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Electrochemically Grown Self-Organized Hematite Nanotube Arrays for Photoelectrochemical Water Splitting

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Hematite nanostructures were electrochemically grown by ultrasound-assisted anodization of iron substrates in an ethylene glycol based medium. These hematite nano-architectures can be tuned from a 1-D nanoporous layer to a self-organized nanotube one if the grown is done onto a bare iron foil substrate or onto an electrochemical pretreated one, respectively. Depending upon the pre-treatment conditioning, the self-organized nanotube layer consists of nanotube arrays with a single tube inner diameter of approximately 40–50 nm and wall thickness of 20–30 nm. Their morphological, structural and optoelectronic properties are studied. The photoelectrochemical properties of the resulting hematite nanostructures are studied from the point of view of their application as photoanodes in splitting of water. Through the photocurrent transients for the three nanostructured hematite type electrodes under study, the rate constants k_{tr} and k_{rec} corresponding to the rate constant of charge transfer and recombination processes have been determined. In all cases, the potential value where $k_{tr} > k_{rec}$ was attained at more negative values than the reversible potential of water oxidation, indicating a photocatalytic effect. All samples show a maximum IPCE value between 350 and 375 nm, being the samples pretreated at -1.0 V which shows the highest IPCE value: 45% at 375 nm.

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In the last years, hydrogen energy has found increased attention as a renewable and clean energy source.^{1–5} Among many methods, solar hydrogen generation by photoelectrochemical (PEC) water splitting is a particularly attractive one because of the environmental friendless and the abundance of water and solar energy without emission of pollutants.^{1–5} Since 1972, when the pioneering work on PEC water splitting was reported by Fujishima and Honda,⁶ a wide range of materials has been investigated. In fact, semiconductor materials such as TiO_2 , SrTiO_3 , WO_3 , ZnO , BiVO_4 and Cu(In,Ga)Se_2 ^{3,4,7–10} have been used for the development of photoanodes in PEC cells.

Compared to these materials, $\alpha\text{-Fe}_2\text{O}_3$ (hematite), has a narrower band-gap (1.9–2.2 eV), which allows to harvest up to 40% of the incident solar radiation. Furthermore, $\alpha\text{-Fe}_2\text{O}_3$ is a promising semiconducting material for photoelectrochemical and photocatalysis applications due to its stability, abundance and environmental compatibility, as well as convenient position of the valence band.^{3,11–23} In spite of the good properties presented by the $\alpha\text{-Fe}_2\text{O}_3$, several problems must be solved in order to convert this material in an optimal one for certain applications. For instance, two of these problems correspond to: i) the very short hole diffusion length (20 nm,²⁴ 2–4 nm)²⁵ compared to the light penetration depth ($\alpha^{-1} = 118$ nm at $\lambda = 550$ nm), which results in the rapid non-radiative electron-hole recombination inside the semiconductor, and ii) poor electrical conductivity.^{26–28} Two approaches have been taken to tackle the short minority carrier diffusion length and the poor electrical conductivity and then improve the PEC performance of the hematite photoelectrodes. Briefly, the two strategies adopted have been: i) doping with different elements (to improve the conductivity of hematite), and ii) structural enhancement (to increase the surface area and reduce the distance of photogenerated minor charge carriers have to travel for collection).^{21,22,26–29} The second approach to increase PEC activity of hematite photoelectrodes involves the use of several nanostructured hematites.^{26–28} In fact, these nonideal

optoelectronic properties above mentioned require an electrode morphology with all materials 5–10 nm from the charge transfer interface (semiconductor-liquid junction), but still containing sufficient material to absorb all possible solar photons (equivalent to a ca. 400 nm compact film). Nanostructured are thus highly attractive morphologies for enabling a high photon harvesting efficiency with hematite³⁰ by decreasing electron-hole recombination.

Following this nanostructuring strategy, several attempts can be encountered in the literature for preparing nanostructured hematite thin films with ultrahigh surface roughness,^{3,30} hematite nanorods and nanowires,³¹ and nanotubes.^{26,27,31,32} In this sense it must be pointed out that because the electrical conductivity of hematite is highly anisotropic,²⁶ charge transport is hindered at the interfaces between the crystallites with different crystallographic orientations. Consequently, in contrast to nanoparticle film, one-dimensional (1-D) nanostructures such as nanorods, nanowires and nanotubes, with larger surface area and high aspect ratio, could improve the transportation of charge carriers (providing a direct conduction path for charge carriers), and then reducing the recombination losses at grain boundaries.²⁶ Moreover, in the 1-D structures, the hole diffusion pathway in the radial direction can be compatible with its short diffusion length so that the effect of hole diffusivity limitation can be minimized.³³ In consequence, one-dimensional nanostructure vertically grown onto a conducting substrate has been proposed as the idealized morphology for a hematite photoanode for water splitting.²⁶ However, based on the constraint of the thickness in the radial direction compatible with the diffusion length (~ 4 –10 nm), hematite nanowires with a very high aspect ratio are needed, which cannot stand individually, perpendicular to the substrate.³³ On the other hand, hematite nanotubes can give better mechanical stability compared to nanowires,³³ and nanotubular architecture gives an extra degree of freedom in its wall thickness that can be varied (in addition to diameter and length) for tuning the required properties.³¹ Furthermore, nanotubes exhibit larger surface area than nanowires for a given diameter and length.³¹ Recently, Mao et al. reported that hematite nanotubes exhibited much higher PEC activity than the hematite nanorods, including an improved photocurrent density, more negative onset potential, better photon harvesting, and

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better charge carrier transfer ability.²⁶ However, overall photocurrents and quantum efficiencies remain still low. So is still needed more work and research on the subject.

In present work, an investigation on the formation of vertically oriented and self ordered hematite iron oxide nanotubular arrays by electrochemical anodization process at room temperature is reported. Hematite nanostructures have been electrochemically grown by ultrasound-assisted anodization of iron substrates in an ethylene glycol based medium. Their morphological, structural and optoelectronic properties are studied. Moreover, the photoelectrochemical properties of the resulting hematite nanostructures are studied from the point of view of their application as photoanodes in splitting of water.

Experimental

Nanostructured hematite layers have been electrochemically grown by ultrasound-assisted anodization of iron foils (Sigma-Aldrich, 99.99%, 0.25 mm) at a potential of 50 V in ethylene glycol (EG; 99.8%, anhydrous), ammonium fluoride (0.5 wt% NH_4F) and wt 3.0% DI water. The anodization experiments were carried out using ultrasonic waves (35 kHz, 70 W) and were carried out for 180 s at a temperature of 50°C. The above process was carried out using a two electrode system (flag shaped 1.0 cm^2 Fe foil as anode and Pt foil, 3.75 cm^2 as cathode; the distance between cathode and anode was kept at 4 cm). Three different iron substrates have been assayed, i.e.: (i) bare iron foils, and pre-treated iron substrates by cathodic polarization for 4 hours in an 0.1 M NH_4F aqueous solution at two different potentials: (ii) -0.8 V and (iii) -1.0 V. The resulting hematite nanostructures (HN) will then be named as: HN(w/o), HN(-0.8 V) and HN(-1.0 V), respectively. The electrochemical pretreatment process of iron substrates was carried out using a conventional electrochemical cell with a three-electrode arrangement. As a reference electrode a $\text{Hg}/\text{Hg}_2\text{SO}_4$ (SME, 0.682 V vs. NHE) has been used, and a platinum spiral and an iron sheet of 1.0 cm^2 constituted the counter and working electrode, respectively. In order to enhance the crystallinity of the as-grown amorphous hematite layers, all the iron oxide nanomaterials have been annealed in a tube furnace Linderberg / BLUE M. model TF55035 C-1, under atmospheric conditions at 500°C for 3 h.

Field-emission scanning electron microscopy (FE-SEM) pictures were obtained on a Helios NanoLab 650, double beam of FEI Company, under the following conditions: Mode II, 2 kV and 100 Pa.

Transmission electron microscopy (TEM) has been carried out with a Philips CM-200 microscope operated at 200 kV. Specimens for TEM were prepared by removing the electrodeposited material by grating with a scalpel, collected and ultrasonically dispersed in 1 mL of ethanol. A small drop of the suspended solution was placed onto a porous carbon film supported on a TEM nickel grid, and was dried in air prior to observation.

Structural characterization of the nanostructured hematite layers was examined by X-ray diffraction (XRD) by using a PANalytical, model EMPYREAN diffractometer at the low angle configuration using $\text{CuK}\alpha$ radiation, the working parameters of the copper tube have been settled at 45 kV and 40 mA.

The potentiodynamic j/E profiles of the hematite electrodes tested in this work under continued and chopped white light illumination have been carried out by using 1000 W Hg:Xe 6295 ORIEL INSTRUMENTS lamp.

The action spectra of the incident monochromatic photon to current conversion efficiency (IPCE) for the hematite nanostructured electrodes were measured over the wavelength of 430–730 nm with an IPCE measurement system (CIMPS-2, Zahner, Germany). In the wavelength region from 360–430 nm, the IPCE measurements have been carried out by using light-emitting diodes (LEDs) with different wavelengths.

Results and Discussion

Electrochemical growth process of $\alpha\text{-Fe}_2\text{O}_3$ nanostructure formation.— As has just been said in the experimental section,

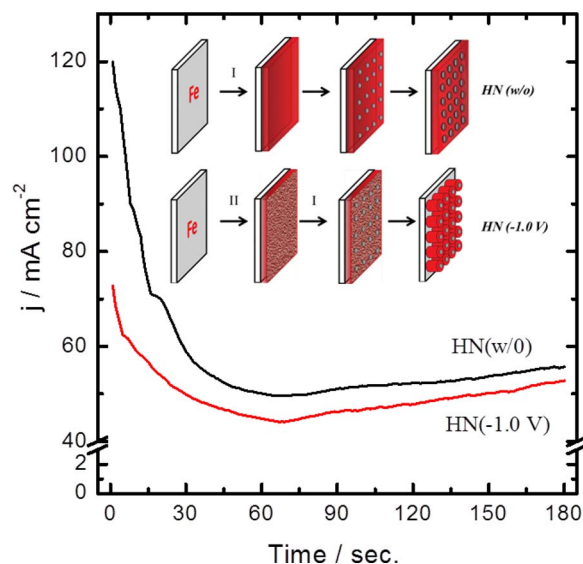


Figure 1. Current transients obtained during the electrochemical grown of the hematite nanostructures by ultrasound-assisted anodization of iron substrates, at a potential of 50 V, for a bare iron foil and a pretreated one HN(-1.0 V) substrates. Inset: scheme showing the different hematite nanostructure architecture evolution as the electrodeposition time progresses, for two different iron substrates, i.e.: one without any pre-treatment and the other with a HN(-1.0 V) or HN(-0.8 V) pre-treatment. In the first case the hematite nanostructure evolves to a nanoporous structure, while in the second case evolves to a nanotube architecture. (I) Ultrasound-assisted anodization of iron foil. (II) Pre-treatment HN(-1.0 V) or HN(-0.8 V).].

hematite nanostructures have been electrochemically grown by ultrasound-assisted anodization of iron substrates at a potential of 50 V in EG+0.5 wt% NH_4F + wt 3.0% DI water. Anodization was carried out for 180 s at a temperature of 50°C (ultrasound: 35 kHz, 70 W). Three different iron substrates have been assayed, i.e.: (i) bare iron foils, and iron substrates electrochemically pretreated for 4 hours in an 0.1 M NH_4F aqueous solution at two different potentials: (ii) -0.8 V and (iii) -1.0 V. The resulting hematite nanostructures (HN) will then be named as: HN(w/o), HN(-0.8 V) and HN(-1.0 V), respectively. See a scheme of the whole process in the inset of Fig. 1. Those pre-treatment potential values correspond to the initiation of the iron localized corrosion process in the aqueous electrolytic media, indicated above. Then, this pretreatment induces the formation of a passive film containing fluoride anions, which in turn induce the formation of defects and strains in the oxide layer. These sites will actuate as active centers for the self-organized hematite nanotube arrays formation. On the other hand, the current transients registered during the ultrasound-assisted anodization of the three iron substrate systems (HN(w/o), HN(-0.8 V) and HN(-1.0 V)), have been very similar to the ones reported by other authors.³⁴ Figure 1 shows the current transients obtained during the electrochemical grown of the hematite nanostructures by ultrasound-assisted anodization of iron substrates, at a potential of 50 V, for a bare iron foil and a pretreated one HN(-1.0 V) substrates. An appreciable difference between these two transients can be seen at the initial stages of the process, exhibiting the transient corresponding to the HN(w/o) sample greater current values than the HN(-1.0 V) one. The last can be due to the fact that the HN(-1.0 V) sample begin the ultrasound electrochemical process with a previously grown passive layer.

Morphological and structural characterization of the hematite nanostructures.— Figure 2 shows illustrative FE-SEM images of nanostructured hematite samples HN(w/o), HN(-0.8 V) and HN(-1.0 V). These FE-SEM micrographs show the effect of the electrochemical pretreatment of the iron substrates on the final morphology of the nanostructured hematite layer. In fact, it can be seen that

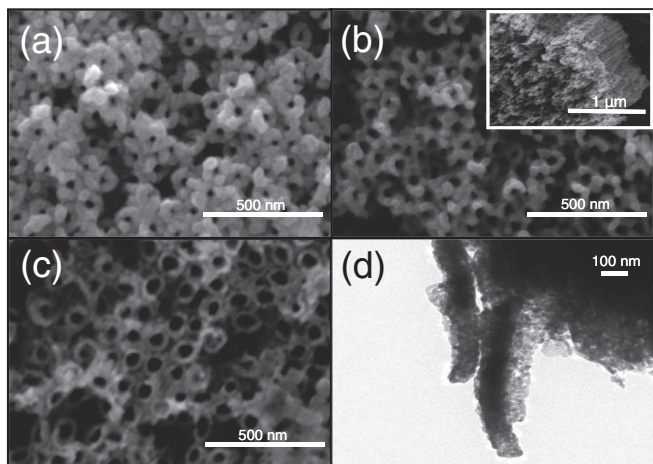


Figure 2. Top view FE-SEM images of nanostructured hematite samples: (a) HN(w/o), (b) HN(−0.8 V) and (c) HN(−1.0 V). The inset of Figure 2b shows a tilted FE-SEM micrograph view with of HN(−0.8 V) sample, tilt angle of 45°. (d) TEM micrograph of single hematite nanotubes extracted from sample HN(−0.8 V).

the hematite nano-architecture can be tuned from a 1-D nanoporous layer (sample HN(w/o)), to a self-organized nanotube one (samples HN(−0.8 V) and HN(−1.0 V)). Furthermore, the effect of this iron substrate electrochemical pretreatment can also be seen in the morphological properties of these self-organized hematite nanotube layers (see Figures 2b and 2c). The nanoporous sample (see Fig. 2a) is characterized by pores of a mean diameter of 30 nm and an interpore distance of 150 nm. The self-organized nanotube layer (see Fig. 2b and 2c) consists of nanotube arrays with a single tube inner diameter of approximately 40 nm and 50 nm, and average spacing of approximately 100 nm and 90 nm for the samples HN(−0.8 V) and HN(−1.0 V), respectively. The wall thickness of the hematite nanotubes is approximately 30 nm and 20 nm for the samples HN(−0.8 V) and HN(−1.0 V), respectively. Also its 1-D character is clearly seen in the cross-sectional tilt FE-SEM image of a HN(−0.8 V) sample in the inset of Fig. 2b, that shows well-developed nanotubes perpendicular to the substrate. It can be seen that in this case the length of the hematite nanotubes is approximately 1 μm. Figure 2d shows a TEM micrograph of single hematite nanotubes extracted from sample HN(−0.8 V), indicating a nanotube diameter of 100 nm.

In order to study the structural properties of the nanostructured iron oxide films, X-ray diffraction experiments have been carried out. This X-ray diffraction characterization showed that the as-grown iron anodic films were amorphous (i.e.: no significant crystalline oxide structure was found), in agreement with previously published works for quite similar ethylene glycol anodic iron films.^{35,36} Thus, to improve their crystallinity they were subjected to thermal treatment. Figure 3 shows a typical X-ray diffraction pattern of an annealed nanostructured iron oxide sample electrochemically grown onto an iron substrate pretreated at −1.0 V (HN(−1.0 V)). It can be seen that all diffraction peaks (except the peaks of the substrate and a magnetite secondary phase), can be indexed to the rhombohedrally centered hexagonal structure of Fe_2O_3 ($\alpha\text{-Fe}_2\text{O}_3$, hematite), which are in agreement with standard reported values,³⁷ see JCPDS pattern at the bottom of Fig. 3. All samples are polycrystalline, and the broadening of the diffraction peaks demonstrates the nanocrystalline character of nanostructured $\alpha\text{-Fe}_2\text{O}_3$ layers. An average crystallite size could be obtained using the Scherrer formula³⁸ for the crystallite size broadening of diffraction peaks: $D = 0.94 \lambda / \beta \cos \theta$, where λ is the X-ray wavelength, θ is the Bragg angle, and β is the FWHM of the diffraction peak. By applying the above mentioned Scherrer equation, typical crystallite size values of 20–23 nm have been estimated from (110) diffraction peak for the hematite films, irrespective of the electrochemical pretreatment at which the iron substrate used

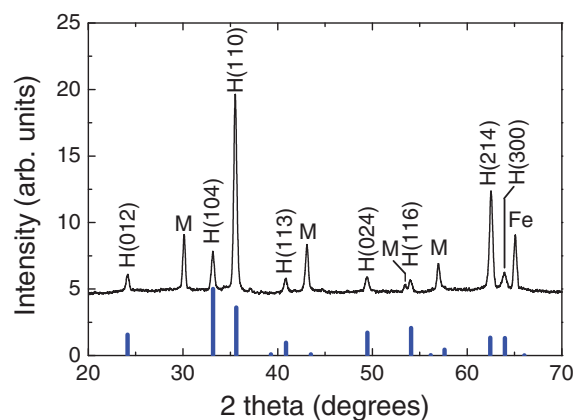


Figure 3. X-ray diffraction pattern of an annealed nanostructured iron oxide sample, electrochemically grown onto an iron substrate pretreated at −1.0 V (HN(−1.0 V)). JCPDS pattern of rhombohedrally centered hexagonal structure of Fe_2O_3 ($\alpha\text{-Fe}_2\text{O}_3$, hematite), is also shown for comparison at the bottom of the Figure. (Fe) and (M) indicate the diffraction peaks originated from the iron substrate and magnetite impurity phase, respectively.

has been submitted. Moreover, it can be appreciated in the XRD diffraction pattern depicted in Fig. 3, that in contrast to the powder diffractogram $\alpha\text{-Fe}_2\text{O}_3$ JCPDS pattern, the relative intensity of the (110) plane, is anomalous with respect to the other planes, evidencing a preferred crystallographic orientation along the [110] direction. To quantitatively investigate the degree of preferred orientation, the diffraction peak intensity ratio of the (110) to respect to the (104), i.e.: $r = I(110)/I(104)$, has been calculated and compared to the JCPDS standard ratio intensities: $r_0 = I_0(110)/I_0(104) = 0.72$.³⁷ In the case depicted in Fig. 3, an r value greater than 0.72 has been obtained ($r \sim 3.0$), indicating a strong preferential orientation of the [110] axis vertical to the substrate.³⁴ Therefore, indicating that the hematite nanotubes grow along the [110] crystallographic direction (as this is energetically most favorable,³⁹ that is, the growth axis is along the c direction.⁴⁰ It is noteworthy to mention that this preferential orientation is the best one for hematite structure with good conductivity.³⁴ In fact, this type of orientation in hematite structure is good for the photoelectrochemical process, where the electron can flow through the (001) basal plane (due to anisotropic conductivity of hematite iron oxide,⁴¹ to the back contact and the hole can still hop laterally between (001) planes to reach the electrolyte interface.^{34,42} On the other hand, along the hematite diffraction pattern, the presence of smaller diffraction peaks corresponding to a minor magnetite (Fe_3O_4) iron oxide phase, can also be seen in Fig. 3. So, in order to study the depth profile (if any), of this magnetite phase through the nanostructured iron oxide, a glancing angle X-ray diffraction (GAXRD) analysis has been carried out onto a typical HN(−1.0 V) sample. Figure 4 shows the diffraction peaks corresponding to the (220) and (104) crystallographic planes of magnetite and hematite iron oxides, respectively, as a function of the omega incidence angle. Moreover, a plot of the intensity ratio of the magnetite (220) diffraction peak to the hematite (104) one ($I_{M(220)}/I_{H(104)}$), as function of the omega incidence angle is presented as inset in Fig. 4. This plot shows that as the incidence angle is higher, the $I_{M(220)}/I_{H(104)}$ ratio increases, indicating the presence of the magnetite phase mainly at the bottom of the hematite nanostructure. In fact, at shallow angles the X-ray beam samples the nanostructured hematite layer, and at progressively higher angles of incidence the X-ray samples the nanostructure bottom (close to the iron substrate). Then, it was shown that the iron oxide nanostructure consists of mainly two layers of different iron oxide compounds, starting from Fe_3O_4 in the bottom to $\alpha\text{-Fe}_2\text{O}_3$ on the surface (top layer). In the basis of this study, a possible scheme of the obtained nanostructure is depicted as inset in Fig. 4.

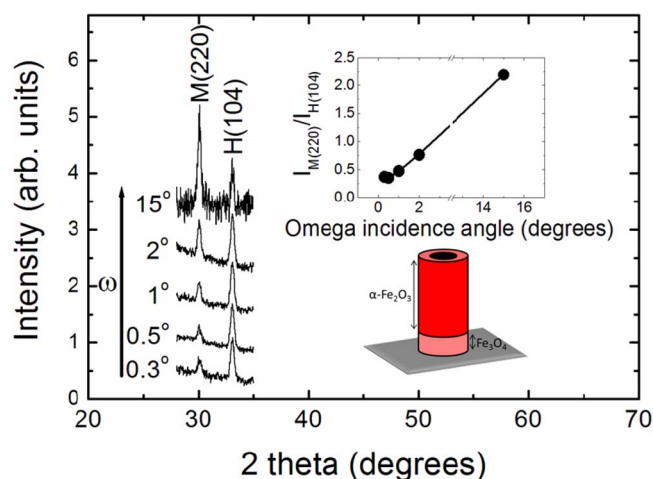


Figure 4. Glancing angle X-ray diffraction (GARXD) pattern of an annealed nanostructured iron oxide sample, electrochemically grown onto an iron substrate pretreated at -1.0 V (HN(-1.0 V)), at different omega glancing incidence angle values. The diffraction peaks corresponding to the (220) and (104) crystallographic planes of magnetite and hematite iron oxides are shown. The inset shows a plot of the intensity ratio of the magnetite (220) diffraction peak to the hematite (104) one ($I_{M(220)}/I_{H(104)}$), as function of the omega incidence angle. Scheme of a single iron oxide nanotube depicting its main phase composition distribution: magnetite at the bottom and hematite in the top layer.

Photoelectrochemical properties of the nanostructured hematite electrodes.— Semiconducting and photoelectrochemical properties of these electrode systems were studied by Mott-Schottky analysis, linear scan voltammetry in the dark and under continuous and chopped illumination photocurrent transients at constant potential and IPCE measurements. First, Mott-Schottky analysis was carried out on the nanostructured hematite samples in order to study their optoelectronic properties (flatband potential (E_{FB}) and the apparent majority carrier density (N_D)). Figure 5 shows the Mott-Schottky plots for the three interfaces studied. It can be seen that all the three systems present a lineal zone with a positive slope, which can be attributed to an n-type behavior. From the extrapolation of the linear region and from the slope of those plots, the flatband potential and the apparent majority carrier density values, respectively, have been obtained; resulting values are depicted in Table I. It can be appreciated that the apparent majority carrier density values are very similar to each other, irrespective of the electrochemical pretreatment. Moreover, the nonlinear behavior that present the Mott-Schottky plot in all potential region assayed would indicate the presence of surface states. For this reason, we determined the capacity of surface states according to the procedure that has been reported by G. Oskam et al.⁴³ To determine surface state den-

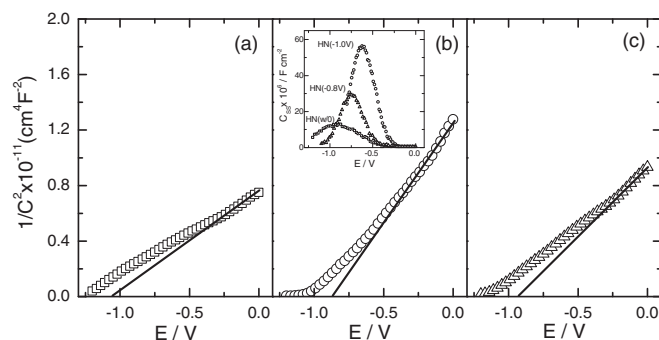


Figure 5. Mott-Schottky plots of (a) HN(w/o); (b) HN(-1.0 V) and (c) HN(-0.8 V) realized in 1 M NaOH, with a frequency of 10 kHz ($\nu = 0.010$ V s $^{-1}$). The inset in (b) shows surface states capacitance as function of the potential.

Table I. Semiconducting and photoelectrochemical parameters of the nanostructured hematite samples under study.

Photoelectrode	E_{FB} / V	N_D / cm $^{-3}$	E_{SS} / V	N_{SS} / cm $^{-2}$
HN(w/o)	-1.05	1.85×10^{20}	-0.95	5.91×10^{11}
HN(-1.0 V)	-0.86	8.88×10^{19}	-0.62	2.55×10^{12}
HN(-0.8 V)	-0.95	1.18×10^{20}	-0.75	1.88×10^{13}

sity, measurements of the parallel capacitance (C_P) at high and low frequencies were carried out. At high frequency (10 kHz), the C_P values correspond mainly to the space charge capacitance ($C_{SC} = C_P$). The surface state capacitance (C_{SS}) at different potentials was evaluated by subtraction of C_{SC} from those C_P values obtained at low frequencies (1 Hz).⁴³ In the inset of Fig. 5 are shown for the three electrodes, the C_{SS} values obtained as a function of potential. From the maximum values of the C_{SS}/E curves ($C_{SS,max}/E$), the density of surface states can be calculated with the following equation:

$$C_{SS,max} = \frac{e^2}{4k_B T} N_{SS} \quad [1]$$

where N_{SS} is the density of surface states, and e , k_B , and T represent the electron charge, the Boltzmann constant, and the temperature, respectively. Furthermore, if we consider the influence of Helmholtz region capacity to be negligible, the energetic position of the surface states (E_{SS}) can be obtained from the difference between the position of the conduction band edge and the potential where $C_{SS,max}/E_{max}$ is located. The E_{FB} , N_D , N_{SS} , and E_{SS} values obtained are summarized in Table I. Table I shows that the values of E_{FB} are shifted toward more positive potentials, with the electrode HN(-1.0 V) which presents the highest E_{FB} . This is important for establishing the overpotential of water oxidation, as will be discussed below. Similarly, the surface states are located within the semiconductor bandgap. However, HN(-1.0 V) sample presents a more positive E_{SS} value, which gives it a more oxidant character.

Figure 6 shows the potentiodynamic j/E profiles of the hematite electrodes tested in this work under continued and chopped white light illumination. For comparison, the inset of Fig. 6b shows the photocurrents under continuous white light illumination of Figures 6a, 6b and 6c re-plotted in a single plot. It can be observed a significant increase in the photocurrent values for the water oxidation in those

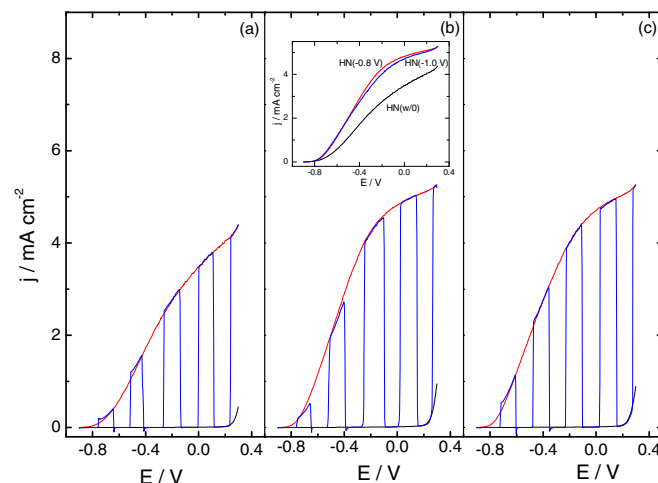


Figure 6. Linear scan voltammetry of hematite nanostructured electrodes: (a) HN(w/o); (b) HN(-1.0 V) and (c) HN(-0.8 V), in the dark (black line), with continuous light illumination (red line) and under chopped light illumination conditions (blue curve). These curves have been recorded at $\nu = 0.025$ V s $^{-1}$ under white light solar simulator (0.5 sun). The inset of Fig. 6b shows the photocurrents under continuous white light illumination of Figures 6a, 6b and 6c re-plotted in a single plot for comparison.

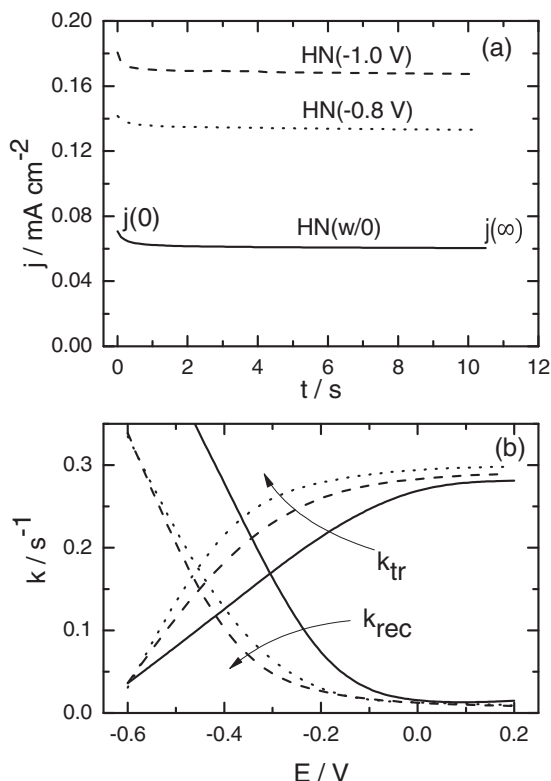


Figure 7. (a) Photocurrent pulses obtained at -0.185 V and (b) k_{rec} and k_{tr} values determined by fitting photocurrent transients obtained at different potentials for HN(w/o), HN(-1.0 V) and HN(-0.8 V) electrode systems. Photocurrent pulses were realized in 1.0 M NaOH using a LED 455 nm (20 mW cm⁻²).

nanostructured hematite electrodes pretreated before their growth. Furthermore, for all electrodes, the photocurrent potential onset (E_{bph}), is achieved at a potential value of $E_{bph} = -0.80$ V. However, when considering the respective E_{FB} values, it can be observed that the overpotential η , ($\eta = E_{bph} - E_{FB}$) follows the sequence $\eta_{HN(-1.0\text{ V})} < \eta_{HN(-0.8\text{ V})} < \eta_{HN(w/o)}$. This fact agrees with the lower wall thickness of the hematite nanotube observed for the electrode HN(-1.0 V). On the other hand, the photocurrent under chopped light illumination presents a low decay during the period light on/light off, and the photocurrent pulse has a value equal to that obtained with continued light illumination. In addition, the photocurrent pulses under chopped light illumination agree very well with the photocurrent under continued light illumination. Also, each photocurrent pulse presents a low level of recombination, as is reflected by the low photocurrent decay after each light pulse. To confirm this behavior, measurements of photocurrent transients at constant potential were made, following the methodology of L. Peter.⁴⁴ Figure 7a shows the photocurrent transients for the three nanostructured hematite type electrodes under study, polarized at -0.185 V (reversible potential of water oxidation), and under a LED light pulse of 455 nm (25 mW cm⁻²). On the other hand, similar photocurrent transient experiments have been performed onto the same nanostructured hematite electrodes and at the same polarization potential, but for a period of one hour, attaining the systems a stationary photocurrent $j(\infty)$. Considering the simple model applied by L. Peter,⁴⁴ which includes a charge transfer process between the electrolyte and the semiconductor and recombination, the photocurrent transients follow approximately well the following equation:

$$\frac{j(t) - j(\infty)}{j(0) - j(\infty)} = e^{-t/\tau} \quad [2]$$

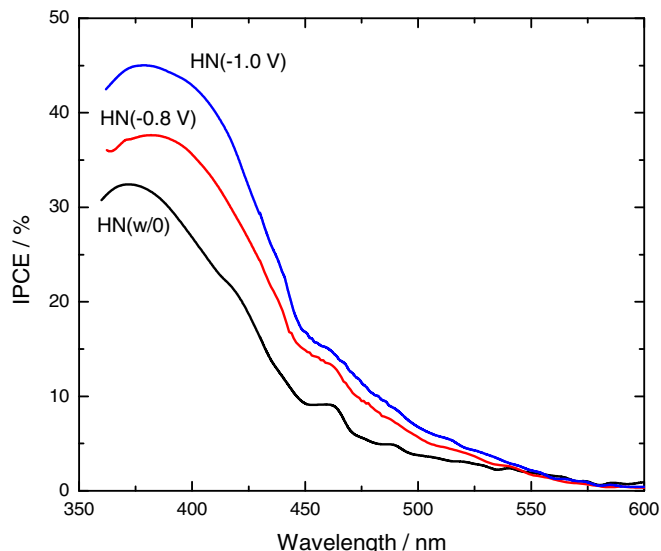


Figure 8. IPCE spectra of nanostructured hematite samples: (a) HN(w/o), (b) HN(-0.8 V) and (c) HN(-1.0 V), collected at 1.23 V vs. RHE.

where the time constant $\tau = (k_{tr} + k_{rec})^{-1}$ and the ratio between steady-state ($j(\infty)$) and initial ($j(0)$) photocurrents is given by:

$$\frac{j(\infty)}{j(0)} = \frac{k_{tr}}{k_{rec} + k_{tr}} \quad [3]$$

Where k_{tr} and k_{rec} correspond to the rate constant of charge transfer and recombination processes, respectively, obtained through Eq. 2. Figure 7b shows the variation of the rate constants obtained from fit of the photocurrent transients at different potentials. It can be seen that as the potential becomes positive there is an increase of the k_{tr} values and a decrease in the k_{rec} ones for the three electrodes studied. However, as the polarization potential is made more positive, k_{tr} values for electrodes HN(-1.0 V) and HN(-0.8 V) grow faster than for the HN(w/o) one. Another aspect that should be noted is the potential value where $k_{tr} > k_{rec}$, i.e.: -0.31 V for HN(w/o) electrode, and -0.45 V for both HN(-1.0 V) and HN(-0.8 V) electrodes. This would be an indication that the hematite electrodes HN(-1.0 V) and HN(-0.8 V) requires less overpotential, or lower band bending to make the charge transfer process to predominate over the recombination one. Nevertheless for the three cases, these potential values are more negative than the reversible potential of water oxidation (-0.185 V vs. MSE), indicating a photocatalytic effect.

Finally, and in order to quantitatively investigate the photoelectrochemical activity of the different nanostructured hematite electrodes as a function of wavelength, incident photon to current efficiency (IPCE) measurements have been performed for the three electrodes assayed and at an applied potential of 1.23 vs. RHE (see Fig. 8). All samples show a maximum IPCE value between 350 and 375 nm, being the sample HN(-1.0 V) which shows the highest IPCE value, 45% at 375 nm. In fact, this is the nanostructured hematite electrode sample exhibiting the thinnest wall thickness (see above, Fig. 2). Moreover, this IPCE value is higher to that previously reported by other authors, see review of Sivula et al.⁴⁵ Above 600 nm, the photoresponse of all the nanostructured hematite electrodes drops to zero, consistent with the bandgap of α -Fe₂O₃. However, a respectable IPCE value of about 10 – 20 can be observed in the 425 – 475 nm wavelength region.

Conclusions

Hematite nanostructures have been electrochemically grown by ultrasound-assisted anodization of iron substrates in an ethylene glycol based medium. Three different iron substrates have been assayed, i.e.: (i) bare iron foils, and iron substrates electrochemically pretreated

for 4 hours in an 0.1 M NH_4F aqueous solution at two different potentials: (ii) -0.8 V and (iii) -1.0 V. This hematite nano-architecture can be tuned from a 1-D nanoporous layer (grown onto a bare iron foil substrate) to a self-organized nanotube one (grown onto a pretreated iron foil). Depending upon the anodization conditions, the self-organized nanotube layer consists of nanotube arrays with a single tube inner diameter of approximately 40–50 nm, and average spacing of approximately 90–100 nm. The wall thickness of the hematite nanotubes is approximately 20 to 30 nm, and depending on the electrochemical pretreatment.

The as-grown nanostructured iron anodic films were amorphous. Thus, to improve their crystallinity they were subjected to thermal treatment. From the XRD analysis a rhombohedrally centered hexagonal structure of Fe_2O_3 (α - Fe_2O_3 , hematite), for all the annealed samples has been determined.

Through the photocurrent transients for the three nanostructured hematite type electrodes under study, the rate constants k_{tr} and k_{rec} corresponding to the rate constant of charge transfer and recombination processes have been determined. As the polarization potential is made more positive, k_{tr} values for electrodes HN(-1.0 V) and HN(-0.8 V) grow faster than for the HN(w/o) one. In all cases, the potential value where $k_{tr} > k_{rec}$ was attained at more negative values than the reversible potential of water oxidation, indicating a photocatalytic effect.

All samples show a maximum IPCE value between 350 and 375 nm, being the samples pretreated at -1.0 V which shows the highest IPCE value, 45% at 375 nm.

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