Influence of the spin deposition parameters and La/Sn double doping on the structural, optical, and photoelectrocatalytic properties of $CoCo_2O_4$ photoelectrodes

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Abstract

In this report, dual bandgap $CoCo_2O_4$ nanostructured films were spin-coated at different preheat temperatures (PHT) using different solution molarities (SM), Sn doping and La/Sn double doping levels. In addition to chemical compositions, various methods were used to investigate the structural, morphological, roughness, and optical properties. All the films are polycrystalline $CoCo_2O_4$, for simplicity Co_3O_4, spinel (AB_2O_4) cubic phase. The doping levels of Sn and La/Sn have strongly affected the surface morphologies and roughness parameters. PHT, SM, Sn% and La% show significant changes in lattice parameters, crystallite sizes, transmittance and reflectance spectra. Two bandgaps were detected in the range of 1.3–1.45 eV and 1.72–2.08 eV. With increasing PHT and decreasing SM, the refractive indices decreased and substantially modified with the inclusion of Sn and La in the matrix Co_3O_4. Among the applied electrodes for photoelectrochemical (PEC) hydrogen generation, the La/Sn-doped Co_3O_4 photocatalyst displays a catalytic H_2 output rate of 134.50 mmol h^{-1}/cm^2 @-1Vwith IPCE% of ~52% @ 460 nm. The supreme values of ABPE% are 3.21%@-0.24V and 3.75%@-0.57V, which are the highest values yet for Co_3O_4-based photocatalysts. Interestingly, this photoelectrode shows photogenerated current densities of $\sim -1.57\,mA/cm^2$ at 0 V and -48.42 mA/cm^2 at -1V, and photocurrent onset over -0.361 V. The PEC surface areas and Tafel slopes are also studied for the identification of the mechanism of PEC H_2 production. The La/Sn doped-Co_3O_4 photoelectrode has been further tested for stability and reusability. This work has provided a new viewpoint to design highly active Co_3O_4-based photocatalysts for solar light-driven H_2 generation.

Keywords: Spinal Co_3O_4 films; Sn/La-doping; Dual bandgap; Hydrogen production; Photoelectrocatalytic activity; Conversion efficiencies.