

Electronic supplementary material

**Solar-driven photoelectrochemical reduction of CO<sub>2</sub> on pyridinyl-immobilized CuInS<sub>2</sub> thin film cathode**

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## **1. Experimental Methods**

All of the reagents used in this study are of analytic grade.

### **1.1 Fabrication of CuInS<sub>2</sub> thin films**

CuInS<sub>2</sub> thin films were fabricated by electrochemical co-deposition of Cu-In alloy layers followed by sulfurization.<sup>S1</sup> A standard three-electrode cell was used; indium tin oxide (ITO) conductive glass (1×2cm<sup>2</sup>), platinum foil and saturated calomel electrode (SCE) were used as the working electrode, counter electrode and reference electrode, respectively. Before each experiment, the working electrode surface was cleaned by ultrasonic washing in ethanol, acetone, and distilled water in turn for three times. Cu-In alloy layers on ITO were prepared using an electroplating bath containing 5 mM CuCl<sub>2</sub>, 5 mM InCl<sub>3</sub>, 0.2 M triethanolamine and 0.010 M sodium citrate. The electrodeposition was conducted potentiostatically for 30 min at 30 °C. After electrodeposition, the Cu-In alloy was annealed with 2 g sublimed sulfur powder at the entrance of a tube furnace in the nitrogen atmosphere at 400 °C for 90 min, CuInS<sub>2</sub> thin films were then obtained.

### **1.2 Characterization of CuInS<sub>2</sub> thin films**

Powder X-ray diffraction (XRD, D/MAX2500, Rigaku, Japan, CuK $\alpha$  radiation,  $\lambda=1.54056 \text{ \AA}$ ) was used to determine the crystal structure, and the crystal size was then calculated from X-ray line broadening using the Scherer equation. The x-ray photoelectron spectra (XPS) were measured by ESCALAB 250 (ThermoFisher Scientific, USA) equipped with x-ray source of twin anode Al K $\alpha$  300W. The XPS spectrometer was configured to operate with 200 eV pass energy for survey, and 30 eV for high resolution scans. All binding energies were calibrated to C1s at 284.6 eV.

### **1.3 Photoelectrochemical reduction of CO<sub>2</sub>**

The photoelectrochemical reduction of CO<sub>2</sub> was conducted by electrochemistry work station CHI650D (Shanghai Chenhua Instrument Co. Ltd., Shanghai, P. R. China) in a quartz glass beaker containing 0.1 M acetate buffer solution and 10 mM pyridine. A standard three-electrode arrangement was used with CuInS<sub>2</sub> thin film (1×2 cm<sup>2</sup>) as a working electrode, graphite sheet as a counter electrode and SCE as a reference electrode. The xenon lamp (AULTT, Beijing, PR China) was used as the visible light source, and the calibrated irradiation intensity is 100 mW/cm<sup>2</sup>.

Prior to the reaction, the electrode had been purged with CO<sub>2</sub> for 30 min. Product analysis was accomplished using gas chromatography-mass spectroscopy. Methanol concentration was measured by a gas chromatography (GC 4000A, East & West Analytic, PR China) with a DB-Wax (Agilent Technologies). The injector temperature was held at 180 °C, the oven temperature was maintained at 60 °C, and the detector temperature was kept at 180 °C. During a typical run, only peaks related to the elution of methanol and pyridine were observed.

When the photoelectrochemical reaction was carried out in the electrolyte containing 0.1 M acetate buffer solution and 25 mM pyridine without the introduction of CO<sub>2</sub>, no methanol was detected, which shows that the addition of acetic acid, sodium acetate and pyridine to the electrolyte could not result in the contamination of trace amount of methanol.

#### **1.4 Electrochemical measurement**

The voltammetric measurement of the illuminated CuInS<sub>2</sub> electrode was conducted in the above setup, and scanning potential was set from -150 to -750 mV (vs. SCE) at 50 mV/s.

The coverage of pyridine on CuInS<sub>2</sub> electrode was measured in an aqueous solution containing pyridine in the above setup by cycle voltammetry method. The coverage can be calculated according to the following equation

$$\Gamma = Q/nAF \quad (\text{Eq. 1})$$

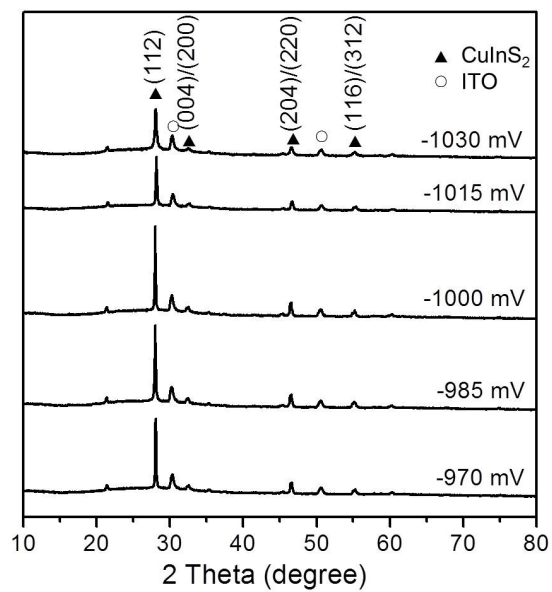
Where  $\Gamma$  (mol/cm<sup>2</sup>) is the coverage of pyridine, Q (C) is the quantity of electricity which can be estimated by integrating the cathodic peak area, n is the number of transferring electrons and is 1 in the reduction of pyridinium, A (cm<sup>2</sup>) is surface area of CuInS<sub>2</sub> electrode, F is Faraday constant (96485C/mol).

The electrochemical impedance spectroscopy experiments were conducted by electrochemistry work station CHI650D. The scanning frequency was set from 0.01Hz to 100 kHz, and the amplitude was 0.1 Hz.

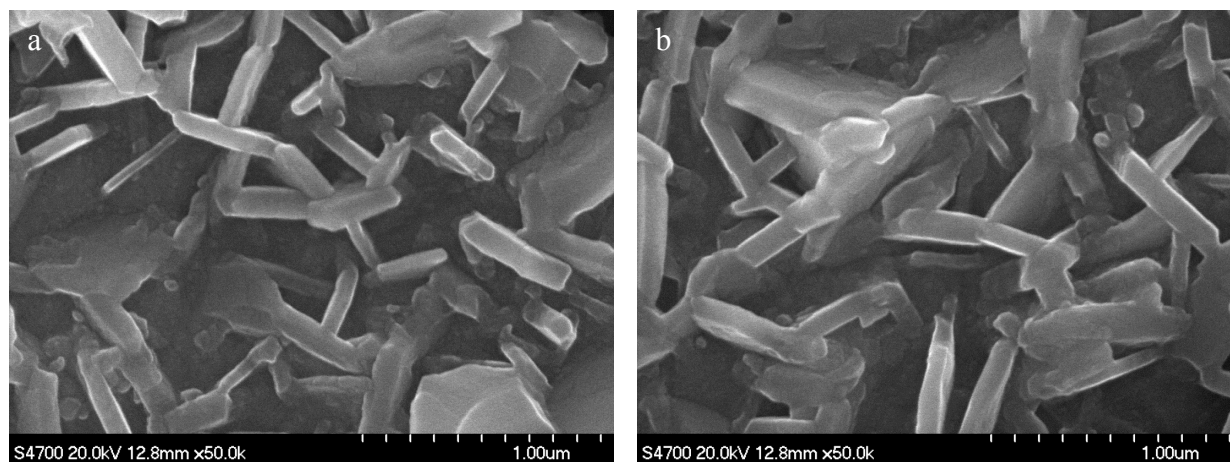
### **1.5 Computational method**

Structure optimizations and energy calculations were carried out with the doubled numerical basis set with d-polarization functions and the generalized gradient corrected functional by Perdew and Wang (PW91).<sup>S2</sup> All calculations were carried out with the DMol program package in the Materials Studio 5.0 of Accelrys Inc.

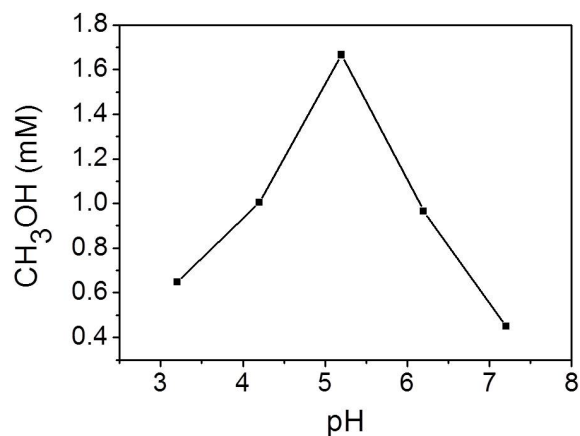
## 2. Supplementary Figures



**Figure S1** XRD patterns for CuInS<sub>2</sub> thin films at various deposition potentials.



**Figure S2** SEM images for CuInS<sub>2</sub> thin film (a) and pyridine-adsorbed CuInS<sub>2</sub> thin film (b).



**Figure S3** Effect of pH value on methanol concentration. Photoelectrochemical reduction experiments are conducted at CuInS<sub>2</sub> thin film photocathode (1×2 cm<sup>2</sup>) at -590 mV (vs SCE) in 0.1 M acetate buffer solution containing pyridine for 7 h, with visible light irradiation of 100 mW/cm<sup>2</sup>.

### 3. Supplementary Table

**Table S1** Equivalent circuit parameters at various applied bias

Applied bias (mV)	$R_e$ (Ohm)	$R_i$ (Ohm)	$R_k$ (Ohm)	$R_m$ (Ohm)	$C_{d1}$ (nF)	$C_{d2}$ (mF)	$C_m$ (mF)
-450	28.51	194.1	307.5	8808	2.465	0.7623	2.184
-550	38.21	180.3	148.7	5739	2.245	0.4812	1.420
-590	37.15	182.0	657.6	3443	2.088	0.3976	1.052
-640	36.63	179.7	439.2	1438	2.105	0.2736	1.344

### 3. References

(S1) Yuan, J.; Shao, C.; Zheng, L.; Fan, M.; Lu, H.; Tao, D.; Hao, C. *Vacuum* **2014**, *99*, 196.

(S2) Wang, Y.; Perdew, J. P. *Phys. Rev. B* **1991**, *44*, 13298.