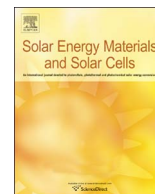




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Tuning orientation of doped hematite photoanodes for enhanced photoelectrochemical water oxidation

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ABSTRACT

The limited conductivity in hematite has been currently considered as a critical bottleneck in improving the efficiency of solar-driven water oxidation. Here we shed light on the improvement of carrier conductivity by combing orientation control and transition metal doping. To rule out the influence of surface facets of hematite when adjusting the film orientation, the hematite photoanode films were fabricated by assembling the spherical particles with single crystalline nature. The doped hematite particles were aligned with (001) plane normal to the substrate by a magnetic field (MF) during the drop-casting process. A considerable improvement in photocurrent density was resulted from the orientation control, which is due to the increased carrier density from Sn doping and efficient charge transportation in the (001) plane observed through electrochemical impedance spectra.

1. Introduction

Photoelectrochemical (PEC) conversion of water or CO₂ to produce hydrogen or carbon-based fuels is a promising technique to capture and store the intermittent solar energy in a sustainable way [1]. The half-reaction of oxygen evolution on photoanode surface provides the electrons that are required to reduce water or CO₂, and the efficiency of the whole reaction is limited by the oxygen evolution reaction (OER) due to its slow kinetics [2]. The development of highly-efficient photoanodes composing of earth-abundant elements is a critical challenge and therefore received extensive research efforts. Hematite (α -Fe₂O₃), with a proper band gap of 2.1 eV allowing the light absorption of incident solar irradiation below 590 nm, is one of the most promising photoanode material candidates [3,4]. However, the reported PEC conversion efficiency of hematite as photoanode are generally much lower than the predicted value. The short hole diffusion length and sluggish reaction kinetics on the surface are the main causes. In the past few years, it has been demonstrated that surface modification using co-catalysts [5–9] or by thermal treatment [10] could effectively shift the photocurrent onset potential by minimizing the overpotential, though fully understandings is still unachieved. As such, the photocurrent density of α -Fe₂O₃ is largely confined by the fraction of photogenerated holes that reach the surface. Improving the carrier conductance is therefore important for enhancing the hematite PEC performance.

Doping strategies are widely adopted to improve the carrier

transport in the α -Fe₂O₃ bulk. Transition metals such as Ti [11,12], Zr [13] Sn [14], and Pt [15] and nonmetal elements [16] have been proven effective for the enhancement of carrier transport by increasing free carrier concentration [17] or the reactivation of the dead layer close to the conducting substrate [11]. Considering that the charge conductance in (001) plane is 10⁴ higher than along the orthogonal directions [18,19], an alternative approach to manipulate the conductivity of α -Fe₂O₃ is tuning the film orientations. By controlling the synthesis conditions, hematite films with preferred orientation have been obtained and the enhanced PEC activity were correlated with the texture effect [20–22]. Unfortunately, adjusting the orientation distribution of the films generally leads to different exposed surface planes. And the dependence of catalytic reactivity of oxide nanoparticles on the exposing facets has been widely observed [23,24]. The concurrence of the two factors brings difficulty to distinguish contributions of surface plane on surface energetics [25] and orientations on charge transport in the bulk. Previously, we demonstrated the role of film orientations on its photoelectrochemical performance by building the films using hematite particles of the same surface structure [26]. However, the photocurrent densities of the aligned hematite photoanodes are still relatively small due to the low electrical conductivity nature of the undoped α -Fe₂O₃.

In this work, we show that photoelectrochemical activity of hematite films could be enhanced by applying both the orientation strategy and doping method. α -Fe₂O₃ films were prepared by assembling single-

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crystalline $\alpha\text{-Fe}_2\text{O}_3$ particles which were prepared with the hydrothermal method. Due to the anisotropy in magnetic susceptibility of hematite, the orientation of the films were successfully manipulated by a strong magnetic field. The effects of Sn doping and (001) preferred orientation on the PEC performance of $\alpha\text{-Fe}_2\text{O}_3$ were discussed, and the correlation between the photocurrent density and conductivity of the film were characterized by the electrochemical impedance spectra (EIS) in detail.

2. Experimental

2.1. Materials and methods

Single crystalline $\alpha\text{-Fe}_2\text{O}_3$ particles were synthesized using hydrothermal method that we previously reported [23] with slight modifications. The mixture of 0.1 M FeCl_3 , 1 wt% PEG 20 K, and 1 wt% NaOH solution was stirred for 30 min before being transferred into a Teflon-lined autoclave for 5 h reaction at 180 °C. The resultant precipitates were washed with acetone and ultrapure water. Sn-doped hematite ($(\text{Fe}_{0.99}\text{Sn}_{0.01})_2\text{O}_3$) particles was prepared by adding 1 mM SnCl_2 into the precursor solution. The hematite particles were assembled onto FTO substrate via drop-casting process during which a magnetic field was applied to assist the orientation control of the film [27], as schematically shown in Fig. S1. The hematite films were annealed under 500 °C for 2 h and then under 800 °C for 10 min.

2.2. Characterization

The hematite films were characterized using FE-SEM (Zeiss EVO18) equipped with EDS, TEM (JEM-2100F), XRD (Rigaku D/max 2500 using $\text{Cu K}\alpha$ radiation) to acquire the chemical and structural information. The UV-vis spectra of samples were recorded on a Lambda 750S UV/Vis Spectrometer with an integrating sphere detector, using a bare FTO substrate as reference. The electrochemical tests were performed in deaerated 1.0 M NaOH electrolyte with a conventional three-electrode on a ZAHNER potentiostat. Saturated Hg/HgO and platinum wire were used as the reference and counter electrode respectively. Hematite electrode was fabricated by establishing contact between the FTO layer and copper wire using silver conductive paint. Exposed areas of the back contact and edges were carefully sealed with epoxy resin.

The working electrode area was about 0.2 cm^2 for electrochemical measurements. Oxygen was detected using a dissolved oxygen analyzer (3-Star, Thermo Scientific) during the chronoamperometric PEC measurement at 1.4 V_{RHE} . The electrolyte was stirred vigorously to assist the diffusion of produced dioxygen. Impedance spectra measurements were performed using 5 mV amplitude perturbation of between 10 kHz and 0.1 Hz. The light source was a 500 W xenon lamp (CEL-HX, ozone free) through AM 1.5 filter with the intensity of 100 mW cm^{-2} .

3. Results and discussions

Fig. 1 shows the top-view morphology of $(\text{Fe}_{0.99}\text{Sn}_{0.01})_2\text{O}_3$ films prepared by drop-casting followed by heat-treatment at 500 °C and 800 °C. It can be found that the films are consisted of oval particles with major and minor axis of 133 nm and 103 nm, respectively. The surface of particles became smooth and the size regrew a little larger (Fig. S2) when the films were calcined at higher temperature of 800 °C. It is worth noting that no noticeable morphology change was observed in the samples prepared under 0 T and 10 T, as shown in Fig. 1. In addition, the Sn content in the particles was about 1 at% from the EDS measurement (Fig. S3). About 5 layers of hematite particles were assembled into the film with thickness about 481 ± 24 nm (Fig. S4).

The $(\text{Fe}_{0.99}\text{Sn}_{0.01})_2\text{O}_3$ particles are further characterized using TEM, as shown in Fig. 2. The size distribution of oval-like $(\text{Fe}_{0.99}\text{Sn}_{0.01})_2\text{O}_3$ particles are identical to the observation in the SEM. The SAED pattern with sharp diffraction spots assigned to $\alpha\text{-Fe}_2\text{O}_3$ reveals the single crystalline feature of the $(\text{Fe}_{0.99}\text{Sn}_{0.01})_2\text{O}_3$ particles (Fig. 2b). The elemental mapping of $(\text{Fe}_{0.99}\text{Sn}_{0.01})_2\text{O}_3$ in Fig. 2c confirms that the Fe and Sn are uniformly distributed in the particles, indicating the uniformly Sn doping. Though the magnetic response of hematite is weak [28], the single crystalline nature of the these particles provides foundations for magnetic alignment when the strength of the field is high enough to suppress the thermal energy.

For photoelectrochemical cell using n-type semiconductor as anode, hole-electron pairs are generated by incident photons. As shown in Scheme 1, holes generated within the $(L+W_{\text{sc}})$ length to the solid-electrolyte interface win the chance of reaching the surface due to the interface electric field. These surface holes participate in water oxidation and release oxygen molecules and the cogenerated electrons move to the counter electrode to produce hydrogen under an appropriate

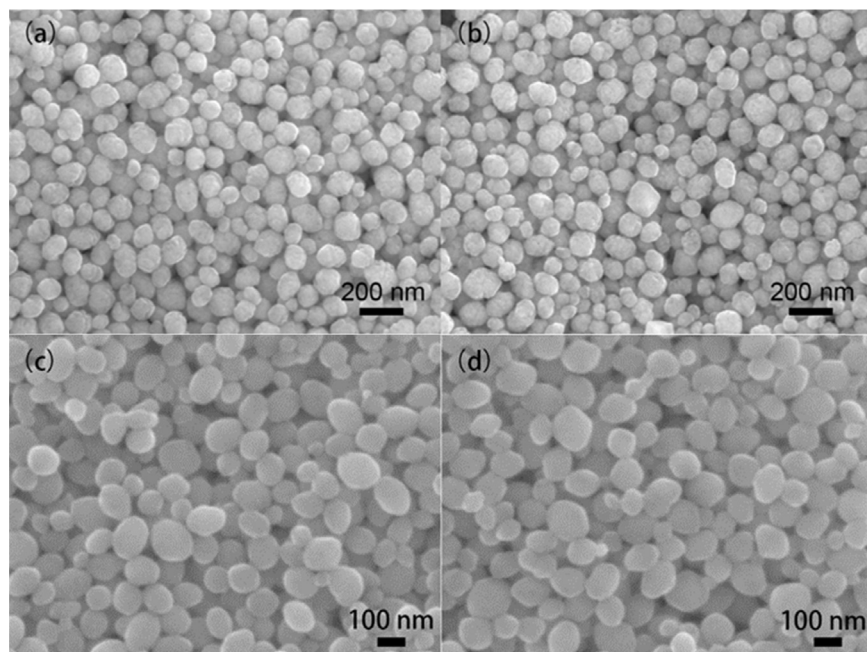


Fig. 1. SEM images of $\alpha\text{-Fe}_2\text{O}_3$ films prepared under magnetic field 0 T (a, c) and 10 T (b, d) by drop casting method and followed by heat treatment at 500 °C (a, b) and 800 °C (c, d).

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