Synthesis and Characterization of High-Aspect-Ratio Hematite Nanostructures for Solar Water Splitting

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Abstract : Nowadays one of the mankind's greatest challenges has been the supply of low-cost and environmentally friendly energy sources as an alternative to non-renewable fossil fuels. Hydrogen has been considered a promising solution, representing a clean and low-cost fuel. It can be produced directly from clean and abundant resources, such as sunlight and water, using photoelectrochemical cells (PECs), in a process that mimics the nature´s photosynthesis. Hematite (alpha-Fe2O3) has attracted considerable attention as a promising photoanode for solar water splitting, due to its high chemical stability, nontoxicity, availability and low band gap (2.2 eV), which allows reaching a high thermodynamic solar-to-hydrogen efficiency of 16.8 %. However, the main drawbacks of hematite such as the short hole diffusion length and the poor conductivity that lead to high electron-hole recombination result in significant PEC efficiency losses. One strategy to overcome these limitations and to increase the PEC efficiency is to use 1D nanostructures, such as nanotubes (NTs) and nanowires (NWs), which present high aspect ratios and large surface areas providing direct pathways for electron transport up to the charge collector and minimizing the recombination losses. In particular, due to the ultrathin walls of the NTs, the holes can reach the surface faster than in other nanostructures, representing a key factor for the NTs photoresponse. In this work, we prepared hematite NWs and NTs, respectively by hydrothermal process and electrochemical anodization. For hematite NWs growing, we studied the effect of variable hydrothermal conditions, different annealing temperatures and time, and the use of Ti and Sn dopants on the morphology and PEC performance. The crystalline phase characterization by X-ray diffraction was crucial to distinguish the formation of hematite and other iron oxide phases, alongside its effect on the photoanodes conductivity and consequent PEC efficiency. The conductivity of the as-prepared NWs is very low, in the order of 10-5 S cm-1, but after doping and annealing optimization it increased by a factor of 105. A high photocurrent density of 1.02 mA cm-2 at 1.45 VRHE was obtained under simulated sunlight, which is a very promising value for this kind of hematite nanostructures. The stability of the photoelectrodes was also tested, presenting good stability after several J-V measurements over time. The NTs, synthesized by fast anodizations with potentials ranging from 20-100 V, presented a linear growth of the NTs pore walls, with very low thicknesses from 10 - 18 nm. These preliminary results are also very promising for the use of hematite photoelectrodes on PEC hydrogen applications.

Keywords : hematite, nanotubes, nanowires, photoelectrochemical cells
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