



# Thermal enhancement of water affinity on the surface of undoped hematite photoelectrodes

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## ABSTRACT

Hematite is one of the most promising semiconductors used to convert solar irradiation directly into chemical energy (molecular hydrogen and oxygen) via water splitting. Although several methods have been developed in the last decades, the repertoire of a method to fabricate hematite electrodes with a large covered area, relative low cost, industrial viability and remarkable properties still remains a challenge. This paper describes a microwave-assisted hydrothermal process to produce hematite films. The photoelectrodes prepared consisted of rods of hematite on the FTO substrate (FTO-fluorine doped tin oxide) forming mesoporous nanostructured. According to the X-ray diffraction data, thin films thermally treated at high temperature grew preferentially to the [110] direction, i.e., growth perpendicular to the substrate. Moreover, high temperature of thermal treatment influenced positively on the stability, current density and charge transfer efficiency of photoelectrodes. The impedance spectroscopy (EIS) data aided us to understand the best photoelectrochemical performance exhibited by hematite electrode synthesized during 2 h with additional thermal treatment at 750 °C. The high temperature treatments seem to promote higher  $N_D$  (charge density) and  $V_{fb}$  values estimated from EIS data, which are related to an efficient photogenerated charge separation ( $e^- - h^+$ ). Additionally, our results suggested that the hematite surface roughness and wettability should be considered as important parameters for producing active electrodes for solar water oxidation. A quasi-super hydrophilic surface observed for electrode sintered at high temperature and illustrated by contact angle images could be favoring solid/liquid interface to increase the surface efficiency for chemical reaction. Finally, this work gives a new insight into the role of high temperatures in the sintering process for the activation of pure hematite photoelectrode surface.

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## 1. Introduction

Iron oxide (hematite) has been attracting the scientific community interest for decades due to its potential to carry out the water oxidation under solar irradiation in a photoelectrochemical cell (PEC) configuration [1–3]. Hematite is an abundant material, has an excellent chemical stability in an aqueous environment and favorable optical band gap that allows it to absorb a wide solar irradiation spectrum. Despite its attractive properties, the poor optoelectronic properties necessitate application of large external potential to split water with solar irradiation assistance, limiting the high performance of this material [4–7]. Since the nanoscience has opened new perspectives [8] and several synthetic routes have been developed to build efficient nanostructured materials for PEC

applications many advances were reported [9–14]. Despite recent advances, more fundamental research to understand the hematite's properties and limitations is needed in order to make real progress in making PEC economically viable [5,15–19]. Indeed, it is a consensus in the scientific community that the state-of-art in this field is to find ways to selectively change or overcome one limitation without adversely altering the other properties [20–23]. Therefore, the experimental effort is being focused on developing strategies to reach the perfect harmony between nanostructured morphologies and active surfaces for chemical reactions as predicted by theoretical calculations [4,24]. Bard and Hardee through chemical vapor deposition (CVD) reported the first performance of hematite films in a PEC [25,26]. Nowadays, aqueous chemical routes under hydrothermal conditions have been considered a very promising and versatile method to synthesize films with innumerable morphologies at relative low cost and easily scalable [27–30]. In addition to the development of synthetic routes, investigations have been carried out in order to activate the surface of electrodes prepared with a wide variety of morphologies.

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Usually the studies are being conducted by modifying the substrate-electrode interface or electrode surface: (i) by adding dopants [31–42] (ii) by depositing a very thin under [43,44] or overlayer [45–47] of a photosensitive material such as a different type of metal or metal oxides [48]; and (iii) by using high temperatures [11,49,50], and with different atmospheres of thermal treatment for increasing the efficiency of photogenerated charge separation [51]. In particular, a promising performance of pure hematite electrodes on solar water oxidation has been achieved when these materials are subjected to a high temperature of thermal treatment. For instance, Sivula and coworkers [11] demonstrated an improvement on the photoactivity of mesoporous hematite electrodes prepared by a colloidal method at a high temperature (800 °C) of sintering. The authors attributed this improvement on the photoactivity to the optimization of the sintering process at high temperatures that caused unintentional diffusion of atoms from the conducting layer of the substrate into the hematite layer. They suggested that this unintentional doping was responsible for the changes in the particle size, optical and structural properties, which led to a better performance of the pure hematite electrodes. The high temperature of sintering and unintentional doping of hematite electrodes were also a subject of investigation conducted by Leite and coworkers [52]. The pure hematite electrode were prepared by using colloidal methods and sintered at 1000 °C for 4 min. By combining high-resolution transmission electron microscopy and scanning transmission electron microscopy with analytical capability the authors observed that the enhancement on pure hematite photoactivity is related to the beneficial effect of a preferential growth of a hematite film along the (110) axis. Additionally, in this study it was found a clear indication that the unintentional doping consisted in the migration of atoms (Tin) from the conducting layer present on the substrate. However, they believed that it has no a significant effect on the water oxidation performance of hematite electrodes.

Although enhancements of efficiency in the solar driven water splitting have been achieved by using pure hematite electrode and innumerable investigations into fundamental properties were reported, a true understanding of the use of high temperature during the sintering process is needed.

In this context, a novel strategy to synthesize in a single-step nanostructured iron oxide thin layer onto conductor glass substrates free from templates under microwave-assisted hydrothermal conditions was described. The enhancement on the solar water oxidation activity of FTO-hematite photoelectrodes arose from a significant change in the surface-electrolyte affinity caused by the high temperature of the thermal treatment. Additionally, the effect of the temperature and preparation time on the properties of FTO-hematite photoelectrodes were investigated by several techniques. This work will give a new insight into the role of high temperature of sintering process on the surface activation of pure hematite photoelectrode.

## 2. Experimental

### 2.1. Fabrication of the hematite electrode

The iron oxide electrodes were prepared from an aqueous solution (deionized water with resistivity greater than 15 MΩ cm) containing ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O, Mallinckrodt, 97%) and sodium nitrate (NaNO<sub>3</sub>, Merk, 99.5%), with pH 1.5 adjusted by adding chloride acid (HCl, Nuclear, 36.5–40%). Aluminum borosilicate and pure silica glass modified with fluorine-doped tin oxide (FTO), as the conductive layer (Solaronix R<sub>Q</sub>=10–15 Ω cm<sup>-1</sup>) was used to build iron oxide films. The FTO glass substrate was cleaned with a solution containing water and

neutral soap 5% (Dextran) at 100 °C for few minutes and then washed several times with deionized water ( $\rho=15 \text{ M}\Omega \text{ cm}$ ). After the cleaning process, the FTO substrate was immersed in a special bottle (20 mL capacity) containing 15 mL of iron-precursor solution. This system (bottle-solution-FTO glass substrate) was subjected to a hydrothermal treatment in a microwave machine (Monowave™ 300, ANTON PAAR) at 100 °C for two or six hours under controlled pressure. Subsequently, the substrate covered by a yellow layer was cleaned with deionized water to remove residual salts of the solution and then thermally treated at different temperatures (550 °C/4 h or 750 °C/30 min) in a muffle furnace (EDG 3P-S).

### 2.2. Characterization

The structural characteristics of the iron oxide electrode were analyzed by X-ray diffraction (D8 Discover-Bruker using Cu K $\alpha$  radiation) in a  $2\theta$  range from 20° to 80° with a step size of 0.02° measured every 20 s. The optical properties were evaluated by using a Varian Cary 50 spectrophotometer (from 200 to 1000 nm). The film morphology and thickness were characterized by scanning electron microscopy (SEM, JSM-6010LA, JEOL at 10 kV). The water affinity with electrode surface was conducted after the samples being dried for several hours. The Atomic Force Microscopy (AFM) images were obtained on Agilent 5500 microscope operating in intermittent contact mode (Tapping Mode). The AFM images were taken by scanning 10  $\mu\text{m}^2$  areasin triplicate. By using the AFM images, the root mean square (RMS) roughness values of each sample were estimated with the Gwyddion software and presented here the average value [53]. Static contact angles of a sessile drop at three different points of each electrode were measured by using a commercial drop shape analysis system (Attension Optical Tensiometer, Theta Lite, KSV/CAM101) at ambient temperature. The variation of the contact angle was evaluated during 60 s and the contact angle values are an average between the left and right values in all points.

### 2.3. Electrochemical and photoelectrochemical measurements

Electrochemical measurements were performed in a three-electrode cell with a quartz window coupled with a potentiostat/galvanostat ( $\mu$ Autolab III). For these analyses, the pure hematite electrodes were used as the working electrode, Ag/AgCl in saturated KCl as reference electrode and a platinum foil as counter electrode. Aqueous solution of 1 M NaOH (pH 13.6, Sigma-Aldrich, 99.9%) was used as electrolyte. The linear sweep voltammetry measurements were carried out in the dark and under simulated sunlight conditions at a scan rate of 50 m s<sup>-1</sup>. Chronoamperometry measurements were carried out at 1.23 V<sub>RHE</sub> under simulated sunlight conditions. The sunlight irradiation was simulated by using a 450 W xenon lamp (Osram, ozone free) coupled with an AM 1.5 filter. The light intensity was set to 100 mW cm<sup>-2</sup>. The potentials measured in Ag/AgCl electrode were converted into the reversible hydrogen electrode (RHE) scale according to the Nernst equation (1):

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E_{\text{Ag/AgCl}}^{\circ} \quad (1)$$

where  $E_{\text{RHE}}$  is the converted potential vs RHE.  $E_{\text{Ag/AgCl}}^{\circ} = 0.1982 \text{ V}$  at 25 °C, and  $E_{\text{Ag/AgCl}}$  is the potential experimentally measured against the Ag/AgCl reference electrode. The electrochemical impedance spectroscopy (EIS) measurements were carried out in a potentiostat/galvanostat (Autolab PGSTAT129N) coupled with a Faraday cage. The Mott–Schottky analyses were performed at a DC potential range of 0.2–1.8 V<sub>RHE</sub> with an AC potential frequency of 10 kHz under dark conditions and the amplitude of the AC potential was 10 mV. Mott–Schottky plots ( $1/C^2$  vs  $V$ ) were plotted from EIS data.

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