

Short communication

Effect of anodizing temperature on surface morphology evolution of sputtered hematite films: A potential post-treatment method for further photoelectrochemical performance enhancement



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ABSTRACT

In this study, effect of anodization temperature on the photoelectrochemical (PEC) performance of nanostructured hematite films prepared by anodizing the sputtered iron films on the fluorine-doped SnO₂ glass substrate was investigated. It was noted that increasing the anodization temperature would induce the hematite nanostructure developing from film-like to nanorod morphology. Importantly, this morphology transformation is noted to accompany with the enhanced PEC performance up to 0.59 mA/cm² (nanorod structured anodized at 60 °C). Our results clearly demonstrated that the potential of post-treatment using anodization to further enhance the PEC performance of hematite films.

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Since Fujishima and Honda demonstrated the photoelectrochemical (PEC) water splitting reaction by shedding ultraviolet light to a TiO₂ electrode [1], a vast amount of researches have been carried out to improve the conversion efficiency for the perspective of mitigating the global warming [2,3]. In addition to TiO₂, several other promising photocatalysts have been synthesized and intensively explored [4–13]. Among them, α -Fe₂O₃ (hematite) exhibits several advantages such as its narrow band gap (~2.0 eV) for harvesting visible light (~40%), stability in electrolyte, low cost, non-toxic and environmental compatibility [4,9–11,14]. However, at current stage its PEC performance is significantly limited by factors including a very short excited state lifetime, low conductivity and poor minority charge carrier mobility (0.2 cm² V⁻¹ s⁻¹) which result in a small hole diffusion length (2–4 nm) [4,9–11]. In order to enhance the PEC performance of α -Fe₂O₃ photoelectrode, a

wide variety of methods have been proposed and substantially supported by subsequent experiments. For example, it is experimentally demonstrated that morphology control is capable of greatly enhancing PEC performance of hematite electrodes. This is because the anisotropic conductivity of hematite that the conductivity of charges transporting within the (110) plane is approximately 4 orders of magnitude higher than parallel to [001] [15]. Accordingly, higher PEC performance is always observed in hematite films possessing a low-dimension structure [16–21]. For instance, Mohapatra et al. anodized α -Fe₂O₃ ultrathin nanotubes on Fe foils with constant potential of 50 V for 13 min in an ethylene glycol solution containing 3 vol% water and 0.5 wt% NH₄F and found that as-anodized α -Fe₂O₃ nanotubes showed a PEC performance (1.41 mA/cm²) higher than other structured specimens [17]. Rangaraju et al. used a two-step electrochemical anodization process to prepare a two-layered iron oxide nanostructure (a top layer of nano-dendrite morphology and a bottom layer of nanoporous morphology) and they observed a remarkable photocurrent density (1.8 mA/cm²) in 1.0 M KOH solution [18]. They attributed the observed high photocurrent density to the better photocatalytic

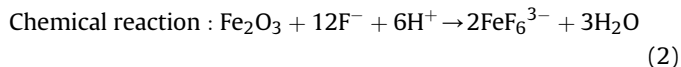
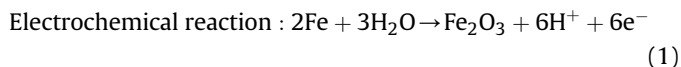
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activity of nano-dendritic iron oxide and better electron transportation behaviour of vertically oriented nano-channels [18]. Chang et al. reported α -Fe₂O₃ nanorods prepared from RF-sputtered Fe films on F-doped SnO₂ (FTO) glass substrates through electrochemical anodization using 50 V [19]. They focused on water content effect on morphology and reported the α -Fe₂O₃ nanorods to exhibit a photocurrent density of 0.72 mA/cm² at 0.5 V [19]. Wu et al. reported α -Fe₂O₃ nanotubes on Fe foil via anodization and they found the voltage and water content can affect the morphology of α -Fe₂O₃ nanotubes [20]. These successful cases arise an interesting research topic to explore that whether anodization could be an effective post-treatment method that could further enhance PEC performance by turning the morphology of hematite films.

To answer this question, efforts were carried out to anodize the sputtered iron films at different temperature in this study. Sputtering is a technique known to produce a relatively uniform and condense film while conversely it indicates that morphology control is difficult to achieve during the sputtering process [22]. Accordingly, post-treatment using anodization is likely to provide an opportunity to adjust the morphology of a sputtered film [23]. Note that although the anodization is not a new technology [17–20], studies regarding its application in post-treatment are rarely found in literature. As shown in Fig. 1, we first prepared Fe films on fluorine-doped SnO₂ (FTO) glass substrate (the FTO substrates were heated and equilibrated at 300 °C with a rotating rate of 20 rpm) using DC magnetron with 100 W DC power in a high vacuum chamber (Fig. 1(a)). In the end of sputtering, these samples were anodized via a two-electrode configuration in a 100 mL solution containing 95 mL ethylene glycol, 0.05 M ammonium fluoride (NH₄F, Showa, 99.0%) and 5 mL ultrapure water, where the Pt foil functioned as the cathode and the Fe film as the anode separated by 30 mm (Fig. 1(b)). The anodization temperatures were varied from 20 to 80 °C with fixed bias of 20 V for 1–3 min with stirring at 100 rpm. These anodized samples were then annealed at 550 °C for 2 h under air ambient condition with the heating and cooling rate at 10 °C/min (Fig. 1(c)). All samples were characterized using scanning electron microscope (SEM, Hitachi S4800), D2 Phaser diffractometer (Bruker, X-ray diffraction), UV–visible spectrophotometer (Vary 100 scan) while their electronic property (Mott-Schottky plots) as well as PEC performance was conducted using a home-made photoreactor (AUTOLAB Model PGSTAT 30, Fig. S1).

Mechanism of anodization of α -Fe₂O₃ nanostructures was suggested by following two reactions [17,19].



Prior to exploring effect of anodization temperature, a preliminary study was conducted to evaluate the effect of anodizing time on morphology evolution of Fe₂O₃ nanostructures at 20 °C. As shown in Fig. S2, the current density dropped significantly from 400 to 100 mA/cm² at stage I, which is due to the occurrence of electrochemical reaction mainly. In this stage, a Fe₂O₃ passive layer was formed on the Fe film [17–19]. At stage II (58–120 s), a steady state of constant current density (80 mA/cm²) was reached. In this period of time, electrochemical reaction and chemical reaction occurred simultaneously and achieved equilibrium lead to the constant current density. Importantly, dissolution and etching of Fe₂O₃ passive layer on the nanostructures occur at stage II [18,19], which is defined as the anodization time of our system. Further current density dropping to 50 mA/cm² at stage III is attributed to the over-etching that may occurred and the FTO expose to the F-containing ethylene glycol solution lead to the lowest current density of the entire anodizing process [19]. Accordingly, stage I (t = 0–57 s) and stage III (t = 121–180 s) weren't selected for conducting following anodization experiments. Fig. 2(a–g) show morphology evolution of hematite nanostructures as a function of anodization temperature, respectively. In Fig. 2(a), the morphology of un-anodization sample (reference) is mainly covered by irregular particles with a mean size approximately 560 nm. In the end of 2 min anodization at 20 °C, a coarse surface appears containing irregular nanoparticles (approximately 295 nm) as indicated by Fig. 2(c). Fig. 2(e–g) show morphology evolution of samples anodized at 40, 60 and 80 °C for 2 min, respectively. When anodized at 40 °C, the morphology of sample contains nanoparticles with an average particle size around 450 nm (Fig. 2(e)) while that anodized at 60 °C exhibits Fe₂O₃ nanorods with an average diameter of 125 nm (Fig. 2(f)). It is noted that over etching the nanorods due to high anodizing temperature would lead a great fraction of FTO surface exposed and therefore compromises the photocatalytic activity of hematite electrodes (80 °C, Fig. 2(g)). This observation may be attributed to that at higher anodizing temperature, the etching rate of Fe₂O₃ is faster, simply due to the enhanced diffusion rate of etched Fe ions having higher thermal kinetic energy. Based on SEM image, the mechanism involved in anodization can be illustrated as Fig. 2(h).

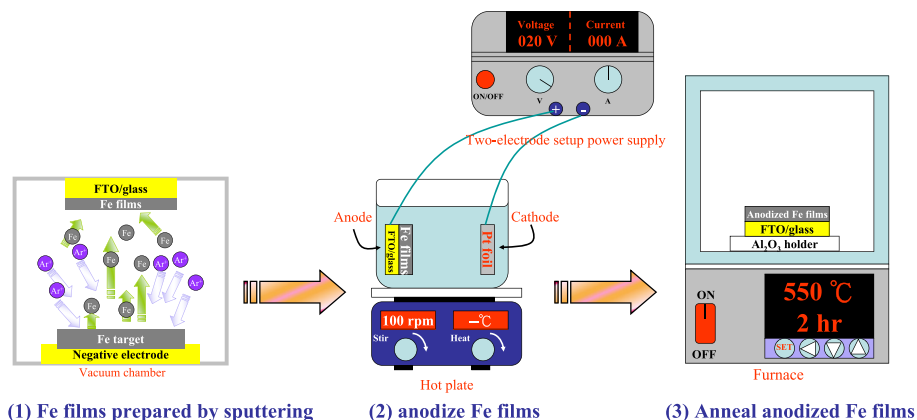


Fig. 1. The schematic illustration of the formation mechanism of Fe₂O₃ via anodization.

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