

Electronic Supplementary Information

for

Enhanced Photoelectrochemical Hydrogen Generation in Neutral Electrolyte using Non-vacuum Processed CIGS Photocathodes with Earth Abundant Cobalt Sulfide Catalyst

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Experimental Section

Deposition of CIGS films: The ESAVD of CIGS thin films in this work was similar to the method used in the previous published work.¹ Cu, In, Ga salts and thiourea were used as the metal sources and S precursor source, respectively. During the ESAVD process, the mixture of precursor solution was atomised to form an aerosol, which was charged under electric field and subsequently directed towards a heated substrate, where it would undergo decomposition and form a stable solid film of CIGS onto the Mo substrate. The as-deposited CIGS films were selenised (with 55 mg Se) in a quartz tube furnace at 550 °C for 30 min.

Deposition of CdS and ZnO: CdS was deposited by chemical bath deposition at 80 °C for 10min in an aqueous solution of 4 mM cadmium acetate hydrate, 4 mM ammonium acetate, 2 mM thiourea, and 0.4 mL ammonium hydroxide solution. Subsequently, a circa 50 nm thick intrinsic zinc oxide (i-ZnO) film was deposited using HHV sputtering system with a RF power of 100 W in the presence of Ar and O₂.

Structural, optical and electrical characterization: The crystal structure of CIGS films were characterized using a X-ray diffraction (XRD) technique with a Bruker D8 discovery diffractometer. Raman spectroscopy measurement was carried out using a micro-Raman spectrometer (Renishaw inVia Raman Microscope) with an excitation wavelength of 514 nm. The microstructure of the CIGSSe films was characterized using a scanning electron microscope (SEM, JEOL JSM-6480LV).

Deposition of Pt: In order to accelerate the H₂ generation process and enhance the kinetics of the water splitting reaction, Pt nanoparticles, which have been widely used as catalysts for water splitting, were deposited on top of the samples by sputtering (CRESSINGTON sputter coater 208HR) for ten seconds. The CIGS photocathode incorporated with Pt nanoparticles was used as a benchmark to compare the PEC properties of the similar CIGS photocathode with low-cost and earth abundant Co-S catalyst.

Deposition of Co-S: The deposition of CoS was conducted according to the electrodeposition method proposed by Sun et al.² The solution composed of 5 mM of cobalt chloride and 0.5 M of thiourea was first prepared. Then the electrodeposition was conducted in a three electrode system with FTO used as the counter electrode and Ag/AgCl as the reference electrode. The consecutive cyclic voltammetry scan was performed from -

1.2 V vs Ag/AgCl to +0.2 V vs Ag/AgCl at a scan rate of 5 mV/s. After three cycles of cyclic voltammetry scan, a layer of cobalt sulfide was deposited on the surface of the samples.

Photoelectrochemical water splitting: CIGS photocathode was used as the working electrode while an SCE electrode and Pt wire were used as the reference and counter electrodes, respectively. To ensure the reproducibility of PEC results, three duplicated samples for each photocathodes were tested. If the electrolyte has a low pH value, it would contain more H⁺ in the solution which could lead to the undesirable photo-corrosion of the photocathode due to the highly acidic environment. While electrolyte with a very high pH value (pH > 10) could also lead to degradation of the photocathode because of the leaching of Se to form H₂Se.³ In our work, pH-neutral electrolyte consisted of 0.5M Na₂SO₄ (pH = 7) was used to avoid any potential degradation issues. The solar water splitting measurements were measured by sweeping the potential from +0.5 to -1.0 V vs. SCE with a sweep rate of 50 mV/s. Such scans were performed both in the dark, under AM 1.5G (100 mA/cm²) irradiation and under chopped AM 1.5G illumination with 2 sec pulses.

References

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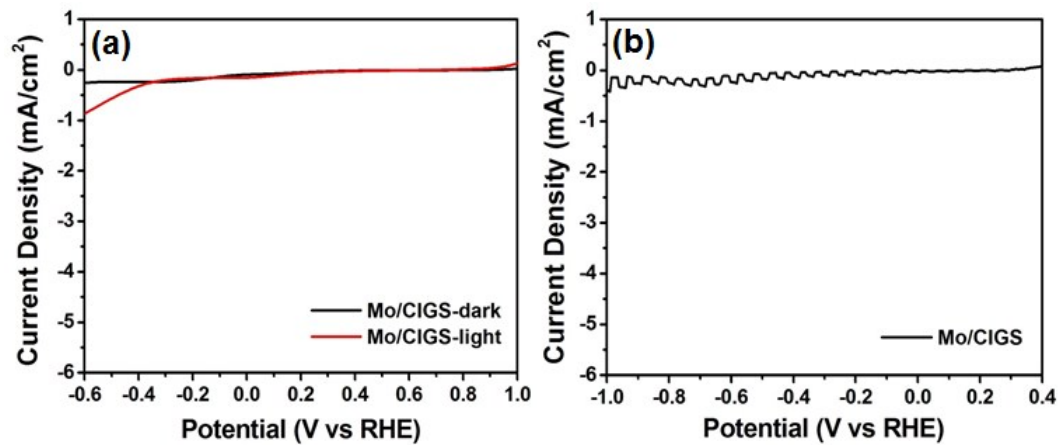


Fig. S1 J-V curves for pure CIGS photocathodes under (a) continuous and (b) chopped AM 1.5G sunlight illuminations.

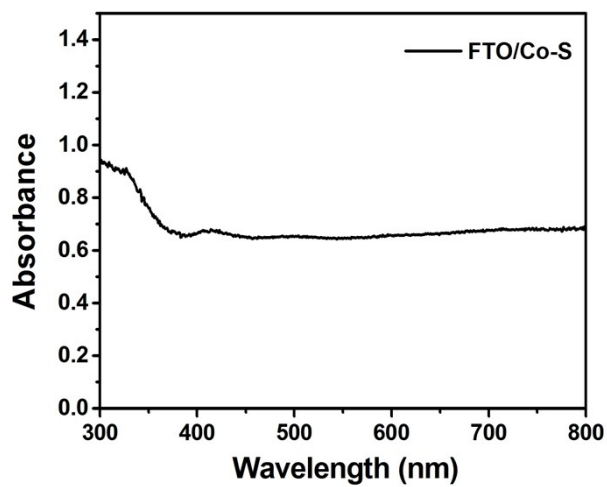


Fig. S2 UV-Vis absorption spectrum for pure Co-S.