## **Experimental Details**

**Chemicals and materials.** Indium (III) chloride tetrahydrate (InCl<sub>3</sub>·4H<sub>2</sub>O), thioacetamide (TAA), hexadecyl trimethyl ammonium bromide (CTAB), potassium bicarbonate (KHCO<sub>3</sub>), ethanol (C<sub>2</sub>H<sub>5</sub>OH), and nafion solution were all purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). All the chemicals were used without further purification. Ultrapure Millipore water (18.2 M $\Omega$ ) was used in all experiments.

Synthesis of pristine  $In_2S_3$  nanosheets. In a typical synthesis, 0.04 mol of  $InCl_3 \cdot 4H_2O$ , 0.06 mol of TAA, and 0.02 mol of CTAB were dissolved in 20 mL distilled water and stirred for 30 min. The mixture was then transferred into a round flask and stirred, followed by being heated to 95 °C and kept for 80 min. After the mixture was cooled down naturally to room temperature, the product was collected by centrifugation at 10000 rpm for 10 min. The precipitate was washed by distilled water three times and ethanol twice to remove any possible ions, and then being dried under vacuum at 40 °C overnight. Finally, the precipitate annealed in N<sub>2</sub> atmosphere at 200 °C to obtain a highly crystalline  $In_2S_3$  nanosheets for further characterizations.

Synthesis of  $In-In_2S_3$  hybrid nanosheets. In a typical procedure, the asobtained pristine  $In_2S_3$  nanosheets was calcined at 600 °C for 2 h in H<sub>2</sub> atmosphere and then cooled down to room temperature.

**Preparation of working electrode.** 3 mg of pristine  $In_2S_3$  or  $In-In_2S_3$  hybrid nanosheets, 12 mg of active carbon, and 90 µL of Nafion solution (5 wt%) were dispersed in 2 mL of ethanol via sonication for 2 h to form a homogeneous ink. Then, 1.5 mL of the mixture was uniformly spread on carbon papers with an area of  $1 \times 1$ cm<sup>2</sup>. The prepared electrodes were dried under ambient environment.

**Electrochemical measurements.** Controlled potential electrolysis of  $CO_2$  was conducted in an H-cell (separated by Nafion 115) containing 40 mL of 1 M KHCO<sub>3</sub> electrolyte under ambient environment. Ag/AgCl (in 3 M KCl solution) electrode and Pt wire were used as the reference and counter electrodes, respectively. We also utilized Au and graphite instead of Pt as counter electrode for experiments, respectively. The activity and selectivity towards  $CO_2$  electrochemical reduction by the use of the different counter electrodes did not exhibit significant differences. This result proved that Pt wire can be used as counter electrode under the effect of proton exchange membrane, which differed from the hydrogen evolution or oxygen

evolution reaction<sup>[S1]</sup>. The potentials were controlled by an electrochemical station (CHI660E). All potentials in this study were measured against the Ag/AgCl reference electrode and converted to the RHE reference scale based on the following equation:  $E(vs RHE)=E(vs Ag/AgCl) + 0.21 V + 0.0591 \times pH$ . The energy efficiency for the conversion of CO<sub>2</sub> into formate was calculated by the following equation.

$$\boldsymbol{\Phi}_{\text{formate}} = \frac{\text{FE (\%)} \times \Delta E_{\text{formate}}^{0}}{\Delta E_{\text{formate}}}$$

 $\Phi_{\text{formate}}$  was the energy efficiency for the conversion of CO<sub>2</sub> into formate.  $\Delta E_{\text{formate}}^{0}$  as the difference between the standard half reaction potentials for water oxidation (1.23 V vs RHE) and the reduction of CO<sub>2</sub> into formate (-0.2 V vs RHE).  $\Delta E_{\text{formate}}$  was the difference between the standard water oxidation potential and the working potential at the cathode, respectively.

The electrochemical reduction of  $CO_2$  was carried out in  $CO_2$ -saturated 1 M KHCO<sub>3</sub> electrolyte (pH = 6.8) in the potential range of -0.7 V to -1.1 V vs RHE atroom temperature. After  $CO_2$  was purged into the KHCO<sub>3</sub> solution for at least 30 min to remove residual air in the reservoir, controlled potential electrolysis was conducted at each potential for 60 min. The oxygen generated at the anode was vented out of the reservoir. The gas products of  $CO_2$  electrocatalytic reduction were monitored by an online micro gas chromatography (GC) (GC2014, Shimadzu, Japan) equipped with a TCD detector every 5 min. The durability tests were conducted at the potential of -1.1 V vs RHE for 8 h. The KHCO<sub>3</sub> solution after electrolysis was collected and analyzed on a 400 MHz NMR spectrometer to quantify liquid products.

Double-layer capacitance ( $C_{dl}$ ) was determined by measuring the capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammogram (CV). The CV ranged from 0.2 V to 0.3 V vs RHE with various scan rates (10, 20, 30, 40, and 50 mV s<sup>-1</sup>). The  $C_{dl}$  was estimated by plotting the  $\Delta j$  ( $\Delta j = j_a$  $j_c$ ) at 0.25 V vs RHE against the scan rates, in which the  $j_a$  and  $j_c$  were the anodic and cathodic current density, respectively. The slope is twice that of the  $C_{dl}$  values. The electrochemical impedance spectra of the pristine In<sub>2</sub>S<sub>3</sub> and In-In<sub>2</sub>S<sub>3</sub> hybrid nanosheets were recorded with AC voltage with 5 mV amplitude at -0.1 V vs RHE within the frequency range from 100 KHz to 100 mHz. In OH- adsorption measurements, N<sub>2</sub>-saturated 1 M KOH was used as the electrolyte and the scan rate was 10 mV s<sup>-1</sup>. The electrochemical impedance spectra nanosheets were recorded at 0 V vs RHE.

Instrumentations. TEM images were taken using a Hitachi H-7650 transmission electron microscope at an acceleration voltage of 100 kV. HRTEM were carried out on a JEOLARM-200F field-emission transmission electron microscope operating at 200 kV accelerating voltage. XRD patterns were recorded by using a Philips X'Pert Pro Super diffractometer with Cu-K $\alpha$  radiation ( $\lambda$ =1.54178 Å). XPS measurements were carried out on a VG ESCALAB MK II X-ray photoelectron spectrometer with an exciting source of Mg K $\alpha$ =1253.6 eV. The binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.6eV. The liquid products were quantified by nuclear magnetic resonance (Bruker AVANCE AV III 400) spectroscopy. Room-temperature UV/Vis diffuse reflectance spectroscopy (DRS) were recorded on a Perkin Elmer Lambda 950 UV/Vis-NIR spectrophotometer. Ultraviolet photoelectron spectroscopy (UPS) tests with photon energy of 21.2 eV were performed at the Catalysis and Surface Science Endstation at the BL11U beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The work functions of pristine In<sub>2</sub>S<sub>3</sub> or In-In<sub>2</sub>S<sub>3</sub> hybrid nanosheets were determined by the difference between the photon energy and the binding energy of secondary cutoff edge.



Fig. S1. Typical TEM image of pristine  $In_2S_3$  nanosheets.



Fig. S2. HRTEM image of the  $In-In_2S_3$  sample in the nanosheet region.



Fig. S3. XPS survey spectra of pristine  $In_2S_3$  and  $In-In_2S_3$  hybrid nanosheets.



**Fig. S4.** S 2p XPS spectra of pristine  $In_2S_3$  and  $In-In_2S_3$  hybrid nanosheets.



**Fig. S5**. The *IR*-corrected linear scanning voltammetry curves of pristine  $In_2S_3$  and  $In_1S_3$  hybrid nanosheets.



**Fig. S6**. Cyclic voltammetric curves in the presence of  $N_2$  and  $CO_2$  over (A) pristine  $In_2S_3$  nanosheets, (B) In-In<sub>2</sub>S<sub>3</sub> hybrid nanosheets.

Potential (vs RHE)	-0.7 V	-0.8 V	-0.9 V	-1.0 V	-1.1 V
pristine In <sub>2</sub> S <sub>3</sub> nanosheets					
FE <sub>formate</sub> [%]	36.5	39.3	52.2	71.9	59.5
FE <sub>CO</sub> [%]	25.9	28.5	21.6	12.0	19.9
FE <sub>H2</sub> [%]	37.6	32.2	26.2	16.1	20.6
In-In <sub>2</sub> S <sub>3</sub> hybrid nanosheets					
FE <sub>formate</sub> [%]	61.6	65.2	73.4	76.0	73.4
FE <sub>CO</sub> [%]	19.5	18.3	14.4	14.0	14.9
FE <sub>H2</sub> [%]	18.9	16.5	12.2	10.0	11.7

Table S1. Summary of the Faradaic efficiencies over pristine  $In_2S_3$  and  $In-In_2S_3$  hybrid nanosheets.



Fig. S7. Faradaic efficiencies for  $H_2$  over pristine  $In_2S_3$  and  $In-In_2S_3$  hybrid nanosheets.



**Fig. S8.** Energy conversion efficiencies for formate production ( $\Phi_{\text{formate}}$ ) over pristine In<sub>2</sub>S<sub>3</sub> and In-In<sub>2</sub>S<sub>3</sub> hybrid nanosheets.



Fig. S9. CV curves of (A) pristine  $In_2S_3$  and (B)  $In-In_2S_3$  hybrid nanosheets with various scan rates.



**Fig. S10**. Current density for carbonaceous product ( $j_{C-product}$ ) normalized by the mass content of In of pristine In<sub>2</sub>S<sub>3</sub> and In-In<sub>2</sub>S<sub>3</sub> hybrid nanosheets.



Fig. S11. Nyquist plots and the corresponding equivalent circuit of the  $In-In_2S_3$  hybrid nanosheets after the 8-h stability test.

## **References:**

[S1] L. Zhang, J. M. T. A. Fischer, Y. Jia, X. Yan, W. Xu, X. Wang, J. Chen, D. Yang,
H. Liu, L. Zhuang, M. Hankel, D. J. Searles, K. Huang, S. Feng, C. L. Brown, X. Yao,
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