

# Synergistic Effect in Plasmonic CuAu Alloys as Co-Catalyst on SnIn<sub>4</sub>S<sub>8</sub> for Boosted Solar-Driven CO<sub>2</sub> Reduction

Zhengrui Yang<sup>1</sup>, Jinman Yang<sup>1</sup>, Kefen Yang<sup>1</sup>, Xingwang Zhu<sup>2</sup>, Kang Zhong<sup>1</sup>, Ming Zhang<sup>1</sup>, Haiyan Ji<sup>1</sup>, Minqiang He<sup>1</sup>, Huaming Li<sup>1</sup> and Hui Xu<sup>1,\*</sup>

<sup>1</sup> School of Materials Science & Engineering, Institute of Energy Research, Jiangsu University, Zhenjiang 212013, China

<sup>2</sup> School of Environmental and Chemical Engineering, Yangzhou University, Yangzhou 225009, China

\* Correspondence: xh@ujs.edu.cn

## Chemicals

L-cysteine, polyvinylpyrrolidone (PVP, M.W. = 55,000), ascorbic acid (AA), KBr, Copper(II)chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O), Tetrachloroauric(III) acid tetrahydrate (HAuCl<sub>4</sub>·4H<sub>2</sub>O), absolute ethanol (C<sub>2</sub>H<sub>6</sub>O), were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Indium chloride tetrahydrate (InCl<sub>3</sub>·4H<sub>2</sub>O), tin (IV) chloride pentahydrate (SnCl<sub>4</sub>·5H<sub>2</sub>O) were purchased from Aladdin China Holding Co., Ltd. (Shanghai, China). Deionized water was used throughout the synthesis. All chemicals were of analytical reagent grade and used without further purification.

## Preparation of SnIn<sub>4</sub>S<sub>8</sub>

Generally, SnIn<sub>4</sub>S<sub>8</sub> was synthesized using a facile hydrothermal synthesis method as follows. First, 0.3506 g of SnCl<sub>4</sub>·5H<sub>2</sub>O, 1.173 g of InCl<sub>3</sub>·4H<sub>2</sub>O were dissolved in 40 mL of deionized water. The mixture finally formed the colorless transparent liquid after magnetically stirring for 30 min to completely dissolved. Next, 0.9693 g of L-cysteine was added slowly to the solution followed by stirring for 30 min. The obtained solution was then transferred into a 100 mL Teflon-lined stainless-steel autoclave and reacted at 160 °C for 24 h. After the mixture was cooled at ambient temperature, the resulting yellow-green precipitates were collected and washed with absolute ethanol and deionized water repeatedly, centrifuged, and then vacuum-dried for 12 h at 60 °C to obtain SnIn<sub>4</sub>S<sub>8</sub>.

## Synthesis of Cu<sub>x</sub>Au<sub>y</sub>-SnIn<sub>4</sub>S<sub>8</sub> hybrid structures

In a typical synthesis, 105 mg of polyvinylpyrrolidone (PVP, M.W. = 55,000), 120 mg of ascorbic acid (AA), and 300 mg of KBr were added to a 100 mL flask with 20 mL of deionized water under ultrasonic treatment for 5 min and then magnetic stirring in an oil bath preset to 80 °C for 10 min. After that, variable amounts of CuCl<sub>2</sub>·2H<sub>2</sub>O solution (0.1 mol/L) and HAuCl<sub>4</sub>·4H<sub>2</sub>O solution (50 mmol/L) were injected into the reaction solution and reacted for 10 min. Subsequently, 100 mg of SnCl<sub>4</sub>·5H<sub>2</sub>O was added to the mixture solution. The reaction mixture was stirred vigorously and reacted at 80 °C in the air for 3 h. Finally, the obtained samples were centrifuged and washed with deionized water, and dried in a vacuum oven at 60 °C for 24 h. The total amount of CuCl<sub>2</sub>·2H<sub>2</sub>O solution and HAuCl<sub>4</sub>·4H<sub>2</sub>O solution is 0.2 mmol. For comparison, a sequence of Cu<sub>x</sub>Au<sub>y</sub>-SnIn<sub>4</sub>S<sub>8</sub> samples was obtained, which were labeled as Au<sub>2</sub>-SIS, Cu<sub>5</sub>Au<sub>1</sub>-SIS, Cu<sub>10</sub>Au<sub>1</sub>-SIS, Cu<sub>15</sub>Au<sub>1</sub>-SIS and Cu<sub>2</sub>-SIS, where x and y corresponding to the molar ratio of CuCl<sub>2</sub>·2H<sub>2</sub>O and HAuCl<sub>4</sub>·4H<sub>2</sub>O, respectively.

## Characterization methods

The phase of samples was indicated by X-ray diffraction (XRD) patterns by A Bruker D8 diffractometer X-ray powder diffraction in the range of 2θ = 10°–80° at a scan rate of

7° min<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) was tested on X-ray photoelectron spectrometer-Thermo Fisher Nexsa. The binding energies obtained in the XPS analysis were corrected with reference to C 1s (284.8 eV). Transmission electron microscopy. The microscopy was examined by scanning electron microscopy (SEM, JSM-7800F, JEOL Ltd., Tokyo, Japan) and transmission electron microscopy (TEM, JEOL-JEM-2100F, JEOL Ltd., Tokyo, Japan). Ultraviolet-visible diffuse reflection spectra (DRS) were obtained using a UV-vis spectrophotometer (Shimadzu UV-2600, Tokyo, Japan) in the range of 200–800 nm; BaSO<sub>4</sub> was used as a reflectance standard material. Photoluminescence (PL) spectroscopy experiments were conducted using a Quanta Master & TimeMaster Spectrofluorometer. The N<sub>2</sub>-sorption measurements were conducted on Tristar II 3020.

### Photoelectrochemical test

The photoelectrochemical properties were measured on the electrochemical workstation (CH Instruments Ins. Austin, TX, USA) with a standard three-electrode system, which consisted of a platinum plate as a counter electrode, a reference electrode using Ag/AgCl electrode (3 M KCl) and catalysts-coated-ITO glass (0.5 cm × 1 cm area). 0.2 M Na<sub>2</sub>SO<sub>4</sub> and a mixture of 5 mM K<sub>3</sub>Fe(CN)<sub>6</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub> (1:1) containing 0.1 mol L<sup>-1</sup> KCl were used in the photocurrent measurement. The working electrode of Mott-Schottky plots was prepared by dropping 5 µL catalyst suspension onto a glassy carbon electrode two times and the electrolyte is the same as that of photocurrent measurement. The catalyst suspension is prepared by dissolving 4 mg of catalyst in 1 mL of ethylene glycol under ultrasound. IPCE can be expressed concretely as follows:  $IPCE = hcI/\lambda J$ , where  $h$  is Planck's constant,  $c$  is the speed of light,  $I$  is the measured photocurrent density at a specific wavelength,  $\lambda$  is the incident light wavelength and  $J$  is the recorded irradiance intensity at a specific wavelength. Linear sweep voltammetry (LSV) tests were conducted in the CO<sub>2</sub>-saturated 0.5M KHCO<sub>3</sub> solution. The Ag/AgCl (KCl sat.) electrode and Pt sheet were adopted as the reference electrode and counter electrode, respectively. Preparation of the working electrode is described as follows: 10 mg of catalyst were dispersed in a solution containing 10 µL of Nafion and 1 mL of ethanol to generate a suspension by sonication. Then, 20 mL of the catalyst ink was dripped onto the carbon paper and dried in air. All potentials were converted into reversible hydrogen electrode values based on equation:  $E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + 0.197 \text{ V}$ .

### Photocatalytic CO<sub>2</sub> reduction measurement

The catalytic activity of catalysts was evaluated by the photocatalytic CO<sub>2</sub> reduction in a 300 mL Labsolar-6A (Beijing Perfectlight, Beijing, China) closed system, matching with a 300 W Xenon lamp (PLS-SXE3, Beijing Perfectlight). The light intensity is 916 mW/cm<sup>2</sup>. In a typical process, 10 mg of the as-prepared catalyst was uniformly dispersed by adding 4 mL of TEOA and 12 mL of deionized water. After that, the high-purity CO<sub>2</sub> was injected into the reaction system and the pressure of the whole reactor was kept at 80 kPa. The above operation was repeated three times. The photocatalytic reaction temperature was maintained at 5 °C by cooling the water circulation system which can promote the adsorption of CO<sub>2</sub>. After the reaction, the gas products were quantified through Gas chromatography (GC-2014, Shimadzu, Kyoto, Japan). To ensure the accuracy of the test results, each activity experiment was conducted at least three times.

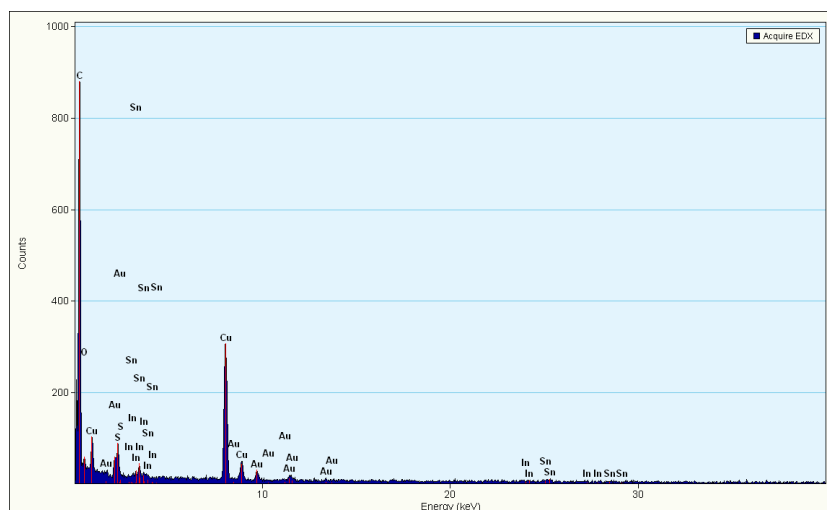


Figure S1. Energy dispersive spectrometer of  $\text{Cu}_{10}\text{Au}_1\text{-SnIn}_4\text{S}_8$ .

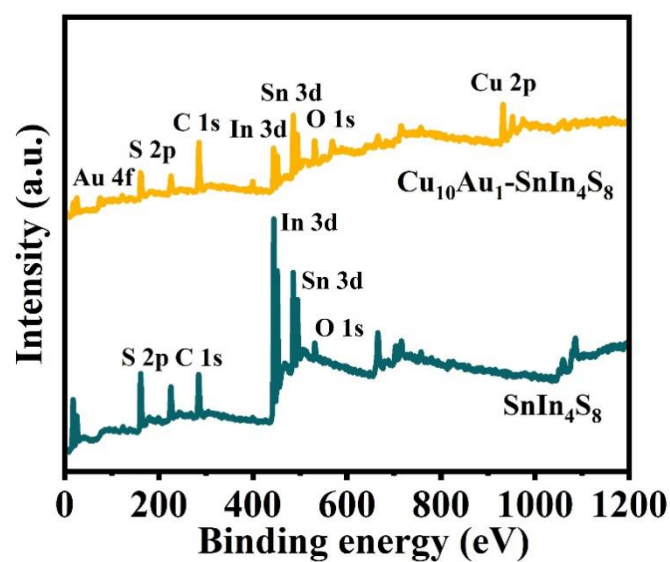


Figure S2. Survey spectra of  $\text{SnIn}_4\text{S}_8$  and  $\text{Cu}_{10}\text{Au}_1\text{-SnIn}_4\text{S}_8$ .

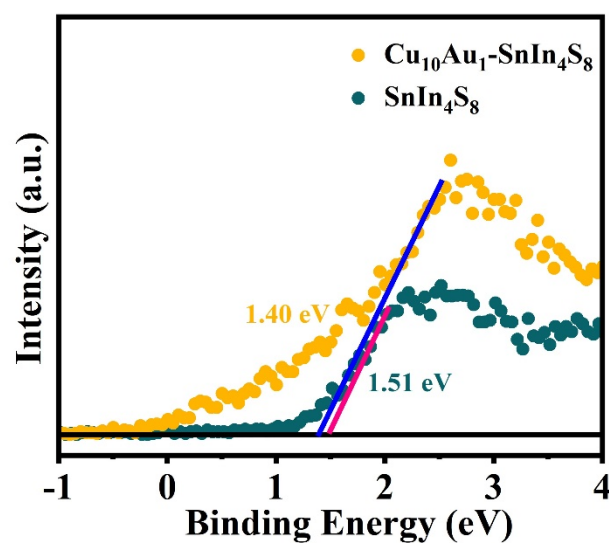
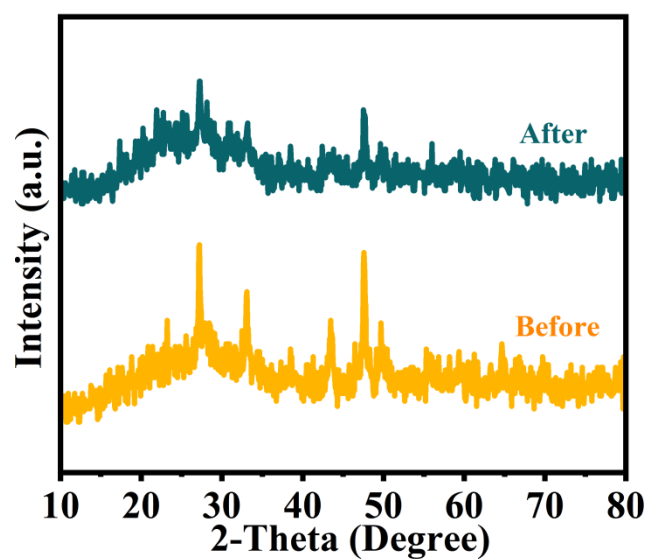
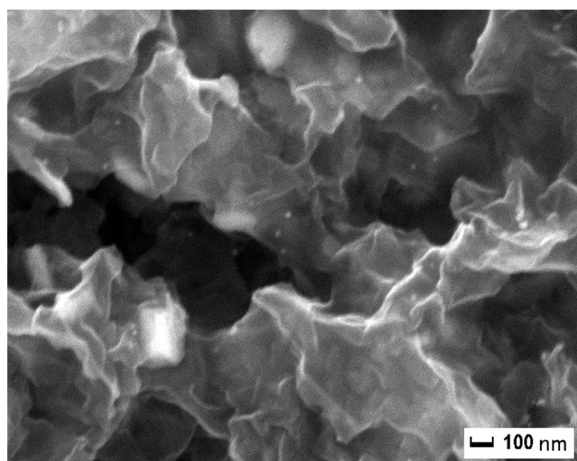


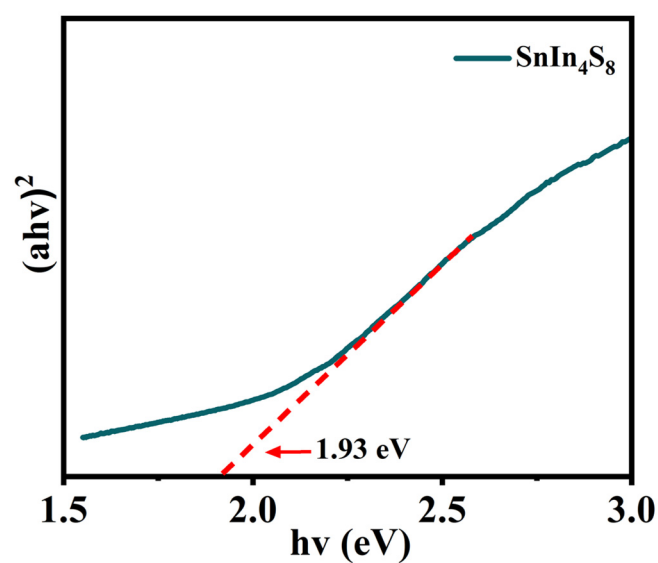
Figure S3. XPS valence band spectra of  $\text{SnIn}_4\text{S}_8$  and  $\text{Cu}_{10}\text{Au}_1\text{-SnIn}_4\text{S}_8$ .



**Figure S4.** XRD patterns of  $\text{Cu}_{10}\text{Au}_1\text{-SnIn}_4\text{S}_8$  before and after photocatalytic  $\text{CO}_2$  reduction reaction.



**Figure S5.** SEM image of  $\text{Cu}_{10}\text{Au}_1\text{-SnIn}_4\text{S}_8$  after photocatalytic  $\text{CO}_2$  reduction reaction.



**Figure S6.** Tauc plots of  $\text{SnIn}_4\text{S}_8$ .

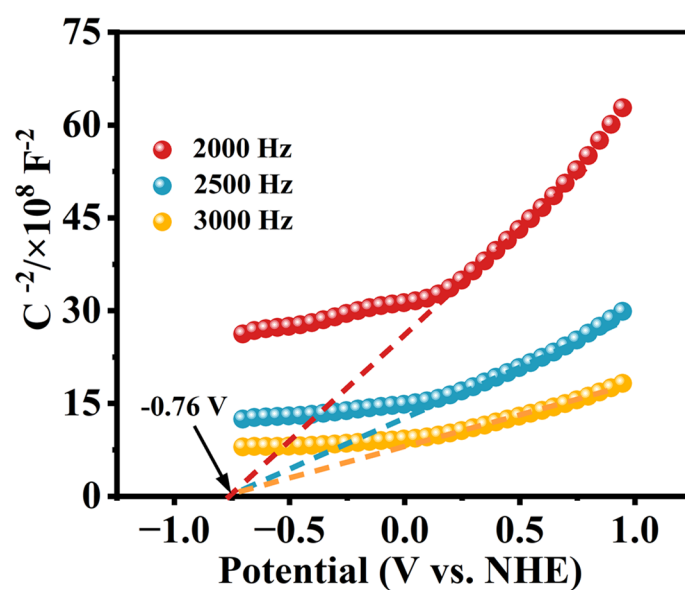


Figure S7. Mott-Schottky plots of SnIn<sub>4</sub>S<sub>8</sub>.

Besides, the latest photocatalysts for CO<sub>2</sub> reduction and their abilities are listed in Table S1. The performance of Cu<sub>10</sub>Au<sub>1</sub>-SnIn<sub>4</sub>S<sub>8</sub> is in a competitive position.

**Table S1.** Comparison of the CO<sub>2</sub> photoreduction performance of Cu<sub>10</sub>Au<sub>1</sub>-SnIn<sub>4</sub>S<sub>8</sub> catalyst with other catalysts.

	light source	Experimental conductions	Activity ( $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ )	Reference
Cu <sub>10</sub> Au <sub>1</sub> -SnIn <sub>4</sub> S <sub>8</sub>	300 W Xe lamp	H <sub>2</sub> O, TEOA	CO: 27.87	This work
In <sub>2</sub> S <sub>3</sub> -CuInS <sub>2</sub>	300 W Xe lamp	CoCl <sub>2</sub> , 2,2-bipyridine, TEOA, MeCN	CO: 19	[48]
WQDs/CdIn <sub>2</sub> S <sub>4</sub>	300 W Xe lamp	water vapor	CO: 8.2 CH <sub>4</sub> : 1.6	[49]
In <sub>2</sub> O <sub>3</sub> /In <sub>2</sub> S <sub>3</sub>	300 W Xe lamp	H <sub>2</sub> O	CO: 12.22	[41]
TiO <sub>2</sub> -AuCu-V	300 W Xe lamp	H <sub>2</sub> O	CH <sub>4</sub> : 33.5	[22]
CN-PA12	AM 1.5 illumina- tion	water vapor	CO: 5.42 CH <sub>4</sub> : 4.03	[23]
ZnIn <sub>2</sub> S <sub>4</sub> /BiVO <sub>4</sub>	300 W Xe lamp	water vapor	CO: 4.75, CH <sub>4</sub> : 0.5	[50]
ZnIn <sub>2</sub> S <sub>4</sub> / N-doped graphene	300 W Xe lamp	H <sub>2</sub> O	CO: 2.45 CH <sub>4</sub> : 1.01 CH <sub>3</sub> OH: 1.37	[51]
CuInS <sub>2</sub> /Au/g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp 400 nm cutoff fil- ter	water vapor	CO: 2.43 CH <sub>4</sub> : 0.15	[52]