



Full length article

Controlled hydrodynamic conditions on the formation of iron oxide nanostructures synthesized by electrochemical anodization: Effect of the electrode rotation speed



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ABSTRACT

Iron oxide nanostructures are of particular interest because they can be used as photocatalysts in water splitting due to their advantageous properties. Electrochemical anodization is one of the best techniques to synthesize nanostructures directly on the metal substrate (direct back contact). In the present study, a novel methodology consisting of the anodization of iron under hydrodynamic conditions is carried out in order to obtain mainly hematite ($\alpha\text{-Fe}_2\text{O}_3$) nanostructures to be used as photocatalysts for photoelectrochemical water splitting applications. Different rotation speeds were studied with the aim of evaluating the obtained nanostructures and determining the most attractive operational conditions. The synthesized nanostructures were characterized by means of Raman spectroscopy, Field Emission Scanning Electron Microscopy, photoelectrochemical water splitting, stability against photocorrosion tests, Mott-Schottky analysis, Electrochemical Impedance Spectroscopy (EIS) and band gap measurements. The results showed that the highest photocurrent densities for photoelectrochemical water splitting were achieved for the nanostructure synthesized at 1000 rpm which corresponds to a nanotubular structure reaching $\sim 0.130 \text{ mA cm}^{-2}$ at 0.54 V (vs. Ag/AgCl). This is in agreement with the EIS measurements and Mott-Schottky analysis which showed the lowest resistances and the corresponding donor density values, respectively, for the nanostructure anodized at 1000 rpm.

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1. Introduction

Iron oxide nanostructures are promising materials as photocatalysts in different applications such as wastewater treatment [1], gas detection [2], dye sensitized solar cells [3], degradation of organic dye pollutants [4], biomedicine [5], lithium batteries [6] and hydrogen generation [7]. Particularly, hematite ($\alpha\text{-Fe}_2\text{O}_3$) is an attractive oxide form for photoelectrochemical water splitting to convert solar energy into clean and renewable hydrogen fuel [8]. Hematite is the most thermodynamically stable and the most common crystalline structure of the iron oxide under ambient conditions [9,10]. Besides, its band gap ($\sim 2.1 \text{ eV}$) is suitable for visible light absorption (up to $\sim 590 \text{ nm}$). Additionally, its excellent chemical stability, non-toxicity and low cost make hematite be a proper material for photocatalytic applications. However, its efficiency is

limited by several factors such as poor conductivity, short hole diffusion lengths (2–4 nm) and short lifetime of the excited-state carriers (10^{-12} s) [10–23]. In order to overcome these drawbacks different efforts have been focused on nanostructuring the material by electrochemical anodization, which is a process that allows synthesizing different nanostructures directly on the metal substrate (i.e. direct back contact). This method significantly reduces the contact resistance between the nanostructure and the substrate, so the material can be directly used as a photocatalyst avoiding additional processes to join the nanostructure to the metal substrate, which in turn introduces an extra contact resistance to the photocatalyst [13,17,24,25].

Most of the studies related to iron anodization have been carried out under static conditions [24,26–30]. However, some authors studied the influence of stirring the electrolyte with a magnet during anodization in order to improve the diffusion process [17,31]. Nevertheless, in the present work a novel methodology is carried out, that is, stirring the iron rod under a controlled rotation speed during anodization. In this way, on the one hand, the

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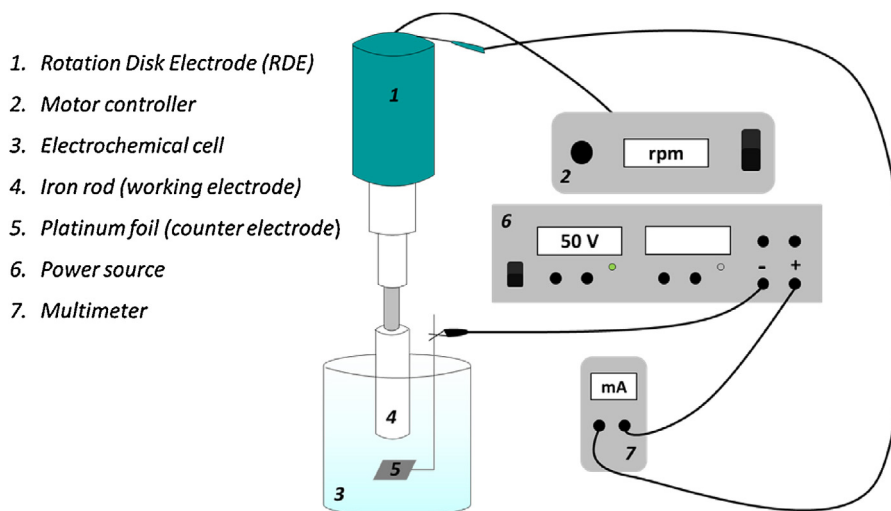


Fig. 1. Illustration of the electrode configuration during the electrochemical anodization.

diffusion process is enhanced and, on the other hand preferential paths are avoided. Furthermore, by controlling the rotation speed of the electrode during anodization, different nanostructures can be obtained. In previous works, the effect of controlled hydrodynamic conditions while stirring titanium, tungsten or zinc rods during anodization was evaluated achieving interesting and efficient nanostructures [32–34]. However, there is no literature concerning iron anodization under hydrodynamic conditions with a rotating anode.

In this study, the effect of controlled hydrodynamic conditions on iron anodization is evaluated. Different rotation speeds of the anode (iron metal) were tested in order to study the synthesized iron oxide nanostructures and determine the most suitable rotation speed in the studied range for obtaining an efficient photocatalyst. The morphology, electrochemical and photoelectrochemical properties of the nanostructures obtained at the different hydrodynamic conditions were characterized by different methods such as Raman spectroscopy, Field Emission Scanning Electron Microscopy (FE-SEM), photocurrent density vs. potential measurements (photoelectrochemical water splitting), stability against photocorrosion tests, Mott-Schottky (MS) analysis, Electrochemical Impedance Spectroscopy (EIS), and band gap measurements.

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2. Experimental

2.1. Electrochemical anodization and annealing treatment

Electrochemical anodization was carried out using 99.9% pure iron rod of 9.5 mm in diameter (an area of 0.7 cm² was exposed to the electrolyte) as working electrode, and a platinum foil as counter electrode. Prior to anodization, the surface of the iron rod was abraded with 220 to 4000 silicon carbide (SiC) papers and degreased by sonication in ethanol for 2 min. After this, the samples were properly rinsed with distilled water and dried in a nitrogen stream.

The electrolyte for the anodization was an ethylene glycol (EG) solution containing 0.1 M ammonium fluoride (NH₄F) and 3 vol% H₂O. The anodization was performed at 50 V for 15 min, and the current density vs. time was continuously measured during the process. In order to evaluate the influence of the controlled hydrodynamic conditions during the anodization process, the iron rod (anode) was connected to a rotating disk electrode (RDE). This RDE is coupled to a motor controller with an accuracy of ±1 rpm in

order to monitor the hydrodynamic conditions of the process. Fig. 1 shows an illustration of the electrode configuration during the electrochemical anodization. Different controlled rotation speeds were applied during the electrochemical anodization, i.e. 0, 1000, 2000 and 3000 rpm, which correspond to the Reynolds numbers of 0, 165, 325 and 490, respectively. The equivalence of the rotation speed with the Reynolds number was calculated as shown in Eq. (1):

$$Re = \frac{\omega \cdot \rho \cdot r^2}{\mu} \quad (1)$$

where, Re is the Reynolds number, ω is the angular velocity expressed in rad s⁻¹ ($\omega = 2\pi f/60$, where f is the rotation speed in rpm), ρ is the electrolyte density in g cm⁻³, r is the radius of the immersed electrode expressed in cm and μ is the dynamic viscosity of the electrolyte in g cm⁻¹ s⁻¹.

Once the anodization was finished, the samples were properly washed with distilled water and dried in a nitrogen stream. Annealing of the as-anodized samples was performed in a tube furnace at 500 °C for 1 h in argon atmosphere. The heating rate was 15 °C min⁻¹ and the samples were cooled within the furnace by natural convection [35].

2.2. Structural characterization

The samples were examined by means of Raman spectroscopy in order to evaluate their crystalline structure. A neon laser 632 nm with ~700 μW was used. Additionally, the morphological characterization of the samples was performed using FE-SEM with an extra high tension (EHT) of 3 kV.

2.3. Electrochemical and photoelectrochemical characterization

Different electrochemical and photoelectrochemical experiments were carried out, such as photocurrent density vs. potential measurements (photoelectrochemical water splitting), stability tests, Mott-Schottky analysis, EIS measurements and band gap measurements.

All the electrochemical and photoelectrochemical experiments were carried out in a three-electrode configuration using the iron oxide nanostructure as the working electrode, a platinum tip as the counter electrode and a silver/silver chloride (Ag/AgCl, 3 M KCl) as the reference electrode. The area of the nanostructure exposed to the test solution was 0.26 cm² and the measurements were conducted in a 1 M KOH solution using an Autolab

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