Research paper

Effects of low temperature annealing on the photo-electrochemical performance of tin-doped hematite photo-anodes

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ABSTRACT

The effects of post-deposition annealing at 400 and 500 °C on the photo-electrochemical performance of Sn^{IV}-doped α-Fe_2O_3 photo-anodes are reported. Samples were fabricated by spray pyrolysis on fluorine-doped tin oxide (FTO) and on titanium substrates. Photo-electrochemical, morphological and optical properties were determined to explain the shift in photocurrent densities to lower electrode potentials and the decrease of maximum photocurrent densities for alkaline water oxidation after annealing. Annealing at 400 and 500 °C in air did not affect significantly the morphology, crystallinity, optical absorption or spatial distributions of oxygen vacancy concentrations. However, XPS data showed a redistribution of Sn^{IV} near Sn^{IV}-doped α-Fe_2O_3 | 1 M NaOH interfaces after annealing. Thus, electron-hole recombination rates at photo-anode surfaces decreased after annealing, shifting photocurrents to lower electrode potentials. Conversely, depletion of Sn^{IV} in the α-Fe_2O_3 bulk could increase recombination rates therein and decrease photon absorption near 550 nm, due to an increased dopant concentration in the semiconductor depletion layer. This accounted for the decrease of maximum photocurrents when electron-hole recombination rates were suppressed using HO_2^- ions as a hole scavenger. The flat band potential of Sn^{IV}-doped α-Fe_2O_3 remained relatively constant at ca. 0.7 V *vs.* RHE, irrespective of annealing conditions.

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1. Introduction

Solar energy harvesting using devices such as photovoltaic modules needs to be coupled to energy storage due to the diurnal and intermittent nature of solar energy. Hydrogen is a candidate for such chemical energy storage, because of its facile oxidation in fuel cells without formation of harmful by-products [1]. Splitting liquid water to produce hydrogen (and oxygen) using solar energy requires a minimum of 1.48 eV under thermoneutral conditions. Prospectively, photo-electrochemical reactors could produce hydrogen directly using solar energy, but photo-electrode materials are yet to be adequately efficient, durable, and produced by an economic fabrication process.

Hematite has been studied extensively as a possible photo-anode material for water splitting [2]. However, it requires an electrical bias to oxidise water effectively as the energy of its conduction band edge is too low and exhibits low energy conversion efficiencies. Numerous approaches for improving this material have been suggested such as doping [3], inclusion of quantum dots [4], improved synthesis pathways such as ALD [5], electrodeposition [6], and high temperature annealing [7] and reductive annealing [8]. In order to enhance the properties of photo-electrodes such as hematite, it is important to understand how the changes produced by different treatments, such as annealing, affect the properties and ultimately their performance. Post-deposition annealing of hematite thin films in air has been suggested as an essential treatment to achieve the adequate crystallinity and decrease concentrations of defects in the structure [9]. Reductive annealing [8] and hydrogen treatment [10] have also been suggested as ways to improve the photo-activity of hematite, creating oxygen deficiencies in its structure and hence improving its conductivity. Other hypotheses have also been proposed to explain the behaviour of hematite after

annealing, ranging from catalytic effects to morphological changes [11].

The substrate used as support for the thin films also needs to fulfil several requirements: mechanical and chemical stability, high conductivity that would minimise in-plane ohmic losses and compatibility with photo-electrodes in terms of interfacial properties of electrical junction formed. Behaviour at elevated temperatures should also be considered when the synthesised films require heat treatment. Traditionally, hematite is deposited on conductive films such as fluorine-doped tin oxide (FTO) or indium tin oxide (ITO) on glass. These substrates are readily available and transparent, which is a useful characteristic for back-illumination. Small electrodes fabricated on these substrates do not suffer from significant ohmic losses and mechanical fragility. However, scale-up of electrodes to > 0.01 m^2 results in electrical potential losses due to relatively low conductivity [12], $8\,\Omega$ per square (FTO, TEC-8 Pilkington) and renders them more easily breakable. Sn^{IV} is also known to interact beneficially with hematite at temperatures $> 600\,°C$ [13,14], demonstrating that FTO and ITO substrates are not entirely inert. Alternatively, hematite has been synthetized on titanium foil due to its chemical stability in alkaline conditions [15] and high conductivity that serves to minimise ohmic losses. However, heat treatment in air causes growth of TiO$_2$ film of several nanometers [16], which could interact with hematite thin films even at 500 °C [15].

Doping of hematite photo-anodes has been suggested as a strategy to improve their electrical conductivity [17] and decrease electron-hole recombination rates in their bulk [2]. This can also be achieved by back-illumination (through the substrate) of un-doped hematite, exhibiting up to 3-fold increase of incident-to-photon current efficiency [18–20], but the high sheet resistance of the required transparent substrate limits scale-up. Conversely, back-illumination has been proved to be counterproductive for doped hematite, the electrical conductivity of which was increased and electron-hole recombination rates decreased in the bulk material, while the sluggish diffusion of holes through the film was the limiting step [21]. A 90% decrease in photocurrent was reported compared with that for front-illumination. Dopants such as Sn^{IV} have been used extensively to enhance photo-activity of hematite photo-electrodes, where Sn^{IV} acts as donor centre after replacing Fe^{III} sites [3]. Sn^{IV}-doped photo-electrodes exhibited higher donor densities of ca. 10^{26} and 10^{27} m^{-3} for doping concentrations between 0.5 and 2% mass [22]. These values are two orders of magnitude greater than for undoped hematite [10,23]. Donor densities reported here (ca. 1.3% mass Sn^{IV} doping) are as high as 10^{25} to 10^{27} m^{-3}. In this case, these unusually high values could have been affected by the concentration of oxygen vacancies in non-stoichiometric hematite Fe$_2$O$_{3-x}$, a higher electro-active area compared to geometrical area, or the presence of chloride ions at the surface [24]. Contrary to the hypothesis that doping with Sn^{IV} affects mainly bulk electron-hole recombination rates, it has been shown recently that it also affects rates of hole transfer and catalysis of the oxygen evolution reaction on hematite photo-anodes [25]. On the other hand, it has been reported that an increase in Sn^{IV} concentrations decreases the absorption of photons substantially in the visible region [3], possibly due to the formation of SnO$_2$, which has a higher band gap (3.5 eV) [26].

To elucidate further the effects of annealing at 400–500 °C of Sn^{IV}-doped hematite on titanium, the performance of spray pyrolysed photo-anodes was assessed as a function of several properties. The understanding of these effects could also clear the path to the improvement of existing models of photocurrent prediction in photo-electrochemical reactors. The quality of such models relies critically on the accuracy of the parameters on which they are based; special attention needs to be paid to parameters such as the flat band potential and donor density as several

assumptions, often inappropriate, are made en route to their determination at nanostructured photo-electrodes [27].

2. Experimental

2.1. Photo-anode fabrication

Sn^{IV}-doped α-Fe$_2$O$_3$ photo-anodes were fabricated via spray pyrolysis [15] on TEC-8 fluorine-doped tin oxide (FTO) on glass (Hartford Glass Inc., USA) and titanium foil (0.74 mm, 99.4% Alfa Aesar). Titanium substrates (10 mm × 60 mm) were polished on an automated polishing machine (Buehler) with polishing paper grade 400, 800, 1200 and finally with aqueous dispersion of < 300 nm alumina particles. Then, substrates were degreased with acetone, immersed in 0.5 M oxalic acid overnight to minimise the oxide layer thickness, rinsed with acetone and ultra-sonicated in de-ionised water, as for FTO substrates, a few minutes prior to spray pyrolysis. The precursor solution for spray pyrolysis comprised 0.1 M FeCl$_3$.6H$_2$O (99.99%, Sigma Aldrich, UK) and 6×10^{-4} M SnCl$_4$ (99.995% Sigma Aldrich, UK) dissolved in ethanol absolute (AnalaR Normapur, VWR). Sn^{IV} concentration corresponds to 1.3% doping by mass. The precursor was nebulized with a quartz spray nozzle (Meinhard, USA) at a height of 150 mm above the surface of the substrate. The nozzle movement was controlled by WinPC-NC CNC Software (BobCad-CAM, USA). The precursor solution was delivered using a syringe pump at 2 cm^3 min^{-1} and pressurised air was supplied at 345 kPa. Substrates were placed on a hotplate at 480 °C and took approximately 15 min to reach that temperature. Next, 40 passes of the nebuliser over the substrate were programmed to obtain 47 ± 6 nm thick hematite films, which was measured with a profilometer (TencorAlphastep 200 Automatic Step Profiler) in a previous study [28]; each pass took 1 minute with a resting time of 1 minute between passes, and a total time of ca. 90 min. Samples were cooled to 200 °C before being removed from the hotplate to continue cooling at room temperature.

The post-deposition annealing was done in a pre-heated oven (Elite Thermal Systems, Ltd.) at 400 and 500 °C in air at atmospheric pressure over the course of an hour. Ti|Sn^{IV}-Fe$_2$O$_3$ samples were extracted at 20, 40 and 60 minutes. All FTO|Sn^{IV}-Fe$_2$O$_3$ samples were treated for the full 60 minutes.

In order to minimise dark currents from non-illuminated electrode areas, samples were partially coated using insulating acrylic lacquer (45 kV mm^{-1}, RS component) to obtain an exposed area of 3 mm × 6 mm, corresponding to the dimensions of the incident light beam.

2.2. Photo-electrochemical characterization

Photo-electrochemical characterization was carried out using a photo-electrochemical cell of 60 cm^3 (PVC body with a quartz window). A potentiostat/galvanostat (Autolab PGSTAT 30 + Frequency Response Analysis module, Eco Chemie, Netherlands) was used to control the cell containing Sn^{IV}-Fe$_2$O$_3$ samples as working electrodes, a platinised titanium mesh (Expanded Metal Company, UK) as counter electrode and HgO|Hg as reference electrode (0.913 V *vs.* RHE and 0.109 V *vs.* SHE). 1 M NaOH was used as electrolyte solution, pH of ca. 13.6 and temperature 25 ± 2 °C. H$_2$O$_2$ (30%, AnalaR Normapur, VWR) was added in some cases as sacrificial electron donor at a concentration of 0.5 M.

Cyclic voltammograms were run typically from 0.5 to 2.0 V *vs.* RHE at 10 mV s^{-1} scan rate. Incident photon-to-current efficiencies (IPCE) were measured from 300 to 700 nm in 20 nm increments for 100 s at 1.51 and 1.71 V *vs.* RHE. Data for Mott-Schottky (MS) analysis was obtained from potentiostatic electrochemical