Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Selective etching of metastable phase induced an efficient $CuIn_{0.7}Ga_{0.3}S_2$ nano-photocathode for solar water splitting

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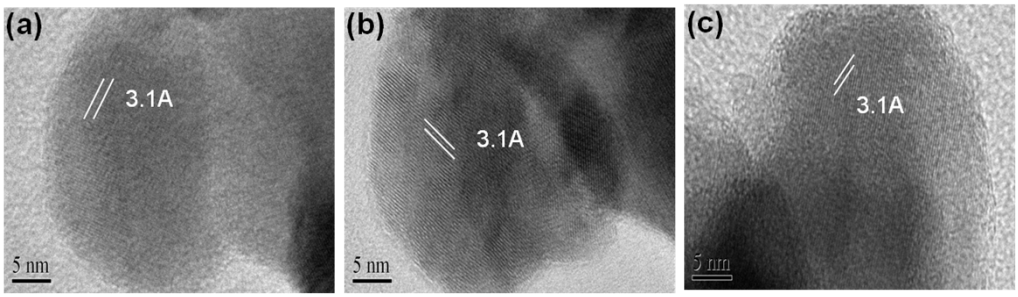

Fig. S1 High-resolution TEM images of the $CuIn_{0.7}Ga_{0.3}S_2$ nanoparticles before etching (a), 0.4 V etching (b), and 0.8 V etching (c).

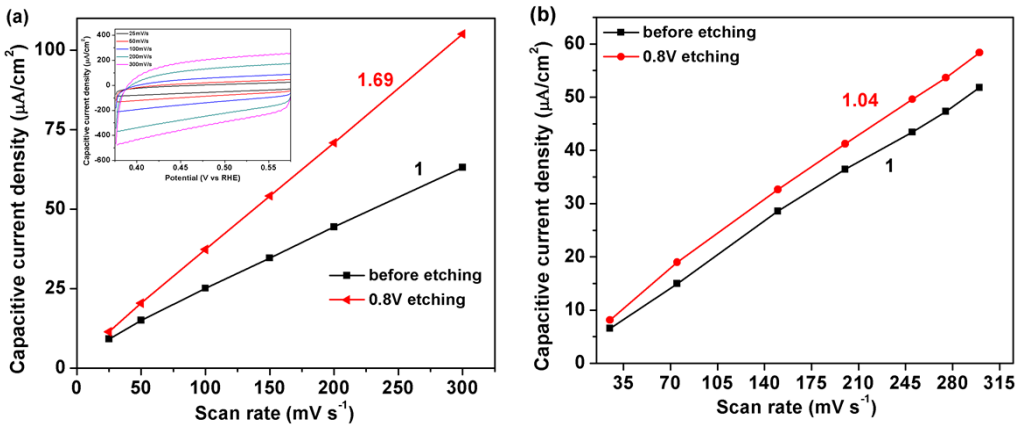

Fig. S2 (a) Relative electrochemical active area measurement of $CuIn_{0.7}Ga_{0.3}S_2$ photocathodes before and after 0.8 V etching: linear relationship between the capacitive current and scan rate for the $CuIn_{0.7}Ga_{0.3}S_2$ photocathodes before and after 0.8 V etching. The inset is the example cyclic voltammograms showing the capacitive current for the $CuIn_{0.7}Ga_{0.3}S_2$ photocathodes after 0.8 V etching at different scan rate from 25 to 300 mV s^{-1}. (b) Plot showing the linear relationship between the capacitive current and scan rate for the Pt/CdS/$CuIn_{0.7}Ga_{0.3}S_2$ electrode before and after 0.8 V etching. The relative electrochemical surface area was determined from capacitance measurements by cyclic voltammetry scan between 0.38 V_{RHE} and 0.58 V_{RHE} in a Na_2SO_4 aqueous solution (0.5 mol/L, pH = 6.5) in the dark. The scan rates were changed from 25 to 300 mV s^{-1}.

Table S1. Surface atomic ratios of the $CuIn_{0.7}Ga_{0.3}S_2$ photocathodes before and after 0.8 V etching by XPS.

Samples	Atomic ratio	
	Cu/(In+Ga)	In/Ga
before etching	0.90	4.29
0.8V etching	1.61	5.20

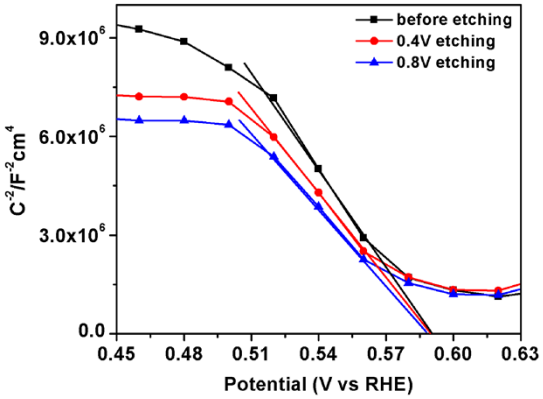

Fig. S3 Mott–Schottky plots of the $CuIn_{0.7}Ga_{0.3}S_2$ photocathodes before and after etching with different potential ranges. The ac amplitude is 10 mV and the frequenciey is 200 Hz.

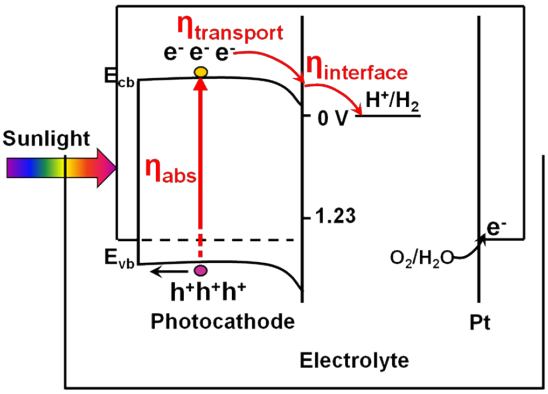

Fig. S4 A schematic diagram of three fundamental processes of photo-generated carriers in a photocathode.

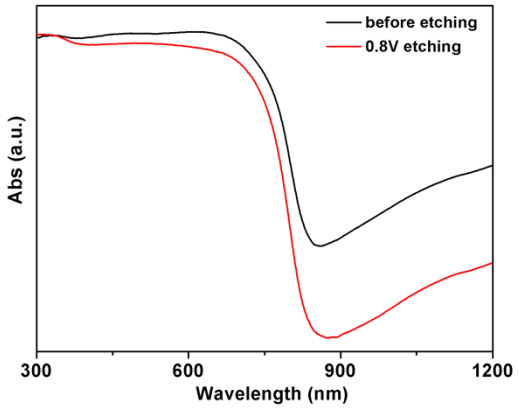

Fig. S5 UV-vis absorption spectra of the $CuIn_{0.7}Ga_{0.3}S_2$ photocathodes before and after 0.8 V etching.

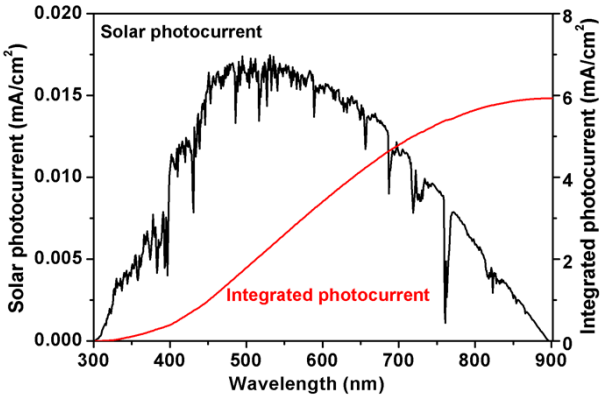

Fig. S6 Integrated solar photocurrent at 0 V_{RHE} by integrating IPCE with the standard solar spectrum.

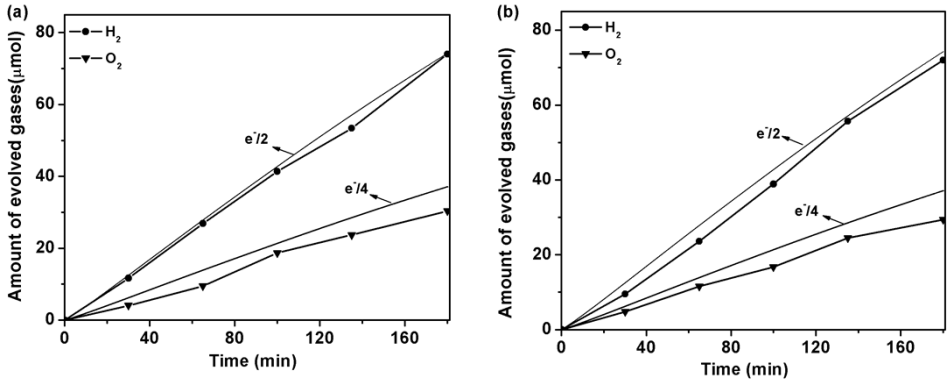

Fig. S7 Time course of hydrogen gas evolution for the Pt/CdS/$CuIn_{0.7}Ga_{0.3}S_2$ photocathode (1 cm^2) before etching at 0 V_{RHE} (a) and 0.4 V etching (b). Light source: AM 1.5G simulated sunlight (100 mW cm^{-2}). The theoretical number of hydrogen and oxygen molecules is denoted by $e^-/2$ and $e^-/4$ respectively.