

## Electronic supplementary information

### Switchable synthesis of p- and n-type Cu-In-S grooved pyramid-like microcrystals for unassisted photoelectrochemical water splitting

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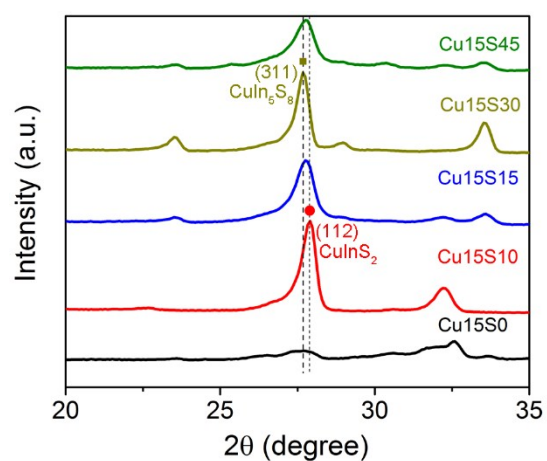
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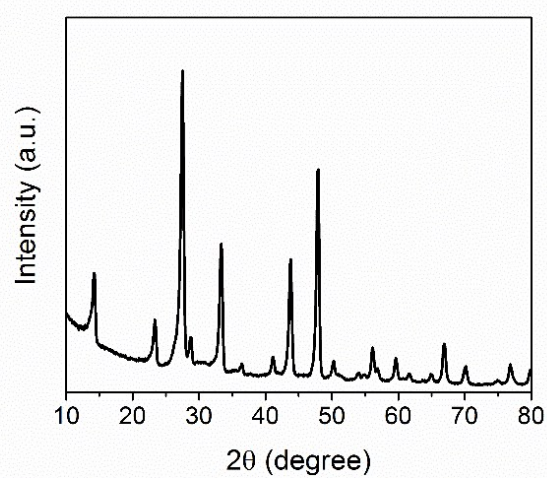
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**Table S1** SEM-EDX results of the Cu-In-S films prepared with different amount of thiourea.

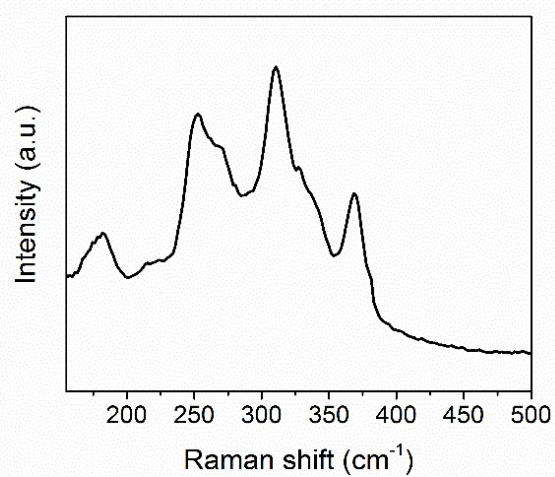
Sample	Cu element	In element	S element
Cu15S0	58.10%	8.07%	33.83%
Cu15S10	21.31%	24.99%	53.70%
Cu15S15	17.48%	27.17%	55.35%
Cu15S30	8.70%	34.87%	56.43%
Cu15S45	16.61%	27.82%	55.57%



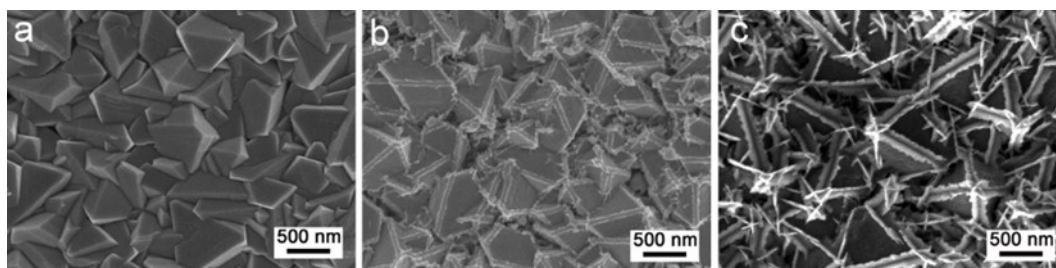
**Fig. S1** The magnified XRD patterns of as-prepared samples.



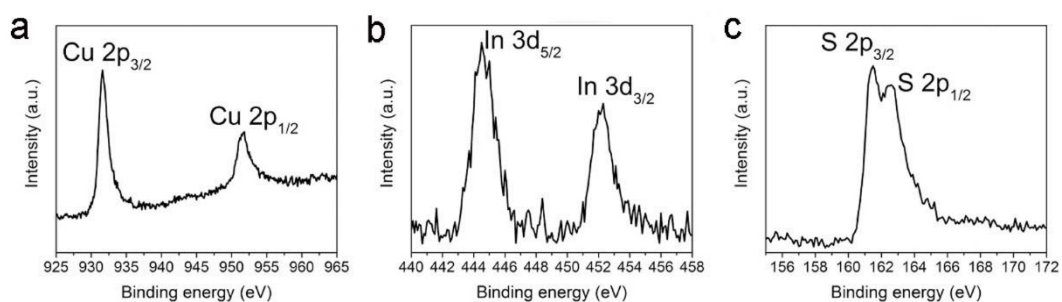
**Fig. S2** XRD pattern of  $\text{In}_2\text{S}_3$  film.



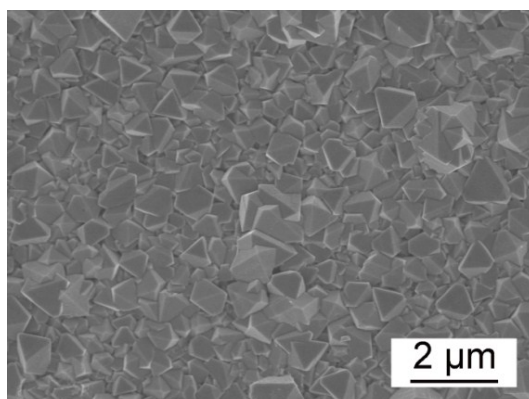
**Fig. S3** Raman spectrum of  $\text{In}_2\text{S}_3$  film.



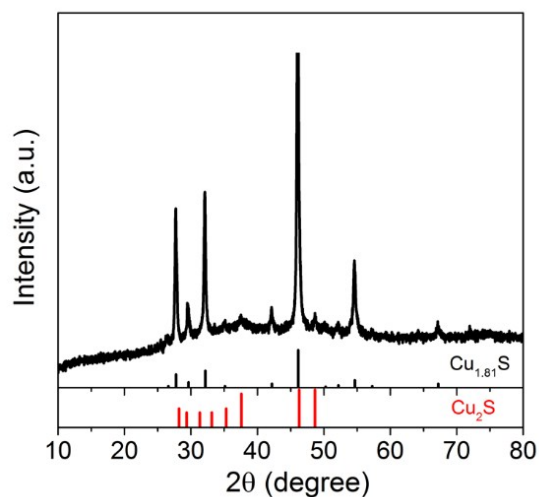
**Fig. S4** Top-view SEM images of (a)  $\text{In}_2\text{S}_3$  film; (b)  $\text{Cu}_{15}\text{S}_{10}$  sample solvothermally treated for 3 h; and (c)  $\text{Cu}_{15}\text{S}_{10}$  sample solvothermally treated for 12 h.



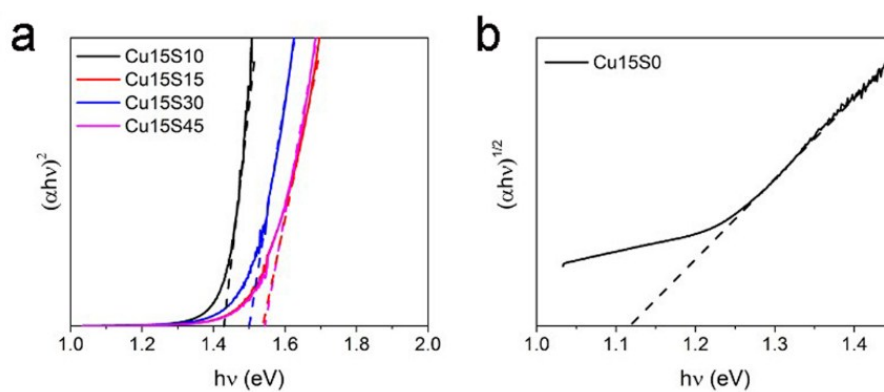
**Fig. S5** XPS spectra of powder extracted from the solution after the solvothermal reaction for preparing  $\text{Cu}_{15}\text{S}_{10}$  sample.



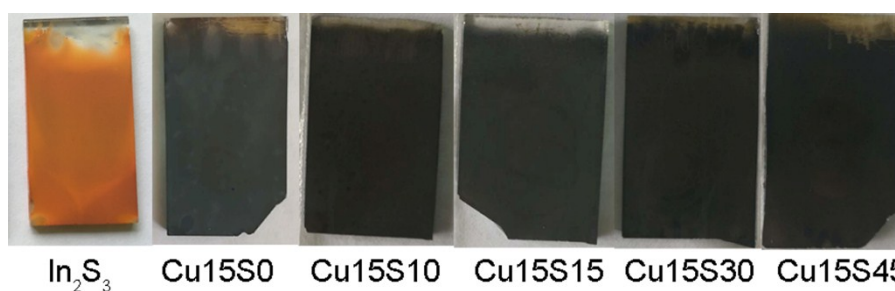
**Fig. S6** Top-view SEM images of  $\text{Cu}_0\text{S}_{10}$  film prepared without adding copper source.



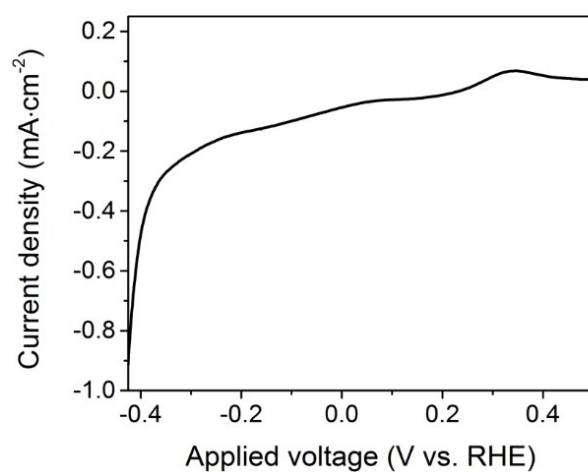
**Fig. S7** XRD patterns of powder extracted from the solution after the solvothermal reaction for preparing Cu15S10 sample.



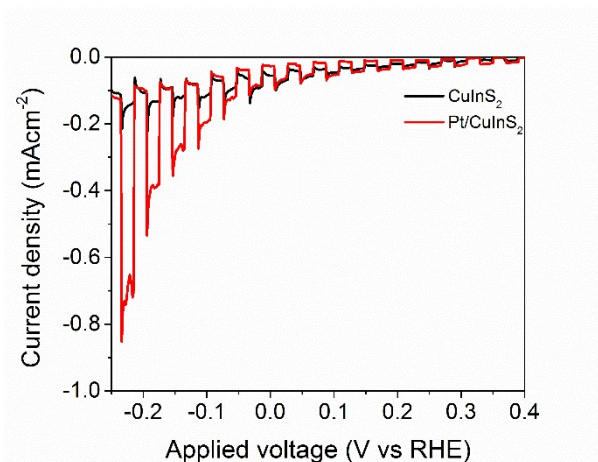
**Fig. S8** (a, b) plots of  $(\alpha h\nu)^n$  vs  $h\nu$  of Cu-In-S films prepared with different amount of thiourea.



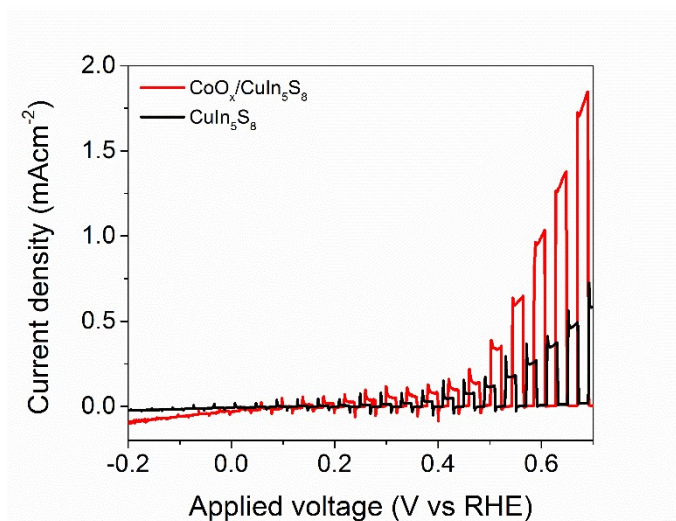
**Fig. S9** Photograph of  $\text{In}_2\text{S}_3$  film and Cu-In-S films prepared with different amounts of thiourea.



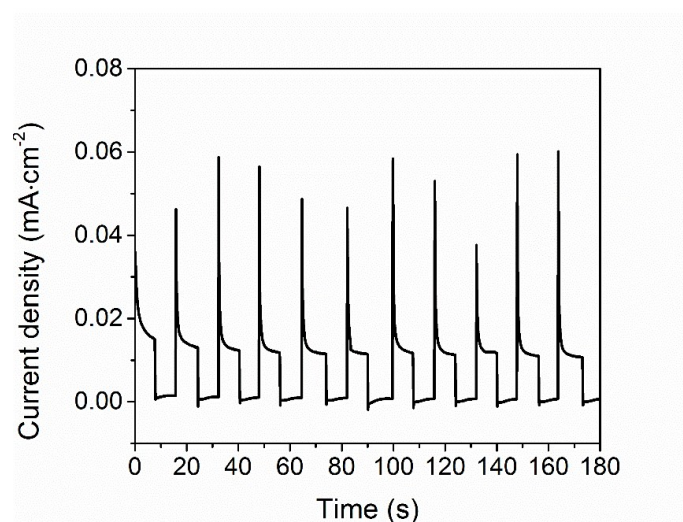
**Fig. S10** Linear sweep voltammetry of CuInS<sub>2</sub> film was measured at 0.1 M Na<sub>2</sub>SO<sub>4</sub> (pH adjusted to 3 by H<sub>2</sub>SO<sub>4</sub>) under chopped irradiation light.



**Fig. S11** Current-potential curves of CuInS<sub>2</sub> and Pt/CuInS<sub>2</sub>.



**Fig. S12** Current-potential curves of CuIn<sub>5</sub>S<sub>8</sub> and CoO<sub>x</sub>/CuIn<sub>5</sub>S<sub>8</sub>.



**Fig. S13** Current-time curve for the tandem PEC cell using CoO<sub>x</sub>/CuIn<sub>5</sub>S<sub>8</sub> photoanode and Pt/CuInS<sub>2</sub> photocathode under light-chopping conditions. The electrolyte is 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH adjusted to 3 by H<sub>2</sub>SO<sub>4</sub>).