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Supporting Information

Facilitating Hole Transfer on Electrochemically Synthesized p-type CuAlO₂ Films for Efficient Solar Hydrogen Production from Water

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Figure S1. Time-profiled changes in currents during electrochemical deposition of Cu(II) and Al(III) onto FTO in water at $-0.31 V_{SCE}$ and DMSO at $-1.91 V_{SCE}$ for 2 h.



Figure S2. (a) XPS and (b) EDX analyses of as-synthesized CuAlO₂ (DMSO/Air) sample.



Figure S3. The XPS O1s spectra of CuAlO₂ sample.



Figure S4. EDX elemental mappings for top views (a–c) and cross-sectional views (d–f) of $CuAlO_2$ (i.e., DMSO/Air sample).



Figure S5. Time-profiled changes in photocurrents during photoelectrochemical H_2 production using CuAlO₂ electrodes at +0.3 V_{RHE} in aqueous KOH solutions (1 M) without and with sulfide, sulfite, or sulfide/sulfite (each 0.5 M).



Figure S6. Comparison of samples synthesized under different conditions for (a) time changes in photocurrents at +0.3 V_{RHE} in aqueous KOH solution (1 M) containing sulfide (0.5 M) and sulfite (0.5 M), (b) H₂ production at +0.3 V_{RHE} , and (c) Faradaic efficiencies for H₂ production at +0.3 V_{RHE} .



Figure S7. Comparison of light-chopped LSVs of $CuAlO_2$ under electrolyte-side and substrateside irradiations in aqueous KOH solution (1 M) purged with N₂. Under the electrolyte-side irradiation, holes must travel a longer distance; under the substrate-side irradiation, electrons travel a longer distance. Considering the transmittance of the substrate (FTO), the incident light intensity decreases by ~20% under the substrate-side irradiation. See Figure S8 for a comparison of the incident light intensities under the two irradiation conditions.



Figure S8. Comparison of normalized light intensities of AM1.5 light in the absence and presence of FTO substrate in front of silicon detector.



Figure S9. Time-profiled changes in photocurrents during photoelectrochemical H₂ production using CuAlO₂ at +0.3 V_{RHE} and Au/CuAlO₂ at +0.3 V_{RHE} and +0.55 V_{RHE} in aqueous KOH solutions (1 M) purged with N₂.



Figure S10. Photoluminescence (PL) spectra of CuAlO₂ and Au/CuAlO₂ films excited at $\lambda = 379$ nm.



Figure S11. Time-resolved photoluminescence emission (400–500 nm) decay spectra of CuAlO₂ and Au/CuAlO₂. Upon excitation at $\lambda = 379$ nm, the emission decays exponentially, with the decay constants estimated by fitting the decay curves to the following equation: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$, where I(t) is the time-dependent photoluminescence intensity, A is the normalized amplitude of the corresponding lifetime component, and τ is the photoluminescence lifetime.



Figure S12. Time-resolved photoluminescence emission decay spectra of FTO only (w/o CuAlO₂) and CuAlO₂ (w/ CuAlO₂). The decay profiles were different each other, suggesting that the shortest decay lifetime component (i.e., τ_1 in Figure S11) is meaningful. Then, we subtracted the IRF from the decay profiles of CuAlO₂ and Au/CuAlO₂ samples and re-fitted the obtained decay profiles. The decay lifetimes (τ_2) of CuAlO₂ and Au/CuAlO₂ were estimated to be 1.706 and 1.513 ns, respectively. Although τ_2 was much larger than τ_1 , the Au underlayer clearly decreased the decay lifetime. This decrease in τ should have resulted from the charge transfer facilitated by the Au layer, leading to a reduction in the charge recombination.