

Synthesis and Photoelectrochemical Characterization of Hematite Based Photoanodes and CFD Simulation Studies in Water Splitting

by

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Abstract

Photoelectrochemical (PEC) water splitting is widely regarded as an effective process for sustainable storage of solar energy as chemical energy in the form of H₂. For application in water splitting, pristine and Sn doped (1%, 3% and 5%) hematite nanoparticles were prepared by hydrothermal process. Structural change from nanorods to nanocorals is seen for the Sn doped hematite products. The Sn 3d XPS peak analysis reveals that Sn has been doped into the hematite lattice. Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS) analysis confirm that 1% Sn doped hematite has the highest photocurrent density (3 mA cm⁻² at 1 V vs. Ag/AgCl) and least charge transfer resistance among the doped products. UV-VIS, Photoluminescence and Mott-Schottky analyses further show that optimum optical and electrical properties are observed for this level of Sn doping. To enhance the PEC performance and study the effect of precursor concentration, NiFe layered double hydroxide (LDH) synthesized in-situ at two different precursor concentrations (low and high) was coated on Sn-doped hematite. A high photocurrent density ca. 2.9 mAcm⁻² at 1.8 V vs. reversible hydrogen electrode (RHE) and a 170 mV cathodic shift in onset potential was recorded for Sn-doped hematite coated with low precursor concentration compared to pristine hematite (0.22 mAcm⁻² at 1.8 V vs. RHE). The enhanced PEC activity can be attributed to the synergistic effect of Sn doping and NiFe-LDH co-catalyst on hematite, which contributes to efficient separation of the photogenerated charge carriers and reduces hole accumulation at the surface. However, for the high precursor concentration case, the formation of a thick film of NiFe-LDH results in a comparatively lower current density (0.85 mA cm⁻² at 1.8 V vs. RHE). The results obtained show that NiFe-LDH can be used as an effective co-catalyst to significantly enhance the charge transport properties of tin-doped hematite. Further, efficient management of the oxygen gas bubbles evolving at the photoanode surface is important for improving the overall performance of a PEC cell. It is desirable to reduce the bubble residence time at or near the electrode surface for promoting an easy electrolyte access to the photoanode surface, thereby enhancing the oxygen evolution reaction (OER) kinetics. Computational fluid dynamics (CFD) simulation results and experimental investigation show an enhanced bubble rise and improved PEC performance with the application of forced convection. This can be attributed to the fact that a higher bubble rise with increased electrolyte inflow velocity reduces the bubble residence time. Moreover, the CFD simulation study conducted shows a reduced bubble adhesion for hydrophilic hematite nanorod arrays, compared to planar morphology of photoanode due to capillary wicking. The developed model predicts that the detachment of the continuous contact between the adhered bubble and nanorod surface results in a reduced blockage of active sites at the bubble base, thereby enhancing the PEC performance. Experimental investigation reveals a 4-fold increment in photocurrent density and reduction in charge transfer resistance for hematite nanorod arrays, compared to planar morphology electrodes. To address the potential drop problem associated with a scaled up (10 cm × 10 cm) photoanode substrate (FTO), a silver mesh thin film was used. Two different patterned silver mesh configurations (square mesh and fine square) were studied, and the simulation results predict an effective electrode area of 100% for oxygen evolution reaction for both the cases.