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Photoelectrochemical studies of oriented 3D crystalline nanorod arrays of hematite

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Abstract – We report two novel aspects relating to the growth of oriented 3D arrays of alpha-Fe_2O_3 nanorods, based on the "purpose-built materials" (PBM) strategy proposed by Vayssieres. Under controlled conditions, the substrate acted as a topographic template and the growth direction of the 3D arrays of alpha-Fe_2O_3 nanorods was unrelated to the crystallographic characteristic of the substrate. The photoelectrochemical response was measured using a standard three electrode configuration cell and the maximum value observed was 3 mA/cm^2 at 0.6 V (was used as reference, Ag/AgCl electrode in KCl satured solution). The crystallographic orientation degree was found to be dominant factor in the control of the photoelectrochemical response in our system.

Photoelectrochemical splitting of water over semiconductor is an effective method for converting solar energy into clean and renewable hydrogen fuel. Since the first report of direct photoelectrolysis of water by light with a TiO_2 as photoelectrode for oxygen evolution connected to a platinum counter electrode for hydrogen evolution many efforts have been dedicated to develop nanostructure materials with higher efficiency conversion. Iron oxide (α-Fe_2O_3 or hematite) photoanode has received considerable attention on account of its abundance, stability, and environmental compatibility, as well as its suitable band gap and valence band edge position. However, independently of the synthetic route proposed to obtain hematite photoanode it has shown poor charge transport due to high rate of recombination and consequently low photoresponse. This dynamics of photogenerated charge in hematite and the high rate of recombination have been constituted the main challenge of scientific community. It is generally accepted that an electron mobility is less than 10^{-2} cm^2.V^{-1}.s^{-1}, the fast electron (e^-) – hole (h^+) recombination resulting in a short carrier diffusion length (in the range 2-4 nm, 20 nm) has been stated which is about 100 times lower than many others oxides (III-V) and slow surface kinetic reaction.

A strategy developed by Vayssieres,[2] called "purpose-built materials" (PBM), appears to be a promising route for growth-oriented 3D crystalline nanorods in several kinds of substrates. This strategy allows one to obtain 3D arrays of several semiconducting metal oxides using controlled aqueous chemical processing at low temperatures (usually in the range of 90-95 °C) and inexpensive precursors.[2] In this work, two new aspects of the PBM strategy were introduced, the topographic template of the substrate for the growth process and the oriented attachment (OA) mechanism controlling the crystal's growth, Figure 2a. A growth process based on the oriented attachment mechanism was proposed to explain this behavior, and this finding, reported here for alpha-Fe_2O, was extended by different authors to explain other metal oxides. The photoelectrochemical response was measured using a standard three electrode configuration cell (Figure 2a) and the maximum value observed was 3 mA/cm^2 at 0.6 V, see Figure 2b, (was used as reference, Ag/AgCl electrode in KCl satured solution). An important parameter to understand the nanorod performance was extracted by XRD diffraction. The crystallographic orientation degree was found to be dominant factor in the control of the photoelectrochemical response in our system. Based on this result and in the literature where the best result found was 2.3 mA/cm^2 at 0.23 V, our nanorods films are good candidate to be applied as photoanode to generate hydrogen by water splitting.

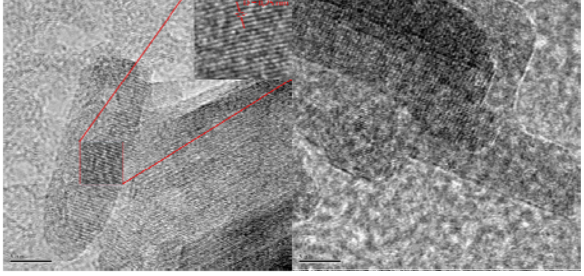

Figure 1: HR-TEM image of alpha-Fe_2O_3 nanorods arrays

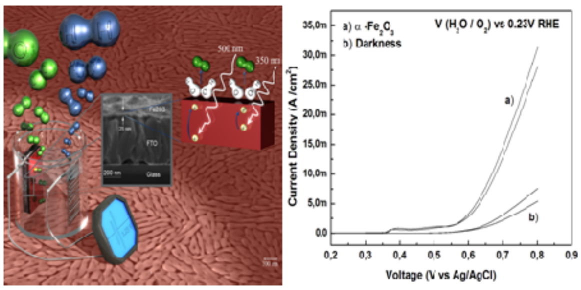

Figure 2: a) Scheme of the photoelectrochemical measurement **b)** Current-Voltage characteristics in darkness and under illumination.

References
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[2] L. Vayssieres, N. Beermann, S. T. Lindquist, A. Hagfeldt, Chem. Mat. 13 (2) (2001)233-235