



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Influence of electrolyte temperature on the synthesis of iron oxide nanostructures by electrochemical anodization for water splitting

Bianca Lucas-Granados, Rita Sánchez-Tovar,
Ramón M. Fernández-Domene, José García-Antón*

Ingeniería Electroquímica y Corrosión (IEC), Instituto Universitario de Seguridad Industrial, Radiofísica y Medioambiental (ISIRYM), Universitat Politècnica de València, Camino de Vera S/n, 46022 Valencia, Spain

ARTICLE INFO

Article history:

Received 11 October 2017

Received in revised form

5 March 2018

Accepted 8 March 2018

Available online xxx

Keywords:

Iron oxide

Nanostructure

Electrochemical anodization

Electrolyte temperature

Water splitting

ABSTRACT

Iron oxide nanostructures are an attractive option for being used as photocatalyst in photoelectrochemical applications such as water splitting for hydrogen production. Nanostructures can be obtained by different techniques, and electrochemical anodization is one of the simplest methods which allows high control of the obtained morphology by controlling its different operational parameters. In the present study, the influence of the electrolyte temperature during electrochemical anodization under stagnant and hydrodynamic conditions was evaluated. Temperature considerably affected the morphology of the obtained nanostructures and their photoelectrochemical behavior. Several techniques were used in order to characterize the obtained nanostructures, such as Field Emission Scanning Electron Microscopy (before and after the annealing treatment in order to evaluate the changes in morphology), Raman spectroscopy, photocurrent vs. potential measurements and Mott-Schottky analysis. Results revealed that the nanostructures synthesized at an electrolyte temperature of 25 °C and 1000 rpm are the most suitable for being used as photocatalysts for water splitting.

© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Nowadays, there is an increasing demand of energy production. Renewable energy sources, such as sunlight, are becoming popular since they can produce clean energy contributing to mitigate the global warming [1–7]. Since Fujishima and Honda in 1972 demonstrated that hydrogen generation was possible by photoelectrochemical water splitting using TiO₂ as a photoanode [8], many efforts have been focused on the photoelectrochemical water splitting

process [1,5,9–12]. Different photoanodes materials have been investigated in recent times for water splitting tests, such as TiO₂ [13], WO₃ [14], ZnO [15] and so on, but one of the best options is iron oxide. In particular, hematite (α -Fe₂O₃) possesses a suitable band gap (~2.1 eV), which can absorb ~40% of sunlight in the visible region [5,16]. Furthermore, hematite is an n-type semiconductor with different characteristics, such as good chemical stability, abundance in the Earth's crust, low cost, non-toxicity and environmental compatibility, which make it suitable for photoelectrocatalysis applications

* Corresponding author.

E-mail address: jgarciaa@iqn.upv.es (J. García-Antón).

<https://doi.org/10.1016/j.ijhydene.2018.03.046>

0360-3199/© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

[17–21]. Nevertheless, some drawbacks, i.e. small hole diffusion length (2–4 nm) and poor minority charge carrier mobility, limit its applications [22–25]. By nanostructuring hematite anodes these challenges can be overcome, making hematite an attractive option for photoelectrochemical applications such as water splitting [20,22,26,27].

Hematite nanostructures can be formed by different methods, i.e. electrochemical anodization [28,29], sol-gel [30,31], hydrothermal method [32,33], electrospinning [34,35], etc. Among them, electrochemical anodization is one of the best techniques because different morphologies for the nanostructures can be obtained by controlling the anodization parameters. Additionally, it is a simple, high controllable, low-cost and attractive method for large-scale production [21,29,36,37]. In previous works, anode rotation speed during the electrochemical anodization process (hydrodynamic conditions were varied from 0 to 3000 rpm) was studied. The conclusion was that hydrodynamic conditions, especially 1000 rpm, enhanced the photoelectrochemical performance of the iron oxide nanostructures [38]. In the present study, electrolyte temperature (from 25 to 60 °C) during electrochemical anodization of iron has been evaluated in order to characterize the formed nanostructures and to analyze their photoelectrocatalytic performance in applications such as water splitting. Moreover, since rotating the anode (iron rod) at 1000 rpm enhanced the iron oxide nanostructures performance, all the work has been carried out under stagnant and hydrodynamic (1000 rpm) conditions, in order to compare the influence of electrolyte temperature under both conditions.

The morphology of the samples has been characterized by means of Field Emission Scanning Electron Microscopy (FE-SEM), the crystalline structure has been examined using Laser Confocal Raman Microscopy, and the different electrochemical and photoelectrochemical properties of the samples have been analyzed by different techniques, such as photocurrent vs. potential measurements (water splitting), photostability tests, and Mott-Schottky (MS) analysis.

Experimental

Synthesis of the nanostructures

Nanostructures were synthesized by electrochemical anodization of iron rods (purity of 99.9%). First of all, the surface of the iron rods was abraded with silicon carbide papers (SiC) from 220 to 4000, sonicated in ethanol for 2 min, rinsed with distilled water and dried in a nitrogen stream. Then, electrochemical anodization of the iron rods was carried out in an ethylene glycol solution containing 0.1 M of ammonium fluoride and 3% vol. of water. Anodization was performed at 50 V for 15 min, and current density vs. time was continuously measured during the process. For each anodization test, the iron rod (9.5 mm in diameter, i.e. an exposed area to the electrolyte during the electrochemical anodization of 0.7 cm²) was used as working electrode and a platinum foil as counter electrode. Different electrolyte temperatures were tested during the electrochemical anodization: 25, 40, 50 and 60 °C. Electrolyte temperature was maintained constant during

anodization by means of a thermostated bath. Furthermore, the nanostructures were formed under both stagnant and hydrodynamic conditions (connecting the anode to a rotating disk electrode (RDE) coupled to a motor controller), in particular at 0 and 1000 rpm, corresponding to Reynolds number of 0 and 165, respectively, since in a previous work the best photoelectrochemical response was achieved for the nanostructures synthesized at 1000 rpm [38].

After anodization, the nanostructures were rinsed with distilled water, dried in a nitrogen stream and annealed in a tube furnace at 500 °C for 1 h in an argon atmosphere. The heating rate was 15 °C min⁻¹ and the samples were subsequently cooled within the furnace by natural convection [39].

Morphological characterization of the nanostructures

The characterization of the morphology of the nanostructures (before and after the annealing treatment) was carried out using Field Emission Scanning Electron Microscopy with an extra high tension (EHT) of 3 kV. The images were acquired at 10,000× and 30,000× magnifications.

Characterization of the crystalline structure

The crystallinity of iron oxide nanostructures was analyzed by means of a Laser Confocal Raman microscope. The characterization was performed using a neon laser 632 nm with ~700 μW.

Electrochemical and photoelectrochemical characterization

All the electrochemical and photoelectrochemical experiments were performed in a three-electrode configuration. The iron oxide nanostructure was the working electrode, a platinum tip was the counter electrode and an Ag/AgCl (3 M KCl) electrode was the reference electrode. The area of the iron oxide nanostructure that was exposed to the solution during the tests was 0.26 cm². The photoelectrochemical experiments were performed using a solar simulator (AM 1.5 conditions at 100 mW cm⁻²).

Photoelectrochemical water splitting tests

Photocurrent density vs. potential plots were performed in 1 M KOH by scanning the potential from -0.4 to +0.6 V at a scan rate of 2 mV s⁻¹, switching the light on and off every 0.02 V (i.e. 0.02 V in the dark and 0.02 V in the light).

Photostability measurements

Photostability measurements were carried out leaving the nanostructures in 1 M KOH solution under simulated AM 1.5 illumination for an hour at an applied potential of 0.35 V (vs. Ag/AgCl). The photocurrent density vs. time was continuously measured in order to check the stability against photocorrosion of the nanostructures.

Mott-Schottky analysis

Mott-Schottky analysis were performed both under dark and light conditions in 1 M KOH solution at a constant frequency value of 5 kHz. The potential was started at the Open Circuit Potential (OCP) value of the sample (roughly 0.3 V) and it was

Download English Version:

<https://daneshyari.com/en/article/7706396>

Download Persian Version:

<https://daneshyari.com/article/7706396>

[Daneshyari.com](https://daneshyari.com)