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Tracking the morphology and phase transformations of anodic iron oxide nanotubes using X-ray spectroscopy

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ABSTRACT

X-ray spectroscopic techniques have been employed to investigate highly ordered iron oxide nanotubes (NTs) prepared by iron anodization in a fluorine-containing electrolyte followed with annealing at elevated temperatures. NTs undergo morphology and phase evolutions from amorphous NTs to single crystalline nanoplates, then nanoflakes, and finally to a polycrystalline film. X-ray diffraction and X-ray absorption near edge structure have been used for the investigation. We show that fluorine incorporation can be used as an effective morphology tailoring tool for the engineering of efficient iron oxide nanostructures.

1. Introduction

In recent years, iron oxide has been shown as one of the most promising energy materials for photocatalysts, lithium ion battery electrodes, and supercapacitors [1–6]. In particular, hematite (α-Fe_2O_3) is especially attractive as a photo-anode due to its abundance, stability in aqueous environments, as well as suitable band gap (~2 eV) and valence band energy for solar water oxidation [1,7]. Multiple methods, such as sol-gel, thermal oxidation, chemical vapor deposition, electrochemical anodization, etc. [8], have been developed to fabricate nanostructured hematite to pursue high photo-conversion efficiency. However, the current status of hematite for water oxidation shows general disappointment due to the poor conductivity and rapid electron-hole pair recombination [8]. Therefore, the fabrication of hematite structure with desired morphology, which exhibits improved conductivity and allows efficient electron and hole separation, should significantly elongate the lifetime of photogenerated charge carriers and improve the efficiency of hematite photoanode [1,7,9].

As in the case of TiO_2, electrochemical anodization shows its robust nature for preparing highly ordered iron oxide nanotubes (NTs) with good geometry and alignment [10–13]. The NT structure thus obtained possesses high surface area and enhanced electron mobility through its tubular tunnel. Nevertheless, as-grown NTs are amorphous, hence thermal annealing is a necessity to initiate hematite crystallization for better photoactivity [7,14]. Meantime, annealing process certainly would sabotage the meticulous nanotubular structure which will suffer the sintering effect, resulting in the degradation of associated photoelectrochemical performance [4,12].

To resolve this dilemma, this work shows for the very first time that a possibility of the morphology tailoring of as-grown iron oxide NTs can be achieved to generate newly alternative hematite nanostructures by taking an advantage of self-doped F^- ions from iron anodization. The associated morphology and phase transformations as well as formation mechanism have been investigated and discussed accordingly using synchrotron soft X-ray spectroscopy.

2. Experimental section

2.1. Sample preparation

Similar to the growth of TiO_2 NTs [15,16], vertically aligned iron oxide NTs were prepared by a multi-step electrochemical anodization procedure. Particularly, a three-step method was applied by using a two-electrode cell, of which the anode was Fe foil (Goodfellow, 0.1 mm thick with a size of ~1 cm × 2 cm) and the cathode

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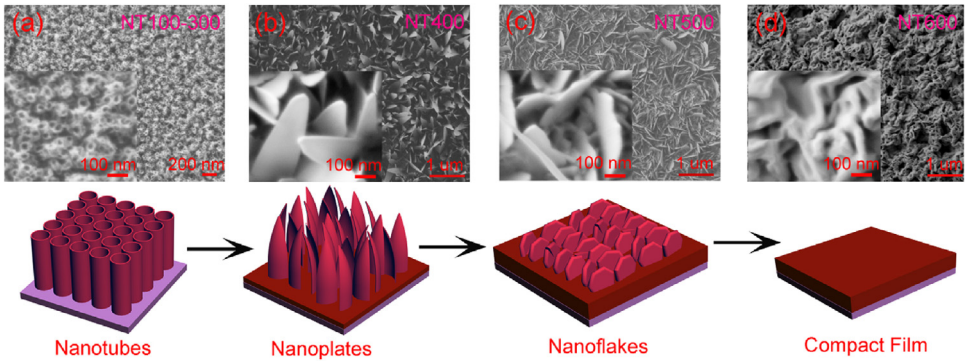

Fig. 1. SEM images (upper panel) of various iron oxide nanostructures with their corresponding schematic views indicated at the bottom.

was a platinum wire. The distance between these two electrodes was ~2 cm. A fluorine-containing electrolyte was used to create the nanotubular structure, which included an ethylene glycol base solution containing 0.3 wt% NH_4F (Alfa Aesar, 98.0% min) and 2 vol% DI water. To obtain the ordered NTs, firstly, Fe foil was anodized at 50 V (Hewlett-Packard 6209B DC power supply) for 10 min under room temperature (20 °C). Then the first layer was ultrasonically removed in DI water. Secondly, the refreshed Fe foil was anodized under the same condition as the first step for 5 min, and the second layer was subsequently peeled off from the Fe substrate by ultrasonication. Lastly, the third-step anodization was performed under the same condition as the first two steps for 3 min. The as-grown NTs were rinsed with ethanol several times and dried in a furnace at 100 °C for 2 h under ambient air, and are henceforth denoted NT100. To initiate the morphology and phase transformations of as-prepared NTs, NT100 was cut into 6 pieces. Of which one was kept without further processing, and the rest five were annealed at 200 °C, 300 °C, 400 °C, 500 °C and 600 °C for 2 h under ambient air with a high heating rate of 10 °C min^{-1}, henceforth denoted NT200, NT300, NT400, NT500 and NT600, respectively.

2.2. Characterization

Morphology characterization and element content analysis using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy were performed using a LEO (Zeiss) 1540 XB SEM facility. X-ray diffraction (XRD) data were recorded using a Rigaku rotating-anode X-ray diffractometer with Co Kα radiation. X-ray absorption near edge structure (XANES) experiment was carried out at the high resolution spherical grating monochromator (SGM) beamline of the Canadian Light Source (Saskatoon, SK, Canada). The Fe $L_{3,2}$-edge, O K-edge and F K-edge spectra were measured with an energy resolution of $E/\Delta E \geq 5000$ [17]. During XANES measurement, surface-sensitive total electron yield (TEY) and bulk-sensitive partial fluorescence yield (PFY) modes were used [15,16]. Of which TEY collected all the ejected electrons from the sample surface and were detected via monitoring the sample neutralization current, PFY recorded the outgoing fluorescent X-rays using four silicon drift detectors. All XANES spectra were normalized to the incident photon flux.

3. Results and discussion

The SEM images of as-prepared NTs and NTs annealed at elevated temperatures are shown in Fig. 1. Clearly, vertically ordered NTs (with an inner tube diameter of ~40 nm and tube wall thickness of ~10 nm) are achieved by Fe anodization (Fig. 1a). Note that no change of morphology is observed for NTs annealed at 100 °C–300 °C, thus only the SEM images of NT100 are shown in Fig. 1a. By contrast, NTs annealed at 400 °C (NT400) and 500 °C (NT500) with a high heating rate of 10 °C min^{-1} show a novel morphology evolution from small NTs to large nanoplates (NPs), and to larger nanoflakes (NFs). Both of these NPs and NFs exhibit a thin nanoarchitecture with a thickness of ~10 nm. It is worth noting that both NT400 and NT500 display a two-layered structure upon the Fe substrate by having the vertically aligned nanostructures on the top and a condensed layer underneath (not shown). In addition, a further increase of annealing temperature to 600 °C demolishes all the nanoarchitectures due to the sintering effect, hence only a compact layer with a sponge-like top morphology resides on the Fe substrate. The relevant schematic views of all these structures are indicated at the bottom side in Fig. 1.

Table 1
EDX results: atomic percentage of elements included in NT100 ~ NT600.

	Fe (Atomic%)	O (Atomic%)	F (Atomic%)	C (Atomic%)	Total (Atomic%)
NT100	62.27	18.40	15.78	3.55	100.00
NT200	59.21	23.99	12.69	4.11	100.00
NT300	46.91	44.40	4.62	4.07	100.00
NT400	41.46	56.43	N/A	2.11	100.00
NT500	40.16	57.70	N/A	2.14	100.00
NT600	39.25	58.28	N/A	2.47	100.00

Table 1 shows the results of elements content from energy dispersive X-ray (EDX) analysis. Four elements as Fe, O, F and C are recorded with their atomic percentages. Note that C is mainly from the carbon tape for EDX measurement. Upon annealing under ambient air, the top layer undergoes oxidation as the Fe at.% decreases whereas the O at.% increases. Interestingly, a large amount of F (~16 at.%) is presented in NT100 while its content drops to ~13 at.% and then to ~5 at.% after annealing at 200 °C and 300 °C, respectively. Persistent results of as-anodized iron oxide films have been shown that a significant amount of iron fluoride locates at the metal/film interface as well as the cell boundaries of tubular oxide layers [13,18], where similar results have been confirmed in as-anodized TiO_2 NTs [15]. More importantly, F no longer exists after annealing at 400 °C or higher where the morphology transformation takes place. Therefore, the presence of F in as-grown NTs together with its interaction with thermal crystallization of iron oxide is the key responsible for the associated novel morphology evolution.

X-ray diffraction (XRD) results are shown in Fig. 2. NT100 ~ NT300 exhibit the amorphous nature of NTs as well as the diffraction peaks from the Fe substrate. After the morphology transformation, both NT400 and NT500 offer the similar diffraction patterns which retain a mixed structure of polycrystalline magnetite and single crystal-like hematite with the predominant (110) lattice plane. As the annealing temperature goes up to 600 °C, other hematite facet planes, including (012), (104), (113), (024), (116) and (300), also pop up while the nanostructure annihilates in NT600. Apparently, phase transition from NT300 to NT400 demonstrates the significance of F: whereas its

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