Hematite nanowires for solar water splitting: development and structure optimization

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Hematite (α-Fe_2O_3) is being investigated for photoelectrochemical solar water splitting since it has a favorable band gap of 2.0−2.2 eV, chemical stability in basic aqueous environments and valence band energy well positioned for the oxygen evolution [1]. As drawbacks, hematite has very limited electron conductivity and has a conduction band edge at an energy level below the reversible hydrogen potential, thus an external electrical bias is required for the hydrogen evolution [1].

Appropriate nanostructured hematite photoelectrodes have been proven useful in increasing the photoresponse performance [2]. If the photoanode is made by an array of nanowires (NWs) in which each NW consists of a sufficiently narrow single crystallite, one-dimensional quantum confinement can occur [3]. Also, it was reported a significant blue-shift for hematite NWs with primary rod diameter of 4-5 nm, with upward shift of the conduction band, which makes direct water reduction possible without the need for an additional bias [4].

In this work, we present an optimization of pulsed electrodeposition (PED) to grow Fe NWs and their consequent oxidation to hematite NWs. The Fe electrodeposition was performed on alumina templates, both by mild and hard anodization processes [5], followed by dendrites formation to reduce the alumina barrier layer in the pore bottom. We were able to achieve the fabrication of highly ordered Fe NWs with lengths ranging from 1 to 10 μm up to 99% pore filling. Furthermore, the nanowires were moulded to increase the surface area. The Fe NWs were then thermally oxidized in an O_2 atmosphere to convert it to α-Fe_2O_3. All the samples were structural, morphological and magnetically characterized using Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS), X-Ray Diffraction (XRD), Vibrating Sample Magnetometer (VSM),

Superconducting Quantum Interference Device (SQUID) and Synchrotron measurements.

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