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Study of the annealing conditions and photoelectrochemical characterization of a new iron oxide bi-layered nanostructure for water splitting

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ABSTRACT

Iron oxide nanostructures have emerged as promising materials for being used as photocatalysts for hydrogen production due to their advantageous properties. However, their low carrier mobility and short hole diffusion length limit their efficiency in water splitting. To overcome these drawbacks, in the present study, we synthesized a new hematite ($\alpha\text{-Fe}_2\text{O}_3$) bi-layered nanostructure consisting of a top nanosphere layer and a nanotubular underneath one by electrochemical anodization. Annealing parameters such as temperature, heating rate and atmosphere were studied in detail in order to determine the optimum annealing conditions for the synthesized nanostructure. The obtained new bi-layered nanostructure was characterized by Field Emission Scanning Electron Microscopy, Raman Spectroscopy, Mott–Schottky analysis and Electrochemical Impedance Spectroscopy. The results show the best water splitting performance for the bi-layered nanostructure annealed in argon atmosphere at 500 °C at a heating rate of 15 °C min⁻¹ achieving a photocurrent density of ~ 0.143 mA cm⁻² at 1.54 V (vs. RHE). The results indicate that the bi-layered nanostructure is an efficient photocatalyst for applications such as water splitting.

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1. Introduction

Iron can be oxidized to different states such as FeO, Fe₂O₃ and Fe₃O₄ [1–3]. Among these oxides, hematite ($\alpha\text{-Fe}_2\text{O}_3$) is the most thermodynamically stable iron oxide under ambient conditions [4,5], and it is a promising material because of its advantageous properties for being used as a photocatalyst in photoelectrochemical water splitting [4–10]. Hematite is an n-type semiconductor with a favorable band gap of ~ 2.1 eV that absorbs light up to 600 nm, collects up to $\sim 40\%$ of the solar spectrum energy and has good chemical stability in a wide pH range. Furthermore, it is an environmentally friendly, non-toxic, abundant and low cost material [1,3–5,7,8,11–22]. However, the efficiency of hematite is limited by some drawbacks such as low carrier mobility (10^{-2} – 10^{-1} cm² V⁻¹ s⁻¹) and short hole diffusion lengths (2–4 nm) that lead to high electron–hole recombination [1,7,12–17,19,21]. Low carrier mobility and short hole diffusion length can cause accumulation of holes on the surface and make the flat band potential

more positive. Therefore, a large anodic bias is required to extract the generated photocurrent [14,23]. At potentials over 1.3 V (vs. RHE) the space charge field can separate the photogenerated charges and it is large enough to block the back flow of electrons induced by accumulated holes at the interface. Furthermore, when the applied potential is higher than this value, the faradaic efficiency loss is reduced considerably [12,24,25].

These issues can be overcome by nanostructuring the material into different nanoarchitectures such as porous structure, tubes, wires or rods [10,12,18,19,21,23,26]. One dimensional nanostructures in a preferred orientation of maximum conductivity could improve charge transport, and the thin walls of some nanostructures enhance hole diffusion [1,27]. Nanostructures of iron oxide have been synthesized by different methods such as sol–gel [28], electrodeposition [29], thermal oxidation [30], electrospinning [31] and electrochemical anodization [32]. Among them, electrochemical anodization can produce nanostructures with high control and it has been widely studied in recent years [1,7,11,13,32–34]. Rangaraju [2] synthesized iron oxide nanotubes by electrochemical anodization in ethylene glycol solution containing NH₄F and water. Lee et al. [7] also studied nanotubular and nanoporous structures by electrochemical anodization in ethylene glycol-based electrolytes. However, bi-

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layered hematite nanostructures synthesized by anodization that combine properties of various nanoarchitectures have not been extensively investigated [1].

After anodization, annealing is required in order to obtain a crystalline nanostructure that can be used as a photocatalyst in water splitting. Some authors [11,35] studied different parameters of the anodization process, e.g. anodization temperature, potential, H₂O concentration, NH₄F concentration and annealing temperature. Nevertheless, some aspects like heating rate or annealing atmosphere need to be studied in detail because annealing is one of the most important processes that determine the physico-chemical properties of the nanostructure [19].

In this study, a novel bi-layered nanostructure consisting of a top nanosphere layer and an underneath nanotubular one was synthesized by electrochemical anodization in an ethylene glycol-based electrolyte containing NH₄F and water. This new double layered nanostructure combines the better photocatalytic properties of the nanospheres with the better electron transport behavior of the directly grown nanotubular structure from the iron substrate [1]. Different annealing conditions such as temperature, heating rate or annealing atmosphere were studied in order to establish the optimum annealing conditions for this nanostructure. The morphology and electrochemical properties of the nanostructure were characterized by different methods such as Field Emission Scanning Electron Microscopy (FE-SEM), Raman Spectroscopy, Mott–Schottky (MS) analysis and Electrochemical Impedance Spectroscopy (EIS). The morphological and electrochemical properties of the nanostructure have been correlated to the results of the water splitting tests in order to evaluate the performance of this new nanostructure as a photocatalyst for hydrogen production. The results obtained from this study imply an improvement in the performance of iron oxide nanostructures used as photocatalysts in applications such as water splitting.

2. Experimental

2.1. Electrochemical anodization

Anodization was carried out using 99.9% pure iron rods (9.5 mm in diameter, i.e. an area of 0.7 cm² was exposed to the electrolyte) as the working electrode, and a platinum foil as a counter electrode. Prior to anodization, the iron rod surface was abraded with 220–4000 silicon carbide (SiC) papers in order to obtain a polished finish. After this, the samples were degreased by sonication in ethanol for 2 min, followed by rinsing with distilled water and drying in a nitrogen stream. Anodization was performed in a solution of ethylene glycol (EG) containing 0.1 M ammonium fluoride (NH₄F) and 3 vol% H₂O at 50 V for 15 min. Current density vs. time was continuously measured during anodization. After anodization, the as-anodized samples were properly washed with distilled water and dried in a nitrogen stream.

2.2. Annealing

Annealing of the as-anodized samples was performed in a tube furnace in order to study different annealing parameters. The evaluated parameters were annealing temperature (300, 400 and 500 °C), heating rate (2, 5, 15 °C/min and nanostructures put directly in the furnace without gradual heating) and annealing atmosphere (air and argon). In all the experiments the samples were cooled within the furnace by natural convection.

2.3. Characterization

The morphological aspects of the resulting samples were examined using FE-SEM. The samples were also examined by Raman spectroscopy in order to evaluate their crystalline structure, using a 632 nm neon laser with ~700 μW. Additionally, different electrochemical and photoelectrochemical experiments were carried out, such as water splitting tests, EIS measurements and MS analysis.

All the electrochemical and photoelectrochemical experiments were performed in a three-electrode configuration using a saturated Ag/AgCl (3 M KCl) as reference electrode, a platinum tip as counter electrode and the iron oxide nanostructures as working electrode. The area of the nanostructures exposed to the test solution was 0.26 cm². The measurements were conducted in a 1 M KOH solution using an Autolab PGSTAT302N potentiostat. The photoelectrochemical measurements were carried out under simulated sunlight conditions AM 1.5 (100 mW cm⁻²).

Photocurrent density vs. potential measurements were recorded by scanning the potential from $-0.4 V_{\text{Ag/AgCl}}$ to $+0.6 V_{\text{Ag/AgCl}}$ with a scan rate of 2 mV s⁻¹. Photocurrent density transients as a function of the applied potential were recorded by chopped light irradiation (0.02 V in the dark and 0.02 V in the light). The experimentally measured potentials vs. Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale according to Nernst equation (Eq. 1)

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \cdot \text{pH} + E_{\text{Ag/AgCl}}^0 \quad (1)$$

where E_{RHE} is the calculated potential (vs. RHE), $E_{\text{Ag/AgCl}}$ is the experimentally measured potential (vs. Ag/AgCl), pH is 14 for the prepared 1 M KOH solution and $E_{\text{Ag/AgCl}}^0$ is 0.207 V at 25 °C for the reference electrode used.

MS plots, in dark and light conditions, were obtained by sweeping the potential from the OCP in the negative direction at 28 mV s⁻¹ with an amplitude signal of 0.01 V at a frequency value of 5 kHz in 1 M KOH. EIS experiments were performed in 1 M KOH at open circuit potential (OCP) and 0.35 V (vs. Ag/AgCl) over a frequency range from 100 kHz to 10 mHz with an amplitude of 0.01 V, in both dark and light conditions. Prior to each EIS test, samples were left in the KOH solution for half an hour (at OCP and 0.35 V, respectively) in order to stabilize them. For the light conditions simulated AM 1.5 illumination was used.

3. Results and discussion

3.1. Process of anodization

Fig. 1(a) shows the current density vs. time during the anodization process and three stages are clearly observed. In the first stage (I), the current density drops quickly from approximately 130 mA cm⁻² to less than 25 mA cm⁻². This decrease is due to the formation of a compact oxide layer (Fe₂O₃) on the iron substrate according to Eq. (2), and consequently, resistance increases immediately.



In the second stage (II), a slow increase in the current density is observed due to the formation of tiny pits on the surface of the compact layer followed by the formation of a nanoporous structure, resulting in a decrease in resistance. This process occurs because the presence of the fluoride ions (F⁻) together with the high applied potential during anodization leads to a partial dissolution of the compact Fe₂O₃ layer, and consequently a

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