

Enhanced Hole Mobility on Electrochemically Synthesized p-type CuAlO₂ Photoelectrodes for Efficient Solar Hydrogen Production

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Delafossite CuAlO₂ photoelectrodes are synthesized via an electrodeposition of Cu(II) and Al(III) onto transparent conducting oxide (TCO) substrates in water and dimethylsulfoxide (DMSO) solvents followed by annealing in air and Ar. Although as-synthesized samples display a unique double layer morphology, their surface property, crystalline structure, and photoelectrochemical (PEC) performance are significantly affected by the synthetic condition. Optimized CuAlO₂ electrodes (synthesized in DMSO and annealed in Ar) possess the suitable energetics for H₂ production under sunlight (optical bandgap of ~1.4 eV and conduction band level of -0.24 V_{RHE}). They exhibit the photocurrent onset potential of ~+0.9 V_{RHE} along with the Faradaic efficiency of ~70% at +0.3 V_{RHE} in alkaline solution (1 M KOH) under simulated sunlight (AM 1.5; 100 mW·cm⁻²). Addition of sacrificial hole scavengers (sulfide and sulfite) significantly improves the PEC performance of CuAlO₂ by a factor of 8 along with the Faradaic efficiency of ~100%. This indicates that the hole transfer limits overall PEC performance. This challenge is addressed by employing a ~150 nm-thick Au film-coated TCO substrate for CuAlO₂ deposition. In the absence of the hole scavengers, the H₂ production with the Au-underlain CuAlO₂ photoelectrode (Au/CuAlO₂) was three-fold higher than that with bare CuAlO₂, while the Faradaic efficiencies at +0.3 and +0.55 V_{RHE} were ~100%. Time-resolved photoluminescence emission decay spectra of CuAlO₂ and Au/CuAlO₂ confirmed the facilitated charge transfer in the latter.