

## Supporting information

# A versatile photoanode-driven photoelectrochemical system for conversion of CO<sub>2</sub> to fuels with high faradaic efficiencies at low bias potentials

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## Experimental details

### Preparation of WO<sub>3</sub>, Sn/SnO<sub>x</sub> films, copper electrode and CuO-Cu<sub>2</sub>O

The WO<sub>3</sub> films were prepared by a polymer assisted deposition method by multiple cycles of precursor coating and annealing as per our earlier reported method. A 10 ml solution containing 1.85 g of ammonium metatungstate (Aldrich) and 1.0 g of polyethyleneimine (Aldrich) was stirred at room temperature for 2 days resulting in a yellowish transparent viscous solution. 5 cm<sup>2</sup> FTO glass (F-doped SnO<sub>2</sub>, Pilkington TEC8) cleaned earlier with water, ethanol and acetone under ultrasonication was coated with the above solution by tape casting method followed by drying in a hot air oven at 80 °C for

30 minutes and further calcinations at 550 °C. The process of coating, drying and calcination was repeated until the optimum number of coating resulting in the highest photocurrent was achieved.

A film of Sn/SnO<sub>x</sub> was electrodeposited on a titanium sheet with an exposed area of 1 cm<sup>2</sup> (Aldrich, 99.7%) in 0.5 M NaHCO<sub>3</sub> under continuous CO<sub>2</sub> purging. The titanium substrate was etched with 20% H<sub>2</sub>SO<sub>4</sub> solution for 5 min prior to electrodeposition using SnCl<sub>2</sub>·2H<sub>2</sub>O (Aldrich, 99.99%) as the source of tin. The electrodeposition was carried out at -0.7 V vs. RHE for 60 min with Pt as the counter electrode. A film of Sn/SnO<sub>x</sub> was electrodeposited on Ti sheet in a 20 mM SnCl<sub>2</sub>·2H<sub>2</sub>O and 0.5 M NaHCO<sub>3</sub> solution under continuous CO<sub>2</sub> purging. In an attempt to obtain the best activity, the amount of 20 mM SnCl<sub>2</sub>·2H<sub>2</sub>O was optimized; *i.e.* 1 ml of 20 mM SnCl<sub>2</sub>·2H<sub>2</sub>O in 75 ml of 0.5 M NaHCO<sub>3</sub> was found to give the highest CO<sub>2</sub> reduction current (Figure S4a).

In the case of copper cathodes, polishing the electrode plays an important role. Initial studies with 0.5 cm<sup>2</sup> copper foils electropolished in orthophosphoric acid at 500 mA cm<sup>-2</sup> for 1 min followed by etching in 1 M HCl for 3 min resulted in up to 56% faradaic efficiencies for CH<sub>4</sub>. However, this polishing method did not produce reproducible results in our studies. Mechanical polishing using diamond and alumina is the recommended procedure for reproducible results. However, with a copper foil mechanical polishing was not convenient and did not produce uniform polishing throughout the electrode. This led us to move on to 'glassy carbon electrode' type copper electrode surrounded by polyether ether ketone (PEEK) body (ALS, Japan). This electrode has a 3 mm diameter of exposed copper having an area of 0.071 cm<sup>2</sup>. Using this electrode, the polishing procedure with diamond, alumina and 1 M HCl gave highly reproducible results. The electrode was mechanically polished using the grit pad, followed by 15 μm, 3 μm, 1 μm diamond polish and then with 0.05 μm alumina polish. Finally the electrode was etched in 1 M HCl for 3 minutes before using for experiments.

Films containing a mixture of CuO and Cu<sub>2</sub>O (Cu<sub>2</sub>O/CuO) was prepared by heating copper foils in air. Copper foils were degreased by ultrasonication in acetone for 30 minutes. It was then etched in 1 M HCl for 30 seconds, washed in distilled water and dried. Finally the foils were calcined at 600 °C for 4

h in air atmosphere resulting in formation of Cu<sub>2</sub>O/CuO on the surface. Ohmic contact was made on one of the sides by scratching off the copper oxides and then using silver paste and copper wire which was then covered using epoxy.

### Physical and electrochemical characterization

The morphology and elemental distribution of the films were analyzed using field-emission scanning electron microscopy (FESEM, JEOL JMS-7401F and Philips Electron Optics B.V. XL30S FEG, operated at 10 keV). The crystal structure of the samples was determined using X-ray diffraction spectrometry (XRD, PW3040/60 Xpert PRO, PANalytical, with CuK $\alpha$  ( $\lambda=1.54056$  Å)). The UV-Vis calorimetry measurements for the quantization of HCOOH were carried out in Shimadzu (Model UV2501PC) spectrophotometer. The UV-Vis diffuse reflectance spectroscopy measurements were carried out using a Agilent Cary 5000 with a DRA 2500 reflectance accessory. The oxidation states of Sn were studied using X-ray photoelectron spectroscopy (EscaLab 220-IXL, VG Scientific, monochromated Al K $\alpha$ ).

Impedance measurements were carried out in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution (pH 7) at an applied frequency of 500 Hz using Ag/AgCl (3 M NaCl) and platinum mesh as reference and counter electrodes, respectively using the Iviumstat potentiostat (Ivium technologies). The flat band potential of electrodes was determined by the Mott-Schottky Equation (1):

$$1/C^2 = (2 / e\epsilon\epsilon_0N_d) [V_a - V_{fb} - kT / e] \quad (1)$$

where C= space charge layer capacitance,  $e$ =electron charge,  $\epsilon_0$ =dielectric constant,  $\epsilon$ =permittivity of vacuum,  $N_d$ =electron donor density,  $V$ =applied potential, and  $V_{fb}$ =flat band potential. The flat band potential ( $V_{fb}$ ) was determined by taking the x intercept of a linear fit to the Mott-Schottky plot,  $1/C^2$  as a function of applied potential ( $V_a$ ).

### Photoelectrochemical CO<sub>2</sub> reductions

The visible light irradiation was carried out using a 500 W Hg lamp (Newport) with a 420 nm cut-off filter and water for IR radiation removal. The photoelectrochemical reactor made of polycarbonate consists of two compartments separated by a Nafion-115 proton exchange membrane (Figure S6). Both the cathode and anode compartment were filled with 40 ml of the electrolyte. The cathode compartment was connected to a gas circulation system with a six-port valve for on-line sampling to a gas chromatograph. The gas circulation system was primarily made of stainless steel tubing. A peristaltic pump (Eyela, Japan) with a Tygon tubing was used for the circulation of the gas. The gas circulation system also contained a pressure gauge and a cold trap maintained at 1 °C to prevent moisture from entering the gas chromatography. The total volume of the gas in the circulation system after filling the reactor with electrolyte was 79 ml. The temperature of the reaction was controlled by partially immersing the reactor in a water bath (not shown in Figure S6) containing mixture of 20% ethylene glycol in water. The temperature of the ethylene glycol-water mixture was maintained by an automated chiller (Lab companion, Model RW-1025G).

Before the start of the reaction, both the electrolyte and the circulation system were purged with CO<sub>2</sub> for 40 min and 10 min, respectively. In reactions involving the copper electrode, the catholyte 0.5 M KHCO<sub>3</sub> was pre-electrolyzed at 0.025 mA using Pt mesh for 150 min under CO<sub>2</sub> purging. Preelectrolysis removes traces of impurity metal ions in the electrolyte which are known to poison the Cu cathode.<sup>1</sup> The closed circulation system and the reactor were filled with CO<sub>2</sub> which was continuously circulated through the electrolyte for the entire reaction period. The reactions were carried out at atmospheric pressure of CO<sub>2</sub> and the bias potentials were applied using a Princeton Applied Research Potentiostat/Galvanostat Model 263A. The photoelectrochemical reactions in WO<sub>3</sub>-Cu and WO<sub>3</sub>-Sn/SnO<sub>x</sub> systems were carried out at 12 °C and 25 °C respectively.

In the case of WO<sub>3</sub>-Cu system, the photoelectrochemical reactions were carried out in 0.5 M KHCO<sub>3</sub> under visible light irradiation ( $\lambda > 420$  nm) using Ag/AgCl as the reference electrode at 12 °C. However, all potentials mentioned in this report are with respect to reversible hydrogen electrode (RHE), converted using pH values according to the Equation (2).

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \times \text{pH} \quad (2)$$

where  $E_{\text{Ag/AgCl}}$  is the potential measured using the Ag/AgCl electrode.

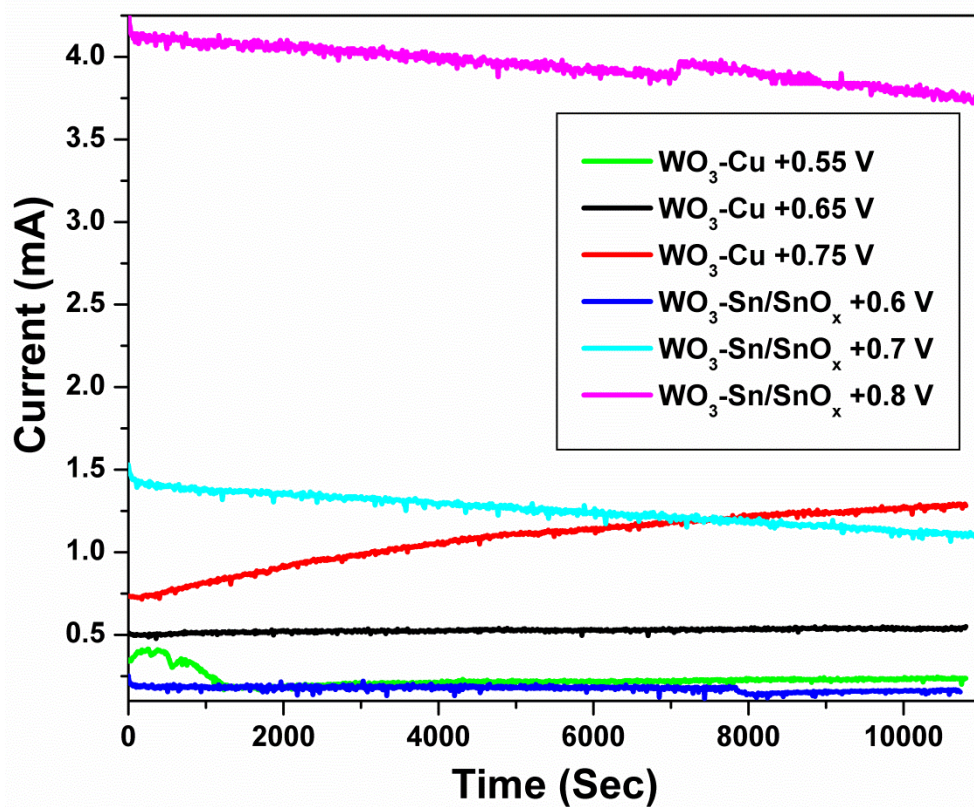
The analysis of the gaseous reaction mixtures containing CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> was carried out using a Supelco Carboxen 1000 packed column and thermal conductivity detector (TCD) in a HP 6890 gas chromatography (GC). The liquid products such as methanol and ethanol were analyzed with an Agilent Porabond Q capillary column and an FID detector. In both columns, high purity Argon was used as the carrier gas. The quantity of formic acid was analyzed by a calorimetric procedure using chromotropic acid.<sup>2</sup>

Further, the faradaic efficiencies (FE) for the different products were calculated based on the utilized charge and the number of electrons required for the formation of the various products according to the Equation (3).

$$\text{FE} = \text{No. of moles formed} \times 100 / \text{theoretical no. of moles} \quad (3)$$

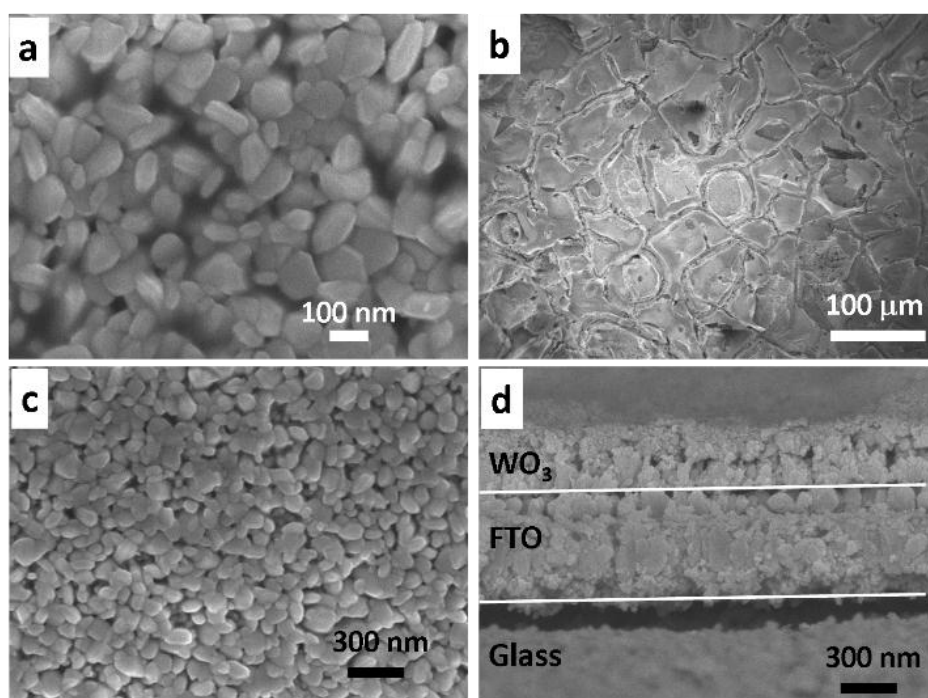
### **Two electrode potential ( $E_{\text{WE}}-E_{\text{CE}}$ ) measurements**

The potential between the working electrode and counter electrode ( $E_{\text{WE}}-E_{\text{CE}}$ ) was measured in a quartz cell under 250 W Xenon lamp irradiation using 0.5 M KHCO<sub>3</sub> purged with CO<sub>2</sub> (pH 7.5) as the electrolyte. The working electrode to counter electrode and working electrode to reference electrode distance was 1 cm. A Bio-logic potentiostat, Model VMP3 capable of sensing the potential of WE and CE simultaneously was used. Ag/AgCl was used as the reference electrode. Platinum mesh electrode was used as the CE for Cu<sub>2</sub>O/CuO.

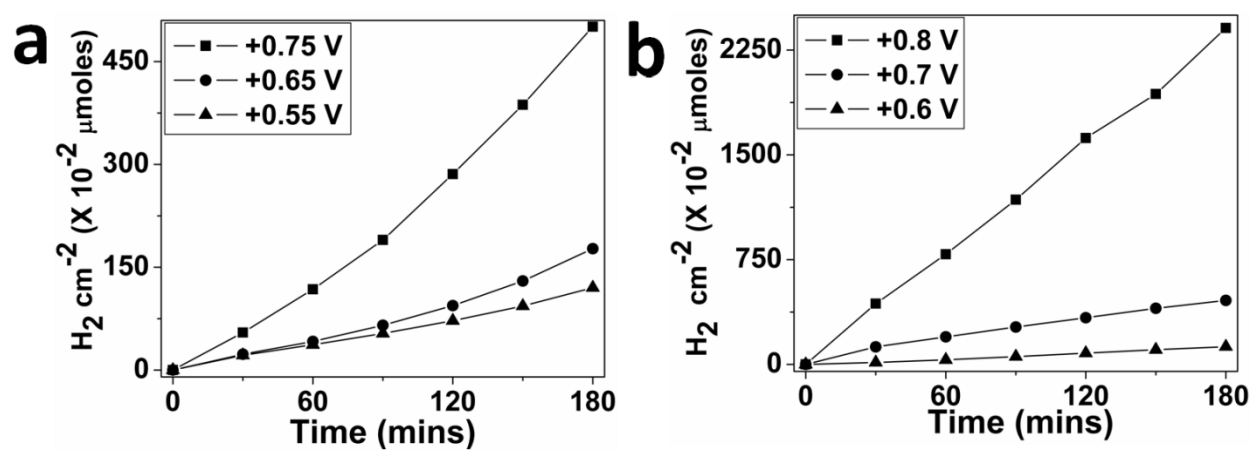


**Figure S1** Chronoamperometry plots of the photoelectrochemical CO<sub>2</sub> reduction reactions carried out using WO<sub>3</sub>-Cu (in 0.5 M KHCO<sub>3</sub>, pH 7.5) and WO<sub>3</sub>-Sn/SnO<sub>x</sub> (in 0.5 KCl, pH 5.2) system at different bias potentials under visible light irradiation ( $\lambda > 420$  nm). The area of the WO<sub>3</sub> photoanode was 4 cm<sup>2</sup>.

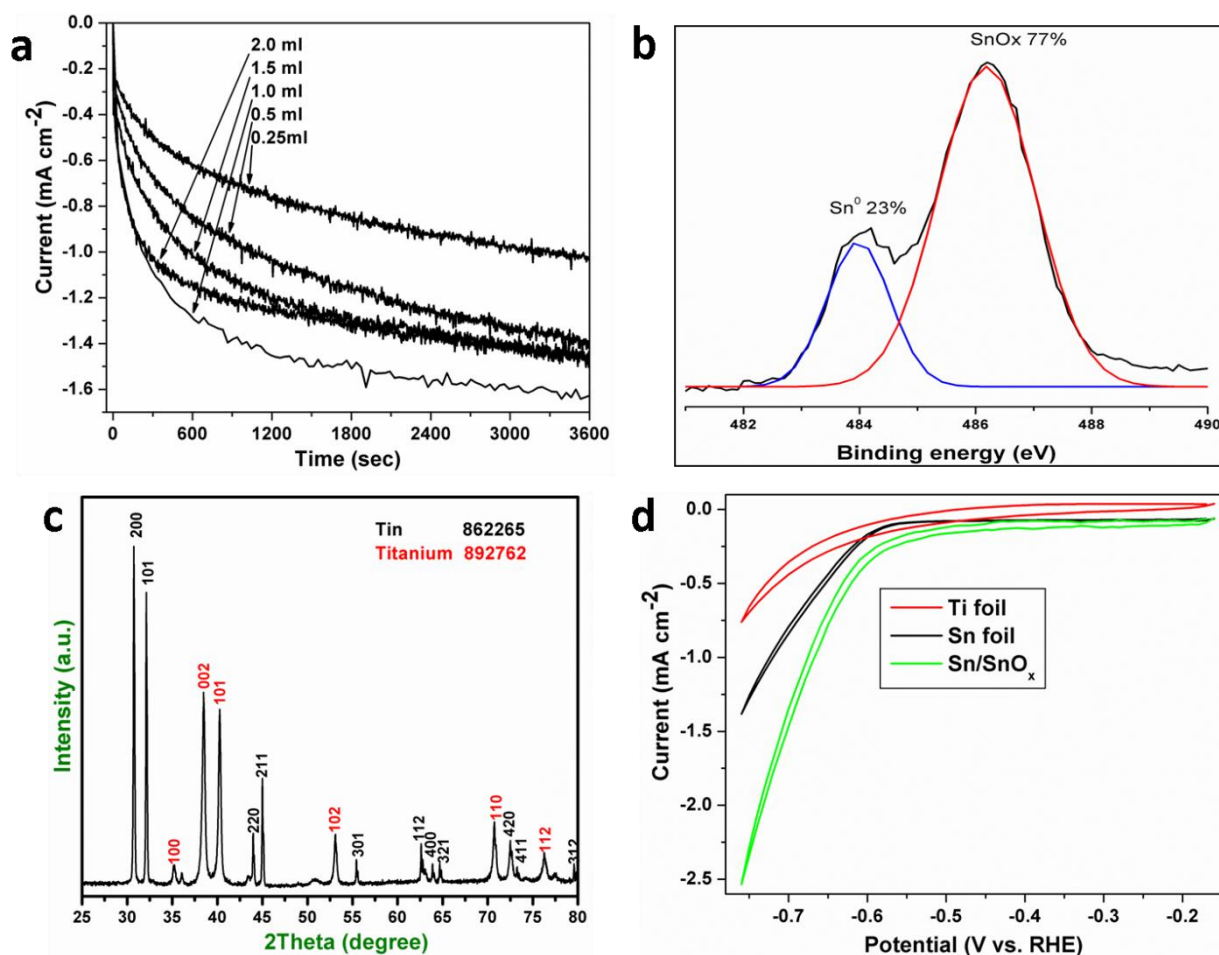




**Figure S2.** Scanning electron microscopy (SEM) images of the WO<sub>3</sub> films at different magnifications.

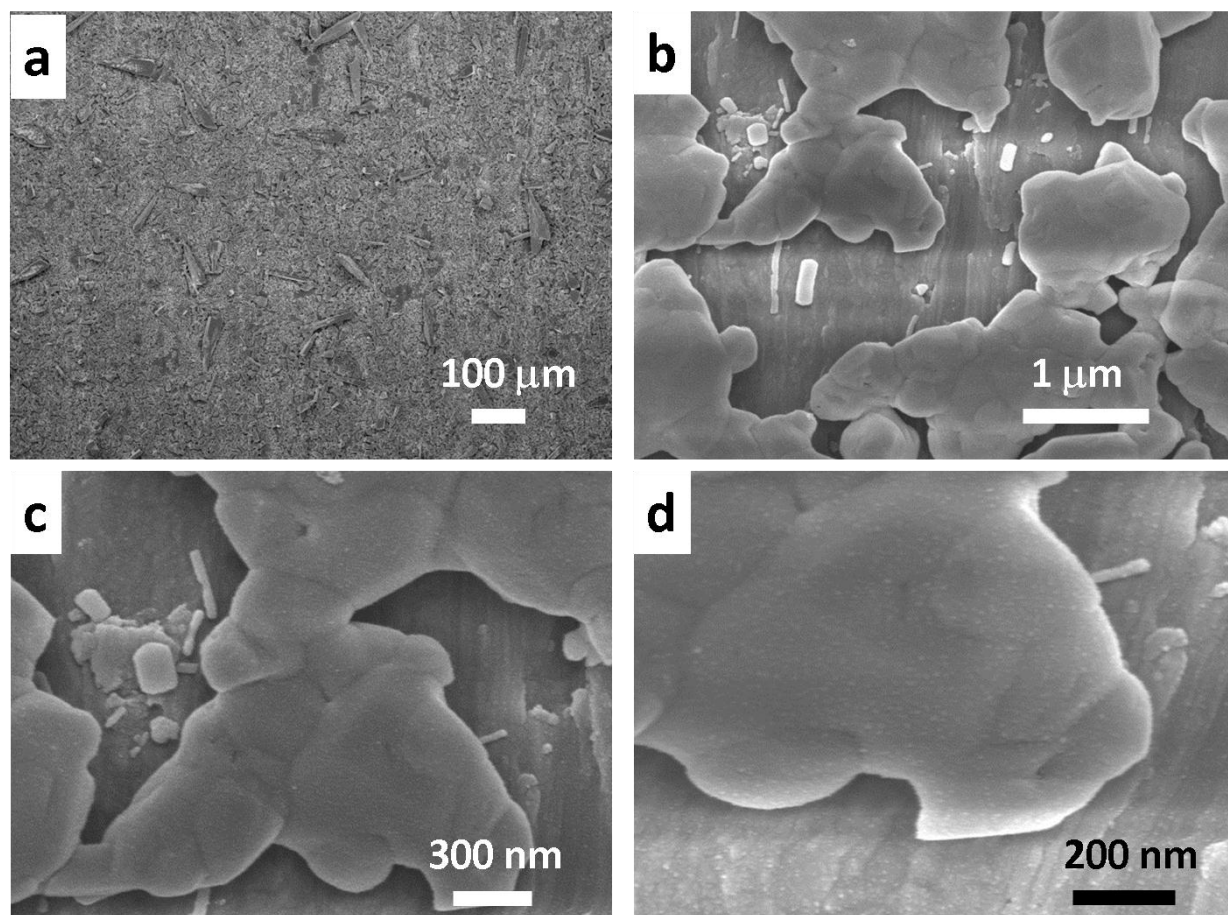


**Figure S3** Amount of H<sub>2</sub> evolved vs. time at different bias potentials for a) WO<sub>3</sub>-Cu system and b) WO<sub>3</sub>-Sn/SnO<sub>x</sub> system

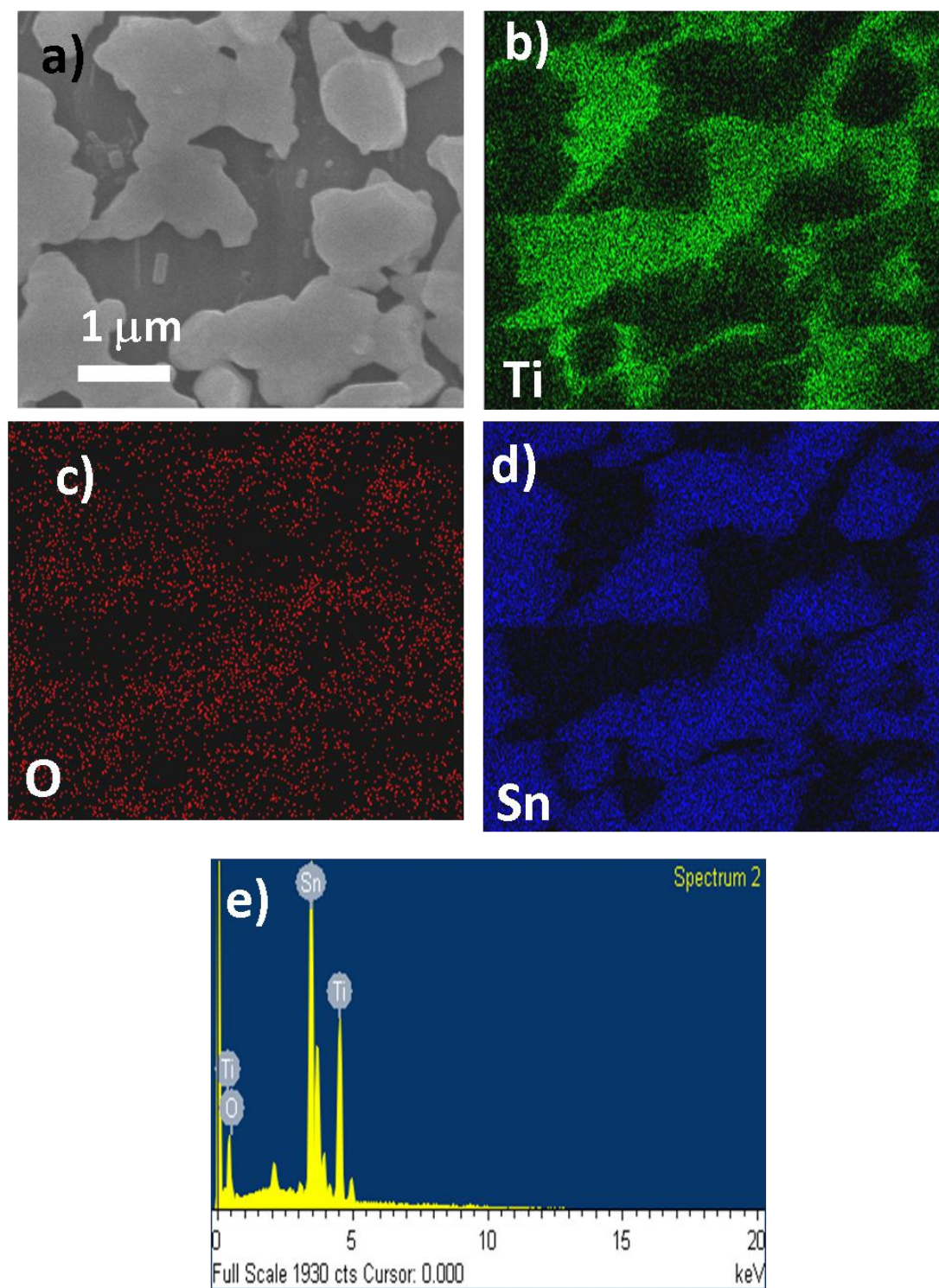


**Figure S4** a) Chronoamperometry of Sn deposition on Ti foil in CO<sub>2</sub> purged 0.5 M NaHCO<sub>3</sub> containing different amounts of 20 mM SnCl<sub>2</sub> · 2H<sub>2</sub>O (pH 7.5) at -0.7 V vs. RHE. b) X-ray photoelectron spectroscopy of Sn/SnO<sub>x</sub> films on Ti substrate. c) X-ray diffraction pattern of Sn/SnO<sub>x</sub> films. d) Cyclic voltammetry (Scan rate 20 mV/s) of Ti, Sn and Sn/SnO<sub>x</sub> in CO<sub>2</sub> purged 0.5 M KCl (pH 5.2) solution.



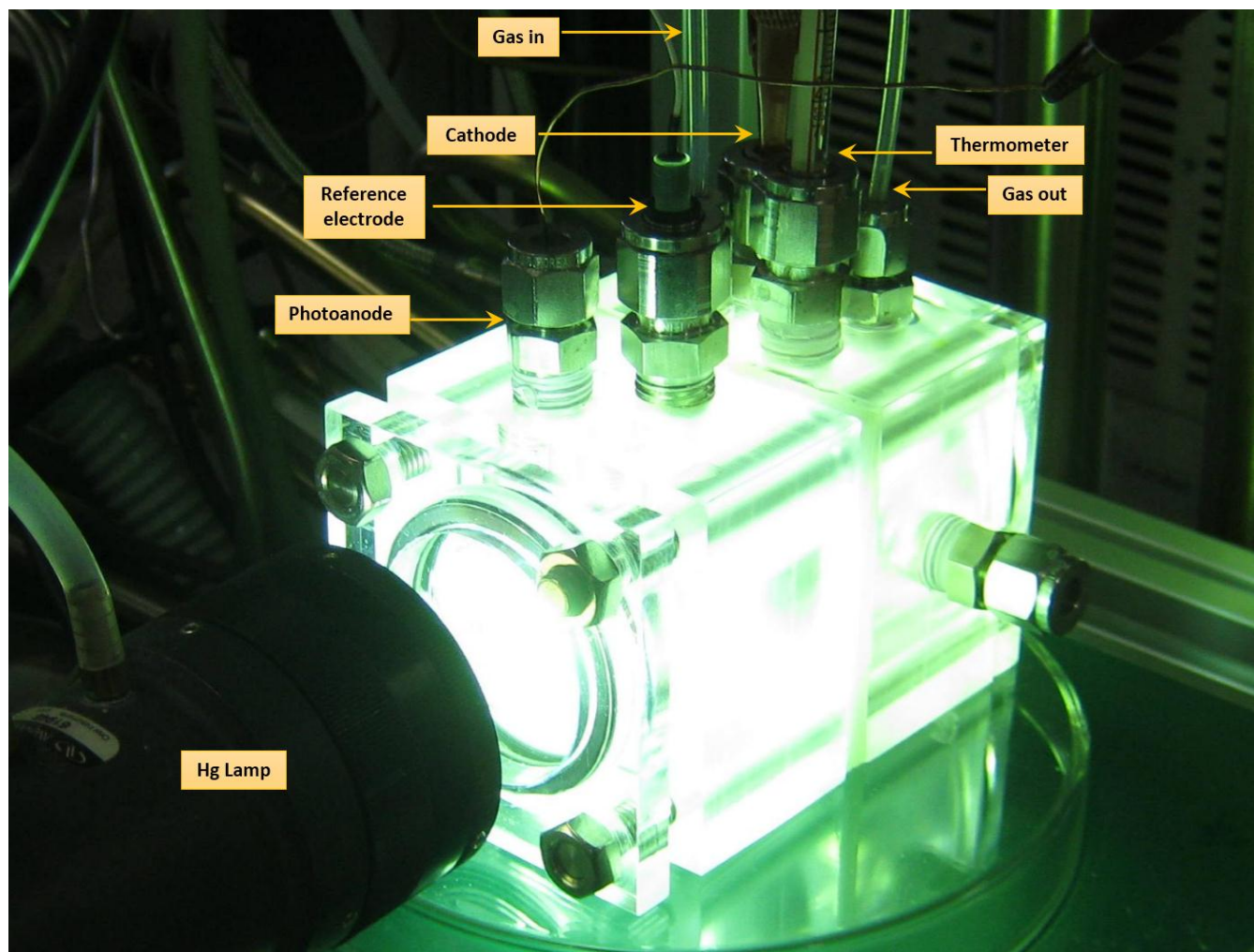


**Figure S5** Scanning Electron Microscopy images of Sn/SnO<sub>x</sub> at different magnifications

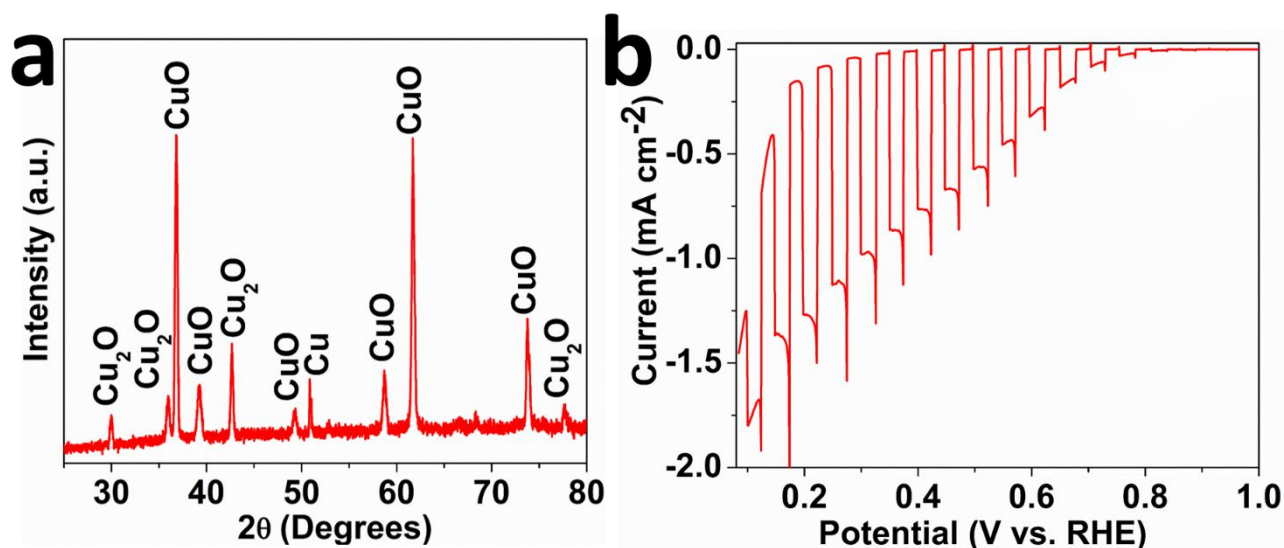


**Figure S6** EDAX elemental mapping and elemental analysis images of Sn/SnO<sub>x</sub> catalysts





**Figure S7** Digital photograph of the photoelectrochemical CO<sub>2</sub> reduction reactor under visible light irradiation ( $\lambda > 420\text{nm}$ )



**Figure S8** (a) X-ray diffraction pattern of p-CuO-Cu<sub>2</sub>O composite and (b) linear sweep voltammetry of the CuO-Cu<sub>2</sub>O in CO<sub>2</sub> purged 0.5 M KHCO<sub>3</sub> (pH 7.5) under 500 W Hg lamp with a >420 nm filter irradiation at a scan rate of 20 mV/s.

## REFERENCES

- (1) Hori, Y.; Konishi, H.; Futamura, T.; Murata, A.; Koga, O.; Sakurai, H.; Oguma, K. "Deactivation Of Copper Electrode" in Electrochemical Reduction of CO<sub>2</sub>. *Electrochimica Acta* **2005**, *50*, 5354-5369.
- (2) Grant, W.M. Colorimetric Microdetermination of Formic Acid Based on Reduction to Formaldehyde. *Anal. Chem.* **1948**, *20*, 267-269.