparticles. The experiment results have shown that the size and shape of nanoparticles were determined by electrochemical deposition conditions including the deposition time, current density, reaction temperature and solution concentration. The proposed electrochemical deposition method has been proven to be a cost-effective, environment friendly and highly efficient approach in fabricating well decentralized $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles for different potential applications.

Key words—Cathodic electrochemical deposition, Hematite nanoparticles, Indium tin oxide electrode.

1. Introduction

Nanoparticles have in recent years been investigated by many researchers due to their attractive properties such as the controllable size, superparamagnetic feature and biocompatibility, which are unable to be obtained with their bulk materials [1-4]. Iron oxide nanoparticles are magnetic materials with unique functions. Their capabilities have been explored in the applications of disease therapy, magnetic resonance imaging (MRI), tissue engineering [5], biosensors, drug delivery [6], data storage and environment protection [7].

There are many different crystalline forms of iron oxides, and they show a variety of physical and chemical properties depending on their chemical compositions and crystal structures [8,9]. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is a half-metallic ferromagnetic oxide with the corundum structures and space group $\text{Fd}\bar{3}\text{m}$. It has the most thermodynamic stable crystallographic phase of iron oxide under ambient conditions and it is also an attractive semiconductor material absorbing the light with the wavelength under 590 nm, which has its potential for photoelectrochemical research into solar energy conversion [10,11]. It has been reported that the nanostructured hematite is suitable for developing multi-junction hybrid photoelectrodes for hydrogen production [12], efficient photoelectrocatalytic water decomposition and organic pollutant degradation [13]. Hematite is a conventional gas-sensing material used to detect combustible gases such as CH_4 and C_3H_8 [14]. It is also used as electrodes in nonaqueous and alkaline rechargeable batteries and has shown a great effect for arsenate (As(V)) adsorption [15]. Furthermore, the nontoxicity, low cost, environment friendly and relatively good stability of the hematite are attractive features for all the applications [16].

Various methods such as electron beam lithography, chemical coprecipitation and hydrothermal synthesis have been developed to obtain iron oxide nanoparticles [11,13,17-20]. However, the equipment of electron beam lithography used for the formation of iron oxides is complicated and the cost is high. The chemical coprecipitation is difficult to control the sizes of particles in the fabrication. The hydrothermal synthesis requires high temperature and high pressure conditions. Although electron beam deposition is widely used to produce thin films of different materials, it can also be used to produce nanoparticles [21-27]. The disadvantages are that it requires a complex system and the process cost is high. In order to precisely control the particle morphologies and shorten the fabrication time, a facile method of electrochemical deposition has been developed for the fabrication of nanoparticles and nanostructured materials. The simple and efficient method can operate at a low temperature and control the composition, crystallinity and deposition property of nanoparticles by properly selecting electrodeposition process parameters [28-30].

Iron oxide films can be obtained by cathodic or anodic electrodeposition. The control of applied voltages and electrolyte compositions is able to produce iron oxide-oxyhydroxide layers in different phases [8]. Schreiber et al. electrodeposited amorphous and nanocrystalline $\alpha\text{-Fe}_2\text{O}_3$ thin films on F-doping tin oxide covered glass substrates [11]. Li et al. reported the electrodeposition of micro-nano sized Fe_3O_4 crystals on self-supported carbon nanofiber buckypapers [31]. Pérez-Villar et al. reported the pulsed electrodeposition technique to prepare iron oxide films without any additional annealing [32]. To date, despite a great deal of work involving the electroplating of iron oxide films and nanoparticles in the literature, electrochemical deposition of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles has not been reported.

In this work, reproducible and homogeneous $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were fabricated on an indium-tin-oxide (ITO) coated glass substrate by cathodic reaction at the temperatures 16.5 °C, 40 °C and 60 °C using a simple one-step electrochemical deposition method. The $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were characterized by Raman spectroscopy and X-ray diffractometer (XRD). A scanning electron microscope (SEM) was used to measure the size and shape of the nanoparticles. The experiment results have shown that the size and shape of nanoparticles can be determined by electrochemical deposition conditions including the deposition time, current density, reaction temperature and solution concentration. The experiment details are described in the following sections.

2. Experimental

2.1 Fabrication of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles

All chemicals in the experiment were used without further purification, and $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were fabricated using the method of cathodic electrochemical deposition in a conventional three-electrode and single-compartment electrochemical cell under the galvanostatic condition and with the solution exposed to the atmosphere. The work electrode was an ITO film coated glass substrate (Area: 1 cm^2 ; square resistance: 8 Ω). The counter electrode was an iron plate and the reference electrode was a standard calomel reference electrode.

The schematic diagram of experiment setup is shown in Fig. 1. One 150 ml glass cell was used in the fabrication. Prior to the electrodeposition, the ITO film coated glass was ultrasonically cleaned by acetone, alcohol (Beijing Chemical Works) and deionized water, respectively. The iron plate was polished with the emery paper and then rinsed with deionized water. The starting materials of ferrous chlorides ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, Xilong Chemical) and ferric chlorides ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Tianjin Kaitong Chemical Reagent) were used. The electrolytic bath in this study was a mixed aqueous solution of FeCl_2 and FeCl_3 , and the electrolyte was not stirred in the whole electrochemical deposition process. Ultrapure water was prepared with the Millipore water purification system. All solutions were prepared from analytical grade reagents.

Hematite nanoparticles were electrochemically deposited with various concentrations of FeCl_2 and FeCl_3 including 4 mM FeCl_2 and 6 mM FeCl_3 , 8 mM FeCl_2 and 12 mM FeCl_3 , and 16 mM FeCl_2 and 24 mM FeCl_3 . The current densities were 1-10 mA/cm^2 and the electrolyte temperature was kept at different constant values during the entire electrodeposition processes from the room temperature (16.5 °C) to 60 °C. The electrochemical deposition was carried out for the different time periods from 0 to 200 s. An electrochemical workstation (Model CHI660D, Shanghai Chenhua) interfaced to a personal computer was used for electrochemical deposition, electrochemical parameter design and data collection. At last, the deposited $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were rinsed with deionized water for a few seconds and then dried in the air at the room temperature.

Fig. 1 The schematic illustration showing the electrochemical deposition process and α -Fe₂O₃ nanoparticles anchored on an ITO film coated glass substrate.

2.2 Characterization

The morphologies and microstructures of the sample surface and cross section were examined by SEM (FEI QUANT-250 FEG) at the 5 kV accelerated voltage. Raman spectra were acquired by the TriVista CRS555 system (Princeton Instruments) with the laser excitation of 532 nm. The crystal phase of samples was characterized with X-ray diffractometry by a Rigaku D/Max2500 using Cu-K α ($\lambda=0.154$ nm).

3 Results and discussions

For the electrolyte used in this study, the reactions involving the formation of α -Fe₂O₃ nanoparticles can be presented by the following electrochemical process. At the cathode, the reduction of water causes the local pH increase according to Eq. (1). Dissolved oxygen is reduced and combined with ferrous iron and ferric iron to form Fe₂O₃ described by Eqs. (2) and (3) [1]. As to the anode reaction, some of the ferric ions are oxidized to ferrous ions, expressed by Eq. (4) [33]. This process promotes the formation of ferric to ferric hydroxides, as shown in Eq. (5). The ferric hydroxides are later converted into Fe₂O₃ (Eq. (6)).

The cathode reactions can be expressed as

The anode reactions can be written as

For determining the composition of the obtained α -Fe₂O₃ nanoparticles deposited on the ITO surface, the Raman spectrum was acquired, as shown in Fig. 2(a). The particles were deposited for 100 s at 60 °C with the current density 10 mA/cm². In the Raman spectrum, the sharp and intense peaks at 213, 274, 391, 477, 585 and 1277 cm⁻¹ are the characteristics of α -Fe₂O₃. This reflects the crystallinity of the obtained nanoparticles [34]. The XRD was also performed for the crystallinity identification of the obtained α -Fe₂O₃ nanoparticles. The XRD patterns are shown in Fig. 2(b). The nanoparticles were deposited for 200 s at 60 °C. The current densities were 1, 5 and 10 mA/cm² in the experiment. The samples obtained from the current density 1 mA/cm² exhibit the diffraction peaks indexed to the α -Fe₂O₃ phase, confirming the formation of α -Fe₂O₃. The XRD intensities of peaks were slightly decreased with the increase of current density. The characteristic peaks of Fe appeared at 5 mA/cm² indicate the changes of crystal structures with the current density.

Fig. 2 (a) Raman spectra of electrochemically deposited α -Fe₂O₃ nanoparticles (deposited for 100 s at 60 °C with the current density of 10 mA/cm²) and (b) XRD patterns of electrochemically deposited nanoparticles formed on the ITO surface with the current densities 1, 5 and 10 mA/cm².

The FEI SEM was utilized to measure the α -Fe₂O₃ nanoparticles anchored on the ITO coated glass substrate. The electrochemical deposition of α -Fe₂O₃ nanoparticles from an aqueous electrolyte can be influenced by a variety of internal and external factors such as the deposition time, applied current density, reaction temperature, solution concentration and electrolyte composition [35]. For the exploration of the effect of deposition time on α -Fe₂O₃ nanoparticles, the galvanostatic deposition was carried out on the ITO coated glass substrates using three different periods of time for 50 s, 100 s and 200 s. All the experiments were performed with the deposition current density 1 mA/cm² at the temperature of 60 °C under the solution concentrations of 8 mM FeCl₂ and 12 mM FeCl₃.

Fig. 3 shows the SEM images of the samples. Fig. 3(a) shows an image of a bare ITO before deposition. It can be seen, from Figs. 3(b)-(d), that the size of α -Fe₂O₃ nanoparticles is increased with the deposition time. The result with the deposition time 50 s is shown in Fig. 3(b). There are a small number of particles observed and the particle size is small. It is found that the acidic aqueous electrolyte solutions of FeCl₂ and FeCl₃ might help activate the ITO layer and form the spontaneous nuclei and isolated α -Fe₂O₃ nanoparticles. As shown in Fig. 3(c), with the increase of deposition time, particles gradually grow up. In Fig. 3(d), the α -Fe₂O₃ nanoparticles are quasi-hexagonal in shape and they are well dispersed. The particles are homogeneous and the surface of ITO coated glass substrate is well covered without any visible cracks or holes.

Fig. 3 The SEM images of α -Fe₂O₃ nanoparticles deposited for the different periods from (a) to (d): 0 (before deposition), 50, 100 and 200 s.

To measure the average particle sizes with the deposition time, the Origin 8.0 and MATLAB were used to compute the sizes of α -Fe₂O₃ nanoparticles. The results were fitted with a linear regression. It is found that there is an approximate linear relation of the averaged particle size Y (nm) with the deposition time X (s), i.e. $Y=0.9627X$. Fig. 4 shows the results. The results could indicate the nucleation formation and the growth mode of α -Fe₂O₃ nanoparticles [31]. In the growth mode, the nucleus density of α -Fe₂O₃ nanoparticles was kept approximately unchanged. The continuous growth of particles might lead to the aggregation of α -Fe₂O₃ nanoparticles. When the ITO layer was fully covered with α -Fe₂O₃ nanoparticles, it might also result in the formation of large polycrystalline clusters [36]. Table 1 shows the measurement results with the average size and size range of the nanoparticles at different deposition times. The average particle size of α -Fe₂O₃ nanoparticles deposited for 200 s is 257 nm.

Fig. 4 Average size of α -Fe₂O₃ nanoparticles as a function of deposition time with the current density 1 mA/cm² and the solution concentrations 8 mM FeCl₂ and 12 mM FeCl₃ at the temperature 60 °C. The error bars show one standard deviation.

Deposition time (s)	Average particle size (nm)	Particle size range (nm)
0	0	0
10	18	10-36
20	21	11-42

30	31	12-51
40	34	15-52
50	38	20-54
60	46	22-88
70	55	26-115
80	78	32-177
90	85	43-175
100	112	43-220
200	257	65-558

Table 1. Average size and size range of α -Fe₂O₃ nanoparticles vs. different periods of deposition time with the current density of 1 mA/cm² and solution concentrations of 8 mM FeCl₂ and 12 mM FeCl₃ at the temperature of 60 °C.

Fig. 5 shows the SEM images of the deposition with different current densities 1, 5 and 10 mA/cm². The deposition to verify the influence exerted by the current density was conducted with the deposition time of 200 s and the solution concentrations of 8 mM FeCl₂ and 12 mM FeCl₃ at the temperature of 60 °C. As shown in Fig. 5(a), the shape of nanoparticles is quasi-hexagonal. When the applied current density is increased, the nanoparticles with irregular and columnar shapes can be observed. The results indicate that the shape of nanoparticles can be influenced by the deposition current density. The morphologies and sizes can be changed with the increase of current densities due to the shifted reaction control. The kinetic to mass transfer could be considered as the implementation of the reaction process. The uneven electric field might be caused by the formed nanostructures on electrode surfaces [1].

Fig. 5 The SEM images of α -Fe₂O₃ nanoparticles deposited with the current densities from (a) to (c): 1, 5 and 10 mA/cm².

Fig. 6 shows the structures of deposited α -Fe₂O₃ nanoparticles at the different temperatures of 16.5 °C, 40 °C and 60 °C for the deposition time of 200 s with the deposited current density of 1 mA/cm², and solution concentrations of 8 mM FeCl₂ and 12 mM FeCl₃. At the room temperature, the deposited nanoparticles were small and dense as the particles were rapidly nucleated and slowly grown. With the temperature increased, the number of nanoparticles was decreased and the shape of nanoparticles gradually became quasi-hexagonal. This indicates the preferred orientation with the corundum type of structures due to the increase of the deposition temperature.

Fig. 6 The SEM images of α -Fe₂O₃ nanoparticles deposited at the different temperatures of (a) room temperature at 16.5 °C, (b) 40 °C and (c) 60 °C.

To explore the effects of solution concentrations, α -Fe₂O₃ nanoparticles were deposited on ITO coated glass substrates with the different solution concentrations of 4 mM FeCl₂ and 6 mM FeCl₃, 8 mM FeCl₂ and 12 mM FeCl₃, and 16 mM FeCl₂ and 24 mM FeCl₃. All the depositions were carried out for the deposition time of 200 s and with the current density 1 mA/cm² at the temperature 60 °C, as shown in Fig. 7. In Figs. 7(b) and (c), there are more big particles and the density of nanoparticles in Fig. 7(b) is larger than that in Fig. 7(c). Compared with Figs. 7(a)-(c), there are no significant differences in the shape between the groups and preferred orientation with the corundum type of structures.

Fig. 7 The SEM images of α -Fe₂O₃ nanoparticles deposited with the different solution concentrations of (a) 4 mM FeCl₂ and 6 mM FeCl₃, (b) 8 mM FeCl₂ and 12 mM FeCl₃, and (c) 16 mM FeCl₂ and 24 mM FeCl₃.

mM FeCl₃, and (c) 16 mM FeCl₂ and 24 mM FeCl₃.

Fig. 8 shows the SEM cross-section image of α -Fe₂O₃ nanoparticles electrochemically deposited on the ITO coated glass substrate and all the as-prepared α -Fe₂O₃ nanoparticles were adherent to the ITO substrate. According to the reference, there are the Frank-van der Merwe, Strabski-Krastanov, Volmer-Weber, polycrystalline, and columnar growth modes for the fabrication of particles and thin films [37]. It is evident from Fig. 8 that the growth mode of the electrochemically deposited α -Fe₂O₃ nanoparticles fits the 3D Volmer-Weber growth mode.

Fig. 8 Cross-section SEM image of α -Fe₂O₃ nanoparticles deposited on the ITO surface for 200 s at 60 °C with the current density 1 mA/cm² and the solution concentrations 8 mM FeCl₂ and 12 mM FeCl₃.

All the results shown above indicate that the α -Fe₂O₃ nanoparticle shapes and sizes are determined by the electrochemical deposition conditions such as the deposition time, applied current density, reaction temperature and solution concentration. The deposition time affects the size of nanoparticles, and the size is increased with the increase of the deposition time. The average particle size and deposition time are linearly correlated under the given conditions. The current density affects the shape of nanoparticles that can be changed from the quasi-hexagonal to irregular shape. The reaction temperature affects the preferred orientation of nanoparticles. With the temperature increased, the number of nanoparticles is decreased and the shape of nanoparticles gradually becomes quasi-hexagonal. For the effect of solution concentrations, there are no significant differences in the shape between the different solution concentrations and the preferred orientation of nanoparticles.

4. Conclusions

Monodispersed hematite nanoparticles were fabricated on the ITO coated glass substrates using cathodic electrochemical deposition. Raman spectroscopy, XRD and SEM were used to characterize the α -Fe₂O₃ nanoparticles. The SEM images show that the size and morphology of α -Fe₂O₃ nanoparticles are determined by the deposition time, current density, reaction temperature and electrolyte concentration. The size of α -Fe₂O₃ nanoparticles is increased with the increases of the deposition time and electrolyte concentration. It is found that the acidic aqueous electrolyte solution can activate the ITO surface, promote the spontaneous nucleation and the growth of isolated α -Fe₂O₃ nanoparticles. The shape and density of particles can be changed by the reaction temperature and electrolyte concentration. Compared to other methods, the electrochemical deposition has been proven to be a cost-effective, environment friendly and highly efficient approach in fabricating nanoparticles with good controllability of the sizes, shapes and crystallinities for different potential applications.

Acknowledgments

This work was supported by International Science and Technology Cooperation Program of China (No.2012DFA11070), EU FP7 (ECROBOT No.318971; BioRA No.612641), EU H2020 (FabSurfWAR No.644971), Changbai Scholar Program of Jilin Province, National Natural Science Foundation Program of China (No.11504030, No.60940035 and No.61176002), Jilin Provincial Science and Technology Program (No.201215136, No.20140414009GH and No.2015-67), and Science and Technology Program of Changchun City (No.11KP04).

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