

Supplementary information

A monolithic and standalone solar-fuel device having comparable efficiency to photosynthesis in nature

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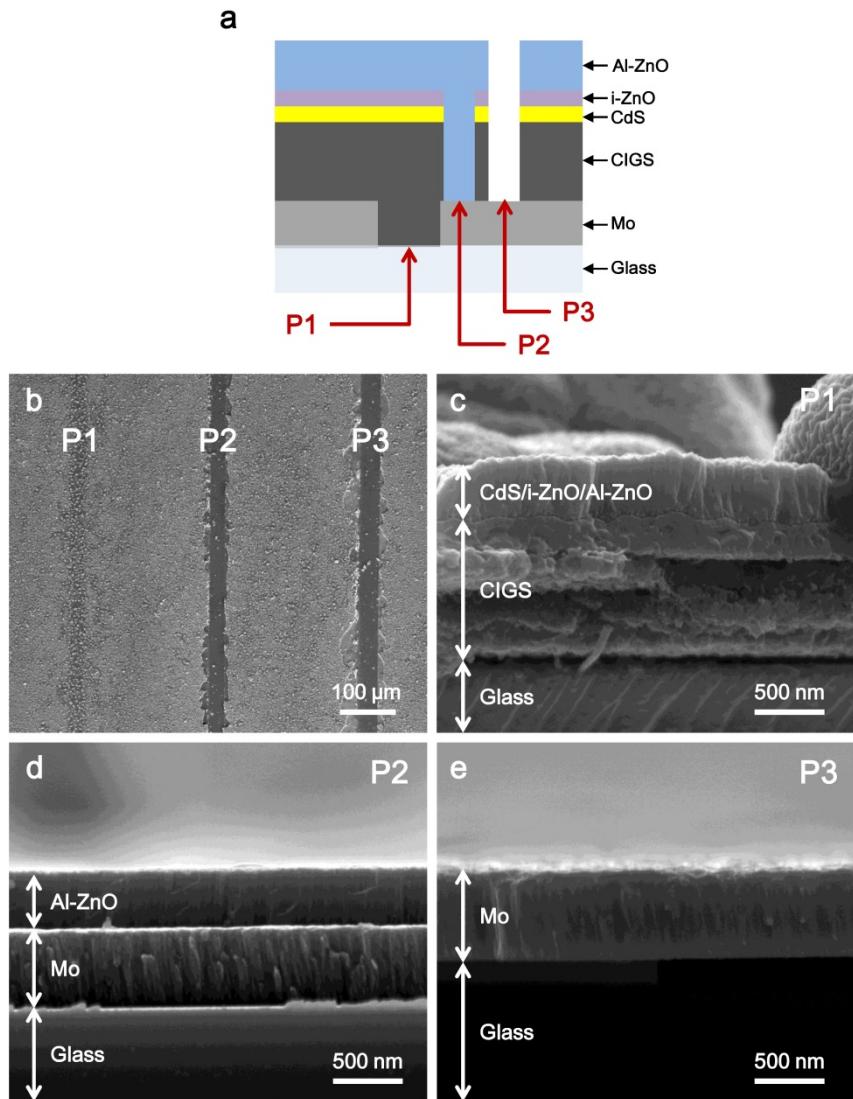


Fig. S1. Schematic diagram (a) and SEM images (b-e) of CIGS module via patterning process. (a) The schematic diagram of the patterns (b) Top view image of scribing region of the CIGS film. (c-e) Cross sectional SEM images of P1 (c), P2 (d), and P3 (e).

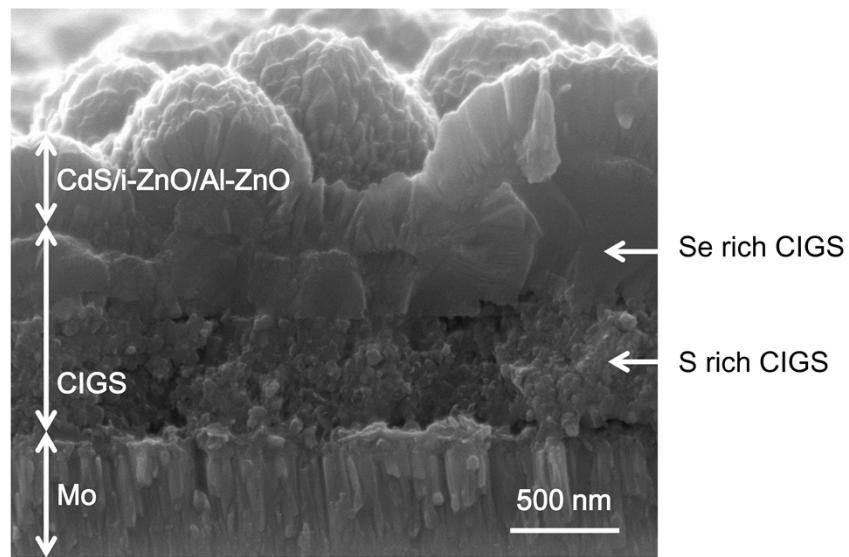


Fig. S2. Detailed cross sectional SEM image of Fig. 3b indicating S and Se rich region in CIGS absorber layer.

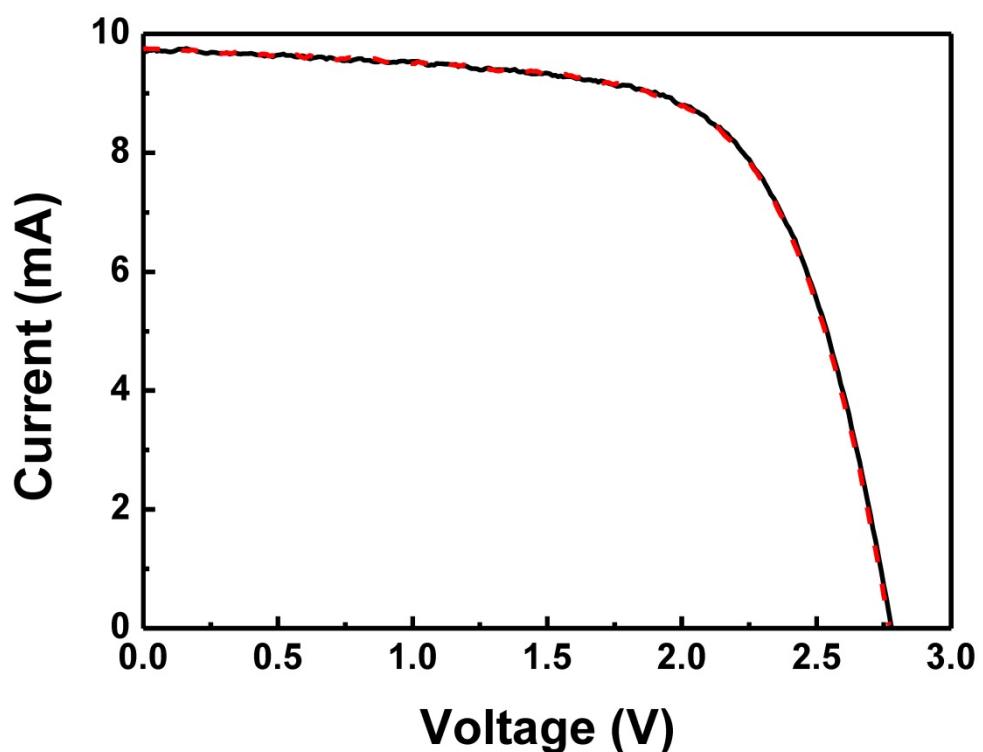


Fig. S3. Current – Voltage (I-V) characteristics of the CIGS module of before (black solid line) and after (red dashed line) the Co_3O_4 catalysts deposition on the rear side of the substrate confirming that the performance of the CIGS module was intact by the Co_3O_4 deposition process.

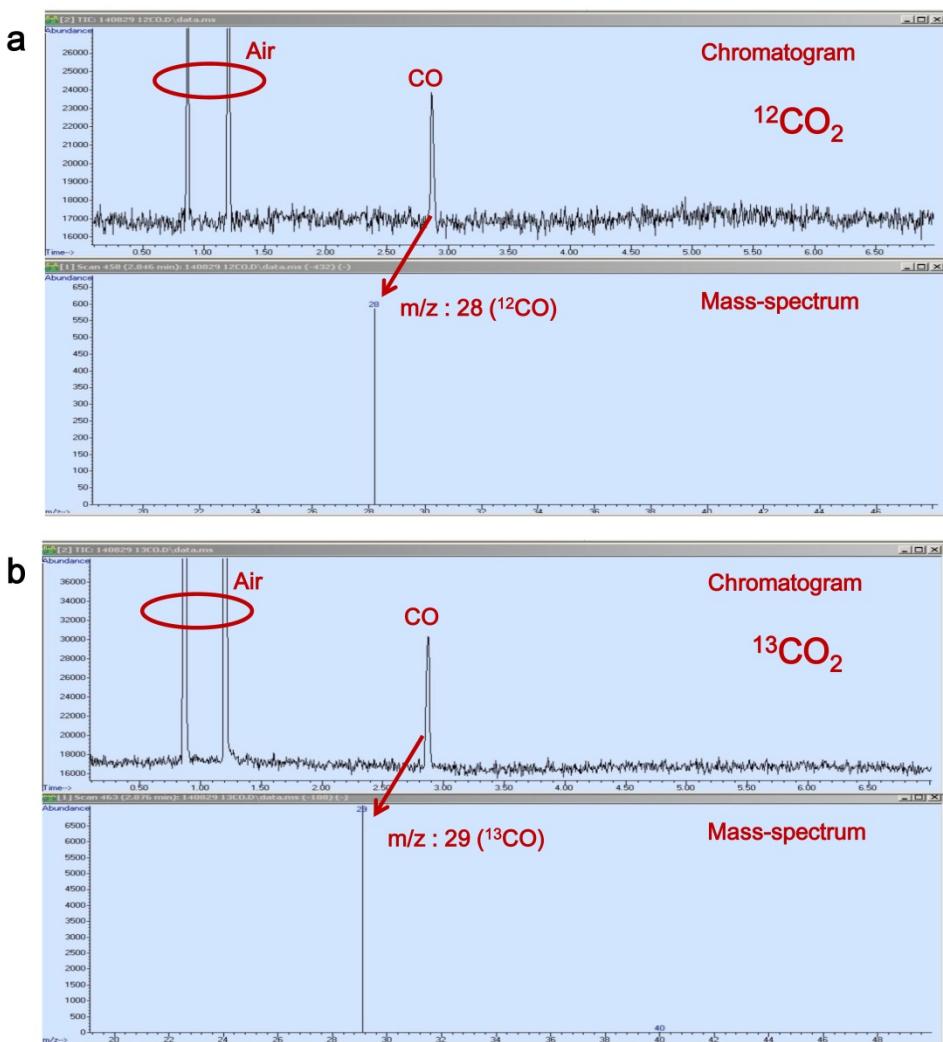


Fig. S4. ^{13}C isotope experiment results. GC-MS spectra of the gas products taken from the cathodic compartment using (a) $^{12}\text{CO}_2$, and (b) $^{13}\text{CO}_2$ gases confirming that CO_2 gas was the carbon source of the produced CO from our solar-fuel device. In order to avoid confusion of overlapping mass-spectrum for ^{12}CO and N_2 , mass spectrum of air was subtracted.

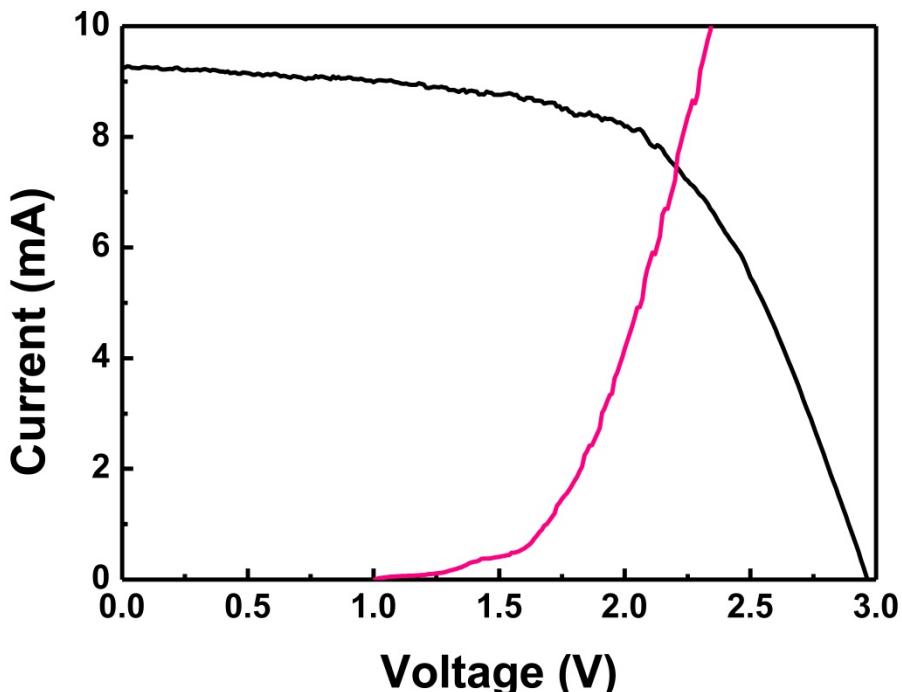


Fig. S5. Two-electrode I-V curve for hydrogen generation from solar water splitting. Black line is CIGS module which had an efficiency of 7.66 % with an open circuit voltage (V_{oc}), short circuit current density (J_{sc}), and fill factor of 2.95 V, 9.22 mA, and 59.2 %, respectively. The pink line is the electrolysis I-V curve with two-electrode configuration with a Co_3O_4 NPs film anode and a Pt cathode.

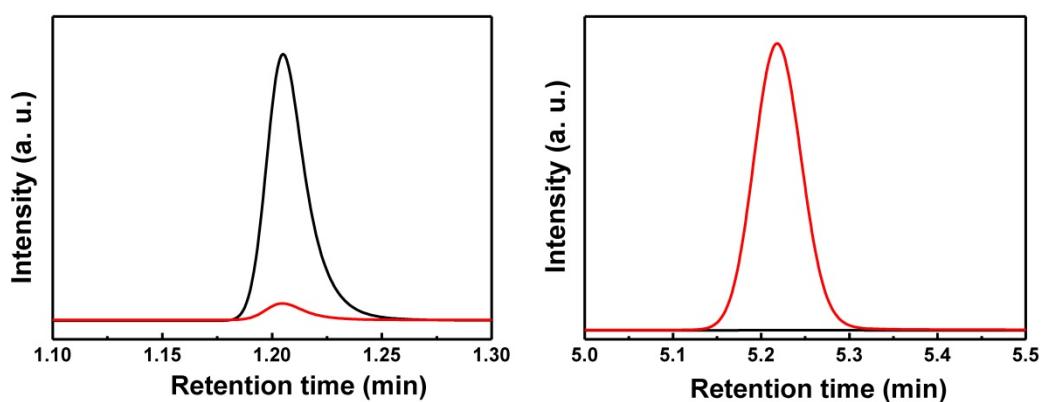


Fig. S6. A typical chromatogram from GC analysis. The red line is a chromatogram from the CO generation device from CO_2 reduction (Fig. 5), and the black line is a chromatogram from the hydrogen generation device from water splitting (Fig. S5).

Table S1. Representative reports of solar-to-hydrogen (STH) conversion efficiency via solar water splitting. (The data are taken from Ronge *et al.*)³⁷

Year	Photo-electrode	Type	Electrolyte	STH Eff.	Ref.
1976	TiO ₂ -GaP	PEC	0.1M H ₂ SO ₄	0.25 %	38
2008	TiO ₂ -CuTiO	PEC	1MKOH(anode) + 0.1M Na ₂ HPO ₄ (cathode)	0.30 %	39
1998	(GaInP ₂ 1jn-GaAs)-Pt	PV+PEC	3M H ₂ SO ₄	12.4 %	16
2010	(WO ₃ 2jn-Si)-Pt	PV+PEC	0.33M H ₃ PO ₄	3 %	40
2012	(WO ₃ 1xDSSC)-Pt	PV+PEC	1M HClO ₄	3.1 %	41
2013	(Co-Pi/W:BiVO ₄ 2jn-Si)-Pt	PV+PEC	0.1M K-Pi	4.9 %	42

Movie S1. The movie shows the solar-fuel device in operation

- (a) An overview of the solar-fuel device for experiment in the dark.
- (b) A lamp is switched on.
- (c) Close up of the cathode for CO generation. CO gas is evolved at the electrode. (The gas product was identified by measuring gas chromatograph).
- (d) Close up of the anode for O₂ generation. The evolved O₂ bubbles attach on the electrode surface.

Supplementary References

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