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Additional Information

# **Iron oxide nanostructures for photoelectrochemical applications: effect of applied potential during Fe anodization.**

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## **Abstract**

In photoelectrochemistry, a suitable photoanode leading to high efficiencies in photocatalytic processes is a research challenge. Iron oxide nanostructures are promising materials to be used as photoanodes. In this work, different potentials during iron anodization were applied to study the properties of the synthesized nanostructures. Results revealed that nanostructures anodized at 50 V presented well-defined nanotubular structures with open-tube tops, and they achieved values of photocurrent density of 0.11 mA·cm<sup>-2</sup> at 0 rpm and 0.14 mA·cm<sup>-2</sup> at 1000 rpm (measured at 0.50 V<sub>Ag/AgCl</sub>), corresponding to the oxygen evolution reaction from water, i.e.  $2\text{H}_2\text{O}+4\text{h}^+ \rightarrow 4\text{H}^++\text{O}_2$ , demonstrating their good photoelectrochemical behavior.

**Keywords:** iron oxide, nanostructure, photoelectrochemistry, anodization, potential.

## 1. Introduction

Photoelectrochemistry is a vigorous research area that studies the nature of the processes occurring when photo-excitation is introduced into the electrochemical system [1,2]. The photoelectric effect was discovered by Becquerel in 1839 [3], who demonstrated that an electric current flows through the external circuit when a silver chloride electrode immersed in an electrolytic solution and connected to a counter electrode is illuminated by sunlight [3,4]. Since then, several research studies have been focused on the conversion of free sunlight into electric power or chemical fuels [5,6]. Photoelectrochemical (PEC) technology comprises the oxidation/reduction reactions between electrochemical active species in solution and photoexcited materials that are produced at the electrode/electrolyte interface upon illumination [7,8]. There are so many photoelectrochemical applications such as dye sensitized solar cells [9], degradation of organic pollutants [10] or water splitting [11]. Among them, splitting of the water molecule into its elemental compounds, i.e.  $H_2$  and  $O_2$ , by using a PEC cell is very interesting. This is owing to the fact that hydrogen is a clean energy source that can be obtained by using solar energy as primary energy input for its production [12].

In PEC cells, photoelectrodes are the most important components and they are determining for the conversion efficiency of the process [13]. In particular, photoanodes for water splitting must be materials that satisfy some characteristics [5,6,14–18]:

(1) A suitable photoanode for water splitting should have a band gap larger than 1.23 eV (the thermodynamically required energy for water splitting into  $H_2$  and  $O_2$ ), but smaller than the energy of a photon in visible light spectrum (2-2.4 eV) in order to ensure the excitation of photogenerated charge carriers.

- (2) The position of the bands of the semiconductor should be adequate, i.e. the bottom level of the conduction band must be less than the reduction potential of  $H^+/H_2$ , while the top level of the valence band must be higher than the oxidation potential of  $O_2/H_2O$ .
- (3) The photocatalyst should have good ability to promote charge separation and fast transport of photogenerated charge carriers from inside of the photoanode to its surface.
- (4) Photocatalysts should have good stability against photocorrosion in extreme conditions (acidic/basic media, high temperatures, etc.).
- (5) Lastly, photoanodes should have high surface area for making easily the access of the water molecules to the photocatalyst, and they should provide enough reactive sites in order to accelerate redox reaction (i.e. split the water molecule).

Since Fujishima and Honda in 1972 reported the study of  $TiO_2$  nanostructures for photoelectrochemical water splitting [19], nanostructures of different oxide metals ( $TiO_2$ ,  $Fe_2O_3$ ,  $WO_3$ ,  $CuO$ ,  $SnO_2$ , etc.) have been widely studied for the same purpose [11,20–22]. This is due to the fact that nanostructures provide high surface area and reactive sites, and they also promote charge separation and transport of charge carriers [23,24].

Among the different metal oxides, iron oxide in its hematite form ( $\alpha-Fe_2O_3$ ) is a promising option owing to their properties [11,18]. Hematite is an n-type semiconductor with a band gap of  $\sim 2.1$  eV which is suitable for visible light absorption (up to  $\sim 590$  nm). Besides, it is a chemically stable, non-toxic, abundant and low cost material [11,25–27]. Moreover, by nanostructuring hematite in nanotubular morphologies, the longitudinal tubular orientation can act as preferred pathways for the electrons transport to the metallic substrate, overcoming then its short lifetime. Furthermore, the thin walls of nanotubular structures also can contribute to enhance the photoelectrochemical

behavior since the short hole diffusion lengths of the hematite can be overcome [28,29]. Because of that, hematite nanostructures are an attractive option for being used as photoanodes in photoelectrochemical applications.

In this study, different potential values were applied during formation of iron oxide nanostructures by electrochemical anodization in order to evaluate its effect in their properties. In spite of the fact that there are abundant literature of the influence of applied potential on anodization of titanium [30–33], there are barely literature about the effect of the applied potential in electrochemical anodization of iron in order to obtain iron oxide nanostructures [34]. In this way, different structural characterizations of the synthesized iron oxide nanostructures have been carried out, i.e. Field Emission Scanning Electron Microscopy (FE-SEM) and Raman spectroscopy. Additionally, photoelectrochemical tests: Mott-Schottky (MS) analysis, photocurrent density vs. potential measurements and stability tests were also performed.

## **2. Experimental**

Iron rod (99.9% pure, ChemPUR) was used as anode in the electrochemical anodization cell with a platinum tip (ChemPUR) as counter electrode, and ethylene glycol (PanReac AppliChem) solution with 0.1 M of ammonium fluoride (Sigma-Aldrich) and 3% vol. of distilled water as electrolyte. Prior to anodization, iron rod was abraded with silicon carbide papers (220, 500 and 4000 grit), sonicated in ethanol for 2 minutes, rinsed with distilled water and dried with nitrogen stream. Electrochemical anodization was carried out at room temperature for 15 min under both stagnant (0 rpm) and hydrodynamic (1000 rpm using a Rotating Disk Electrode) conditions [35,36]. Applied potential during anodization was varied from 30 to 60 V in order to evaluate its effect in morphology and photoelectrochemical properties of the synthesized nanostructures.

Current density versus time evolution was recorded during anodization since these curves reveal information about the nanostructures formation. Once nanostructures were formed, they were annealed in argon atmosphere at 500 °C for 1 hour at a heating rate of 15 °C·min<sup>-1</sup>, and cooled down within the furnace by natural convection [37].

Structural characterization of the nanostructures was carried out by Field Emission Scanning Electron Microscopy (FE-SEM) operating at 3 kV, and by Scanning Confocal Laser Microscopy with Raman Spectroscopy with a neon laser of 632 nm with approximately 700 μW.

All photoelectrochemical experiments were performed in 1 M KOH in a three-electrode configuration with the corresponding nanostructure as the working electrode (exposed area of 0.26 cm<sup>2</sup>), a platinum tip as the counter electrode and an Ag/AgCl (3 M KCl) reference electrode. Simulated sunlight with AM 1.5 illumination (100 mW · cm<sup>-2</sup>) was used for light conditions. Mott-Schottky plots were obtained by sweeping the potential from the Open Circuit Potential (OCP) value (~ -0.3 V for the nanostructures in 1 M KOH) in the negative direction at a scan rate of 28 mV · s<sup>-1</sup>, with an amplitude signal of 0.01 V at a frequency value of 5 kHz. Electrochemical Impedance Spectroscopy (EIS) experiments were performed over a frequency range from 100 kHz to 10 mHz with an amplitude of 0.01 V. Previous to the EIS tests, the samples were left at 0.35 V (vs. Ag/AgCl) under illumination for 1 hour in order to stabilize them. Finally, photocurrent density versus potential measurements were carried out by chopped light irradiation from -0.40 to 0.60 V (0.02 V in the dark and 0.02 V in the light) at a scan rate of 2 mV · s<sup>-1</sup>. Stability measurements against photocorrosion were performed at 0.35 V under illumination for 1 hour.

### 3. Results and discussion

Figure 1 shows the current density vs. time registers during electrochemical anodization of iron at the different applied potentials. All the curves indicated the typical tendency of the formation of iron oxide nanostructures with the three typical stages: (1) formation of a compact oxide layer, (2) tiny pits in the compact layer due to the fluoride ions in the electrolyte and the applied potential that leads to nanoporous structures, and (3) dissolution and cation-cation repulsion; this formation continues until reaching equilibrium between formation of oxide layer and its chemical dissolution, leading to nanotubular structures [34,38].

Registers in Figure 1 indicate that the higher the applied potential, the higher the current density [39]. This phenomenon is because of the fact that when electrochemical anodization is carried out, the presence of fluoride ions ( $F^-$ ) in the electrolyte together with the high applied potential leads to the dissolution of the compact layer as mentioned above. Then, when applied potential increases the dissolution of the oxide layer increases, which in fact results in a decrease in resistance (i.e. an increase in current density) [34]. This tendency is more remarkable at initial states, which indicates that the nanostructures morphology is established basically at initial stages as occurs for other materials, such as  $TiO_2$  nanostructures [30].

Analyzing samples anodized under stagnant conditions (Figure 1 a)), registers illustrate that both formation of the oxide layer and its chemical dissolution are greatly affected by applied potential. At potentials between 30 to 50 V the equilibrium was rapidly achieved and the registers were almost constant, indicating that the formation of nanotubular structures stopped. Whereas, when 60 V were applied, the current density

continued rising with time. This means that the equilibrium was not reached, which in fact implied that a well-defined nanotubular structure was not formed.

For nanostructures anodized under hydrodynamic conditions (see Figure 1 b)), registers indicate that the steady-state was reached for all the samples regardless the applied potential. This is due to the fact that steady-state is controlled by diffusion processes and, since rotating the electrode improves the diffusion processes occurring during anodization, then the equilibrium is reached earlier [40].

Raman spectra of the different samples were similar regardless the conditions applied during anodization. As an example, Raman spectra of samples anodized under stagnant and hydrodynamic conditions were presented in inset of Figure 1 a) and b), respectively. The peaks that appeared at roughly  $229\text{ cm}^{-1}$ ,  $249\text{ cm}^{-1}$ ,  $295\text{ cm}^{-1}$ ,  $414\text{ cm}^{-1}$ ,  $500\text{ cm}^{-1}$ ,  $615\text{ cm}^{-1}$  and  $1317\text{ cm}^{-1}$ , indicated the predominance of hematite as crystalline phase in the structure. However, the peaks at Raman shifts of approximately  $554\text{ cm}^{-1}$ ,  $672\text{ cm}^{-1}$  and  $\sim 820\text{ cm}^{-1}$  were an indicative of the presence of some amount of magnetite in the nanostructures [41–43].

Regarding the morphology of the synthesized nanostructures, Figure 2 shows FE-SEM images acquired at 10,000x magnifications. Insets of Figure 2 show the images acquired at 30,000x magnifications. Samples anodized at 30 V under stagnant conditions (Figure 2 a) showed an initiation layer that partially covered the nanostructures. However, at the same potential but rotating the electrode at 1000 rpm, this initiation layer seemed to disappear (see Figure 2 b), but in this case the nanostructure was not well defined, i.e. the potential was not enough in order to form open-tube top nanotubular structures.

When 40 V were applied during anodization, the initiation layer disappeared for both cases (stagnant and hydrodynamic conditions), but the nanostructures seemed not to be

completely formed, which means that this potential was not enough in order to form well defined nanotubular structures. Figure 2 c) and d) illustrates that under hydrodynamic conditions the nanostructures were more homogeneous and open-tube mouths nanotubular structure started to appear, but the differences in morphology at 40 V were not significant. Nevertheless, in the samples anodized at 50 V there were notably differences between stagnant and hydrodynamic conditions. At 1000 rpm the nanostructure was tubular with an open-tube top and the entire surface was homogeneous, but under stagnant conditions the samples were somewhat stacked. The same phenomenon occurred at 60 V, where the samples anodized at 0 rpm were more stacked than the ones anodized at 1000 rpm. Furthermore, comparing both cases, when potential increased from 50 V to 60 V, the nanostructures were more stacked for the latter. Then, the surface were not as homogeneous as in the case of the samples anodized at 50 V, presenting small etched areas without nanostructures, which could affect negatively the efficiency of the nanostructures as photocatalysts in water splitting. This could be due to the fact that the formation/dissolution rate did not reach the equilibrium, being the dissolution rate faster than the rate of formation of the iron oxide [34].

The differences in morphology according to the different applied potential values imply that there is an optimum range (50-60 V in the case of iron oxide nanostructures anodized for 15 minutes at room temperature) in order to form nanotubular structures. This is in agreement with other authors that studied TiO<sub>2</sub> nanostructures formation by titanium anodization, and they established that there is only a potential range at which ordered TiO<sub>2</sub> nanotubes are formed [30–32].

In order to study the density of defects present in the iron oxide structure of the different samples, Mott-Schottky analysis was carried out in 1M KOH, and results ( $I/Cs^2$  vs.  $E$ )

are plotted in Figure 3. All plots present a positive slope corresponding to an n-type semiconductor [44,45], and the higher the slopes, the lower the donor density values. In this way, donor density values were obtained from the intercept of the linear region in MS plots with the x-axis in Figure 3.  $N_D$  values obtained under dark conditions were lower than that obtained under illumination as expected, since light promotes charge separation in the photoanode.

The highest values of  $N_D$  were achieved for the samples anodized at 30 and 60 V (see Table 1). Since they are too high, some of the defects can act as trap carriers, then reducing the efficiency of the photoanode in photoelectrochemical processes [46]. On the other hand, the nanostructures that possessed lower  $N_D$  values were the ones synthesized at 40 and 50 V (in particular, under hydrodynamic conditions), being in the order of  $10^{19}$  (see Table 1). It was investigated in a previous work [35] that these values are advantageous for the nanostructures since they are in the correct order of magnitude for having good charge separation (but not too high for acting as trap carriers), which is beneficial for photoelectrochemical applications such as water splitting (as it would be discussed later).

Regarding flat band potentials, all values were between -0.6 and -0.8 V (vs. Ag/AgCl) indicating that the electrode rotation speed during electrochemical anodization did not affect considerably the flat band potential. However, an exception is noted for the nanostructure synthesized at 30 V under stagnant conditions, which had lower values in comparison to the rest of the nanostructures. This could be due to the fact that at 30 V the nanostructure was not well defined because 30 V is not high enough to form iron oxide nanostructures by anodization of iron.

Figure 4 shows the Nyquist plots for all the synthesized nanostructures under static (Figure 4 a)) and hydrodynamic (Figure 4 b)) conditions. In first place, it is noticed that, in general, the samples synthesized under hydrodynamic conditions showed less impedance than the ones synthesized under static conditions. This is because the improvement in the diffusion process by rotating the electrode during anodization allows forming more homogeneous and well-ordered nanostructures, then their impedance was lower. In particular, for both static and hydrodynamic conditions the nanostructure that presented the lowest impedance was the one anodized at 50 V. The lowest the impedance they offer, the better the photoelectrochemical behaviour because of the improvement in the charge-transfer processes, which in fact is beneficial for photoelectrochemical applications.

Figure 5 shows Bode-phase and Bode-modulus plots for all the synthesized nanostructures. Bode-phase plots showed two well-differentiated time constants for each nanostructure. However, these two time constants were the result of a time constant at high frequencies and the superposition of two time constants at low frequencies. The experimental data was fitted to an electrical equivalent circuit as Figure 5 c) shows. This circuit is composed by a resistive element ( $R_s$ ) and three groups of resistance-constant phase element (R-CPE). CPE elements were used instead of pure capacitors to justify frequency dispersion and non-ideality. Table 2 shows the values of the different resistances obtained by the fitting of experimental data to the electrical equivalent circuit.

Table 2 shows that all the  $R_s$  values were similar because this resistance corresponds to the solution resistance and the solution was the same for all the nanostructures.  $R_1$  and  $R_2$  are associated with the nanostructures, and then these values were very different according to the studied sample. It is noticed that the samples anodized at 50 V (both

under static and hydrodynamic conditions) offered the lowest resistances, which in fact means that these samples are promising for photoelectrochemical applications. Finally,  $R_3$  values corresponded to the iron oxide compact layer that is underneath the nanostructures because of the formation process. These values were the highest since a compact iron oxide layer is less conductor and then its resistance is much higher than that of the nanostructures.

As mentioned before, iron oxide nanostructures can be used as photocatalyst in different photoelectrochemical applications, such as the splitting of the water molecule. In this case, nanostructures were evaluated by registering photocurrent density versus applied potential in order to evaluate their suitability as photocatalysts for water splitting. Figure 6 shows the results for the nanostructures synthesized under stagnant and hydrodynamic conditions (Figure 6 a) and b), respectively). In both cases, the samples anodized at 50 V achieved the highest photocurrent density values (i.e.,  $\sim 0.11 \text{ mA}\cdot\text{cm}^{-2}$  at 0 rpm and  $0.14 \text{ mA}\cdot\text{cm}^{-2}$  at 1000 rpm, both measured at  $0.52 \text{ V}_{\text{Ag}/\text{AgCl}}$ ), followed by the ones synthesized at 40 V. Note that there were not significant differences between the samples anodized at 30 and 60 V, being the values very similar in all the applied potential range.

In fact, these results are in agreement with FE-SEM images since the samples that showed the most homogeneous and well-defined nanotubular structure were the ones anodized at 50 V (for both stagnant and hydrodynamic conditions). These nanostructures were open-tube top nanotubular in morphology and this fact increased holes diffusion lengths and lifetime of the excited-state carriers, whose generally low values are the main drawbacks of iron oxide nanostructures. Furthermore, the surfaces of the samples anodized at 50 V were the most homogeneous which is beneficial for

photoelectrochemical applications since there are not areas without nanostructures as occurred in the case of 60 V (see Figure 2).

The water splitting results are in accordance with the Mott-Schottky analyses since the nanostructures synthesized at 50 V possessed the optimum values of  $N_D$ , that is, the value that indicates a good charge separation but not too much in order to avoid the defects from acting as trap carriers. Furthermore, water splitting results are also in accordance with the EIS results since they indicated that the samples anodized at 50 V offered the least resistance.

Finally, comparing the results for the samples anodized at 50 V under stagnant and hydrodynamic conditions, it is noticeable that the best results were achieved for the ones anodized at 1000 rpm, since hydrodynamic conditions improved diffusion processes and the formed nanostructures had well defined nanotubular structures with open-tube tops.

Additionally, the stability against photocorrosion of all the samples was tested in 1 M KOH at 0.35 V for 1 hour. Insets of Figure 6 a) and b) show the measurements and all the samples were stable at least for 1 hour in the indicated conditions. Furthermore, the samples were reused for water splitting test, which in turn demonstrates the viability of the usage of the nanostructures as photocatalysts for photoelectrochemical applications.

Actually, the state-of-art of iron oxide based photoelectrodes have achieved photocurrent density values higher than  $4 \text{ mA} \cdot \text{cm}^{-2}$ . However, these results have been obtained for iron oxide nanostructures doped with different elements such as Pt, Co, Ag, Ti and so on [47–50]. This, in fact, increases the complexity and cost of the formation processes. Since iron oxide (in particular in its hematite form) is one of the most promising materials due to its properties, several studies are focused on obtaining iron

oxide nanostructures with simple and low cost methods such as electrochemical anodization. Until the moment, these iron oxide nanostructures achieve current density values in the order of a few  $\text{mA} \cdot \text{cm}^{-2}$  [38,51–54]. Then, the main research objective is to optimize the parameters of the processes to achieve higher efficiencies.

In this study, electrochemical anodization was studied since the main purpose is to optimize the applied potential in order to form iron oxide nanostructures that could be used as photoanodes in water splitting. Results indicated that the best applied potential for the formation of iron oxide nanotubular structures was 50 V anodizing under hydrodynamic conditions. These results allow continuing optimizing parameters of electrochemical anodization in order to approach pristine iron oxide nanostructures to the state-of-the-art of the photoanodes for water splitting.

#### **4. Conclusions**

In the present study, the effect of different applied potentials during electrochemical anodization of iron in order to form iron oxide nanostructures was evaluated. In this way, potentials of 30, 40, 50 and 60 V were applied during the process. Results revealed that the most adequate potential for anodizing iron to form nanostructures was 50 V, for both stagnant and hydrodynamic conditions, the latter achieving the best results. In fact, FE-SEM images revealed a nanotubular structure that enhanced charge carriers, being the main crystalline phase hematite with some amount of magnetite as Raman spectroscopy confirmed. Furthermore, donor density values under this condition were in the order of  $10^{19} \text{ cm}^{-3}$ , which enhanced the photoelectrochemical efficiency of the nanostructure. This was corroborated by water splitting results since the nanostructure

anodized at 50 V under hydrodynamic conditions achieved the highest photocurrent density values ( $\sim 0.14 \text{ mA}\cdot\text{cm}^{-2}$  at  $0.52 \text{ V}_{\text{Ag}/\text{AgCl}}$ ).

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### **Table captions**

**Table 1.** Values of donor density ( $N_D$ ) and flat band potential ( $E_{FB}$ ) obtained for the samples anodized at the different potential values. Simulated AM 1.5 illumination was used for the light conditions.

**Table 2.** Equivalent circuit resistance values for the samples anodized at the different applied potentials (30, 40, 50 and 60 V) under both static and hydrodynamic conditions. Data obtained under simulated sunlight AM 1.5 ( $100 \text{ mW} \cdot \text{cm}^{-2}$ ) at 0.35 V (vs. Ag/AgCl) in 1 M KOH.

### **Figure captions**

**Figure 1.** Current density vs. time measurements during anodization of nanostructures in ethylene glycol based solution with 0.1 M  $\text{NH}_4\text{F}$  and 3 % vol.  $\text{H}_2\text{O}$  for 15 min at different potentials (30, 40, 50 y 60 V) under stagnant (a) and hydrodynamic (b) conditions. Insets show a Raman spectrum of annealed nanostructures as an example.

**Figure 2.** Field Emission Scanning Electron Microscopy (FE-SEM) images at a magnification of 10.000X for the synthesized nanostructures at different potentials (30, 40, 50 and 60 V) under both stagnant and hydrodynamic conditions. Insets show a 30.000x magnification of the images.

**Figure 3.** Mott-Schottky plots obtained under dark (a) and light (b) conditions for the nanostructures synthesized at different potentials (30, 40, 50 and 60 V) under stagnant and hydrodynamic conditions.

**Figure 4.** Nyquist plots obtained under simulated sunlight AM 1.5 ( $100 \text{ mW} \cdot \text{cm}^{-2}$ ) at 0.35 V (vs. Ag/AgCl), for the samples anodized at the different applied potential and under both static (a) and hydrodynamic (b) conditions.

**Figure 5.** Bode plots obtained under simulated sunlight AM 1.5 ( $100 \text{ mW} \cdot \text{cm}^{-2}$ ) at 0.35 V (vs. Ag/AgCl), for the samples anodized at the different applied potential and under both static (a) and hydrodynamic (b) conditions. Electrical equivalent circuit used to simulate the experimental obtained EIS data (c).

**Figure 6.** Photocurrent density vs. potential (water splitting) measurements for the nanostructures synthesized at different potentials (30, 40, 50 and 60 V) under stagnant (a) and hydrodynamic (b) conditions. Insets show stability to photocorrosion tests of the nanostructures.