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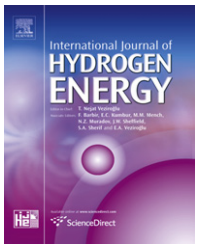

Microwave-assisted low temperature fabrication of nanostructured α-Fe_2O_3 electrodes for solar-driven hydrogen generation

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ABSTRACT

It is demonstrated for the first time that significant enhancement of photoelectrochemical performance could be achieved by using microwave-assisted annealing for the fabrication of α-Fe_2O_3 thin films. The process can also lead to significant energy savings (>60% when compared with conventional methods). Different types of Fe thin films were oxidized using both microwave and conventional heating techniques. The photoelectrochemical performance of electrodeposited, undoped and Si-doped iron oxide samples showed that microwave-annealing resulted in superior structural and performance enhancements. The photocurrent densities obtained from microwave annealed samples are among the highest values reported for α-Fe_2O_3 photoelectrodes fabricated at low temperatures and short times; the highest photocurrent density at 0.55 V vs. $V_{Ag/AgCl}$, before the dark current onset, was 450 $\mu A\ cm^{-2}$ for the Si-doped films annealed at 270 °C for 15 min using microwave irradiation (and 180 $\mu A\ cm^{-2}$ at 0.23 V vs. $V_{Ag/AgCl}$) while conventional annealing at the same temperature resulted in samples with negligible (3 $\mu A\ cm^{-2}$) photoactivity. In contrast, a 450 °C/15 min conventional heat treatment only resulted in a film with 25% lower photocurrent density than that of the microwave annealed sample. The improved performance is attributed to the lower processing temperatures and rapidity of the microwave method that help to retain the nanostructure of the thin films whilst restricting the grain growth to a minimum. The lower processing temperature requirements of the microwave process can also open up the possibility of fabricating hematite thin films on conducting, flexible, plastic electronic substrates.

1. Introduction

Finding a renewable source of energy to replace fossil fuels has been the focus of many research groups around the world. Generation of hydrogen through photoelectrochemcial (PEC) water splitting is one of the most promising alternatives for the production of hydrogen as a fuel. In this method, light is absorbed by a semiconductor electrode which then provides the energy required to break water molecules into hydrogen and oxygen.

Since the pioneering work of Fujishima and Honda in 1972 [1], a variety of semiconductor materials such as $SrTiO_3$ [2], TiO_2 [1,3,4], CdS [5,6], WO_3 [7,8] and Fe_2O_3 [9,10] have been used as PEC water splitting photoelectrodes. The desirable material capable of driving the reactions involved in the photocatalysis of water is required to satisfy several requirements; suitable bandgap, favourable positioning of the band edge energy levels, stability in aqueous environment, abundance and ease of fabrication are considered to be the most important [11]. Iron

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oxide in the form of α-Fe_2O_3 (hematite) is one of the materials which meet most of these selection criteria. So far, however, conversion efficiencies of hematite photoelectrodes have remained relatively low. Slow charge transfer kinetics, low light absorption and short hole diffusion lengths have been generally identified as the factors responsible for the poor PEC performance of hematite photoelectrodes [12,13]. Several different approaches have been investigated to tackle these problems. Doping is believed to increase the conductivity of hematite electrodes and consequently could lead to improvements in photoelectrochemical performance. Recently, attempts have also been made to improve the conversion efficiencies of α-Fe_2O_3 through tailoring the nanostructure of thin films of hematite via processing. Iron oxide electrodes can be deposited either at high temperature using methods such as atmospheric pressure chemical vapour deposition (APCVD) [14,15], aerosol-assisted CVD (AACVD) [16] and spray pyrolysis [10,17] or at low temperature using, for example, electrochemical routes [18,19] and sputtering [20]. The advantage of low temperature fabrication methods is that they are easily transferable at industrial scale and deposition conditions are easier to control comparing to those of high temperature processes such as APCVD. However, these methods generally involve a post deposition annealing process. This step could be very energy intensive and time-consuming. The major drawback, however, is the particle growth and consequent collapse of the nanostructure as a result of the annealing treatment. It reduces the porosity and effective surface area which will in turn affect the PEC performance. This also limits the maximum conversion efficiencies that can be achieved by the photoelectrodes fabricated using low temperature techniques.

Microwave irradiation has shown great potential for the processing of different inorganic solids [21,22] and semiconductor materials such as TiO_2 [23], ZnO [24] and iron oxides [25,26]. Microwave-Assisted hydrothermal processing has dominated the research on preparation of iron oxides [27,28]. Although feasibility of the application of microwave heating in producing different particle shapes such as nanorings [29] sheets and spheres [27] has been reported, the role of microwave heating in altering the photoelectrical properties of iron oxide particles has not been investigated in detail. From the processing point of view, it has been shown that the use of microwave irradiation would lead to shorter synthesis time, higher yields, better particle shape control and chemical plant size reduction [27,29–31]. We present here a facile microwave-assisted method to oxidize electrodeposited Fe films to form hematite thin films which showed enhanced PEC performance. The performance of microwave-prepared films surpassed that of the samples annealed conventionally while a total power savings of >60% was achieved by using microwaves.

2. Experimental

2.1. Sample preparation

Fe was electrochemically deposited on fluorine-doped tin oxide coated (FTO, TEC8, Pilkington Glass, Ltd, St Helens, UK) glass substrates. The area of the film was maintained at 1 cm^2. The FTO substrates were cleaned and sonicated in acetone, ethanol and deionised water (resistivity = 18.2 MΩ) and stored in absolute ethanol. The electrochemical solution consisted of 2 mM $FeCl_3.6H_2O$ (reagent grade, SigmaAldrich, Dorset, UK) in absolute ethanol and stirred at 60 °C for 2 h. The electrochemical deposition of Fe films was performed in a two-electrode configuration where FTO was used as a cathode and a Pt wire as an anode. An applied potential of 6.2 V for 50 s resulted in a black film of metallic Fe (thickness = 100–150 nm) on the FTO substrates. The deposition of Fe film was confirmed by XRD. The films were then washed by deionised water and left in air to dry. In order to study the effects of Si doping on the properties and performance of photoelectrodes, Tetraethoxysilane (TEOS) was used as the source of Si. Solutions with different molar ratios of Si/(Fe + Si) were prepared. A minimum concentration of Si/(Fe + Si) = 10% showed an appreciable improvement in photoperformance. Higher concentrations of TEOS (up to Si/(Fe + Si) = 40%) did not result in any further improvement in PEC performance. Hence all the results reported here are for the films prepared from the solutions with the molar ratio of Si/(Fe + Si) = 10% and that the dopant concentrations mentioned in the paper are for the electrochemical solutions. Doped Fe films were deposited from Si-containing solutions by applying 7 V potential for 50 s to achieve similar thicknesses to those of undoped Fe films.

2.2. Annealing treatments

Thermal oxidation of iron films were carried out using two different methods; conventional and microwave heating. Conventional annealing was carried out in a tube furnace (MTF-10–25–130, Carbolite, Hope Valley, UK); the sample was heated at the rate of 20 °C/min to the desired temperature. Both ends of the tube were kept open to allow for the flow of air. After annealing the furnace was turned off and the samples were left in the furnace to cool down. The temperature of the samples was measured using a k-type thermocouple. Microwave-Assisted annealing was performed using a modified microwave oven (MC8087ARS multimode cavity, LG, Milton Keynes, UK) capable of producing a tuneable continuous power output up to a maximum of 1000 W operating at 2.45 GHz frequency.

Electrodeposited films were placed inside a high purity alumina casket to minimise the heat loss. SiC rods were used as secondary susceptors [32]. The top of the casket had a hole at the centre which allowed for the temperature measurement of the film using a thermal imaging camera (FLIR Thermovision A40, FLIR Systems, West Malling, UK) and temperature was recorded using ThermaCAM Researcher software [33]. Temperature calibration was performed using the melting point of V_2O_5 as described elsewhere [33,34]. The error in temperature measurements is evaluated to be within ±5 °C. Microwave power was manually increased so that the heating rate of 20 °C/min was maintained and the desired temperature was achieved. For the samples annealed conventionally (Conv. Samples), a wide range of temperature–time annealing profiles was examined; temperature was varied from 250 °C to 650 °C at 15, 30 and 60 min annealing times. Microwave-annealed samples (MW samples) were prepared by heating them at 175, 200, 230, 270 and 300 °C at