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PULSED PHOTOELECTRODEPOSITED MOS_X CO-CATALYST OVER SB_2S_3 FILMS FOR IMPROVEMENT OF SOLAR-DRIVEN HYDROGEN EVOLUTION REACTION

Resumo: Harvesting solar energy in photoelectrochemical (PEC) cells stands as a sustainable approach to obtaining hydrogen gas (H_2), which is a clean energy carrier with great potential to be one of the mainstream sources of energy in the future. Among the semiconductor materials studied for application in PEC systems, antimony(III) sulphide (Sb2S3) has stood out as a potential candidate due to its suitable indirect optical bandgap (E_g) of 1.6 eV and high absorption coefficient of 10^4- 10^5 cm^-1 (for photons with energy higher than its E_g)[1]. Additionally, Sb2S3 is a nontoxic material comprised of earth- abundant elements and having the conduction band edge potential suitably positioned for light-driven hydrogen evolution reaction (HER) [2], meaning that this semiconductor can be used as a photocathode in a PEC cell for H2 generation. Despite having these desired properties, the photoelectrocatalytic performance of Sb2S3 features some limiting factors, including poor charge carrier transport and deep intrinsic traps that favour charge carriers' recombination[3]. Herein, electrodeposited Sb2S3 films were superficially modified via pulsed photoelectrodeposition of earth-abundant MoSx co-catalyst and then evaluated for their HER photoelectroactivity. XRD characterisation of the Sb2S3 films indicated the formation of a pure Sb2S3 phase (PDF no. 42-1393). PEC analyses for the Sb2S3/MoSx films have shown a photocurrent density for the HER of −0.74 mA cm^-2 at 0 V vs. RHE in an acidic medium, which is 12.5 times higher than that of the bare Sb2S3 film (−0.059 mA cm^-2). Besides the improvement of photoelectroactivity for HER, the presence of MoSx hindered photocorrosion processes of Sb2S3 films, as evidenced by the percentage photocurrent density decay of Sb2S3/MoSx films (19.9%) which is smaller compared to that of bare Sb2S3 film (23.8%), after elapsed 3500 s of a stability test. Additional analyses based on electrochemical impedance spectroscopy under illumination revealed a decrease in the charge transfer resistance for Sb2S3/MoSx films compared to that with bare Sb2S3, confirming the improved photoresponse of the Sb2S3/MoSx films. Considering these results, it is remarked that the superficial modification of the Sb2S3 films by MoSx co-catalyst stands as a promising approach for improvement of semiconductors' photoelectroactivity and stability for HER, to be considered for large-scale applications.

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