

Supporting Information

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3 **An in-situ spectroscopic study on 2D-CuS/Ti₃C₂ photocatalytic CO₂ reduction to C1 and**

4 **C2**

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1 **Experimental Details**

2 **Chemicals and Materials**

3 Hydrofluoric acid (HF, AR, 40.0%) and aluminum titanium carbide (Ti_3AlC_2 , 98%, 200 mesh) were obtained
4 from McLean Shanghai. Ethylene glycol (EG), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), and copper chloride
5 ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) were from Sinopharm Reagent Corporation. All reagents were of analytical grade and could be
6 used without any further purification.

7 **Synthesis of 2D Ti_3C_2**

8 Firstly, 2 g of titanium aluminum carbide (Ti_3AlC_2) was weighed and Ti_3AlC_2 was slowly added to 40 mL of
9 hydrofluoric acid (HF, 40 wt%) over 10 min. The reaction was stirred at 35 °C for 24 h under a thermostatic
10 water bath, and at the end of the reaction, the precipitate was collected by centrifugation at 3500 rpm and
11 washed repeatedly with deionized water until the pH of the supernatant was neutral. The resulting solid was
12 dried in a vacuum oven at 60 °C for 12 h, and multilayer Ti_3C_2 nanosheets were finally obtained.

13 **Synthesis of 2D CuS**

14 First, 10 mL of water and 30 mL of EG were mixed and stirred until well blended, then 341 mg of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$
15 (2 mmol) and 496 mg of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (2 mmol) were weighed and added to the mixed solution with
16 continued stirring. After the solution was stirred to a yellow-green color, it was transferred to a 100 mL round-
17 bottomed flask and placed in an oil bath at 70 °C and heated for 4 h with constant stirring. At the end of the
18 reaction, the flask was removed from the oil bath, cooled to room temperature and washed several times with
19 ethanol and water, retaining the solids and discarding the supernatant, and dried under vacuum at 60 °C
20 overnight.

21 **Synthesis of 2D/2D CuS/ Ti_3C_2**

22 First, a quantitative amount of multilayer 2D Ti_3C_2 powder was weighed and added to a mixture of 10 mL of
23 water and 30 mL of EG and sonicated for 30 min to form a homogeneous dispersion. Then 341 mg of
24 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2 mmol) and 496 mg of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (2 mmol) were weighed and added to the above
25 dispersion with continuous stirring until the solution turned dark green. It was then transferred to a 100 mL
26 round-bottomed flask and placed in an oil bath at 70 °C with constant stirring and heating for 4 h. At the end
27 of the reaction, the solution was cooled to room temperature and then washed several times with ethanol and
28 water crosswise, retained as a solid and dried under vacuum at 60 °C overnight. A series of 2D/2D CuS/ Ti_3C_2
29 samples, i.e., 4 mmol, 8 mmol, 16 mmol, 24 mmol, and 32 mmol, were prepared by the addition of
30 multilayered 2D Ti_3C_2 powders in different amounts of substances, while keeping the concentration of the
31 CuS precursor (2 mmol) constant. The generated 2D/2D CuS/ Ti_3C_2 nanocomposites were prepared according

1 to the molar ratio of CuS to Ti_3C_2 named as CuS/ Ti_3C_2 (1:n), n=2, 4, 8, 12, 16.

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3 **Material Characterizations**

4 The surface morphology and microstructure of the products were photographed using a FE-SEM, JSM-7001F
5 scanning electron microscope (SEM) from JEOL, Japan. The crystal structure of the product was obtained by
6 X-ray diffraction (XRD) using a Shimadzu XRD-6100 powder model from Tsushima Corporation, Japan. The
7 valence states of the elements were studied by X-ray photoelectron spectroscopy (XPS) using Thermo ESCAL
8 AB 250XI model from Thermo Fisher Scientific, USA. The UV absorption spectra of the products were
9 obtained by a Shimadzu UV-3600 UV-Vis diffuse reflectance spectrometer from Tsushima Corporation,
10 Japan. The fluorescence spectra of the products were obtained by a steady state/transient fluorescence
11 spectrometer model Edinburgh FLS 1000 from Edinburgh Instruments, UK. Electrochemical correlation
12 characterization was carried out by an electrochemical workstation model CHI660E from Shanghai Chenhua
13 Instrument Factory. The in situ infrared characterization of the products was carried out using a diffuse
14 reflectance Fourier transform infrared (FTIR) spectrometer model Nicolet Is10 from Thermo Fisher Scientific,
15 USA.

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17 **Photocatalytic CO₂ reduction**

18 Photocatalytic CO₂ reduction experiments were carried out in a homemade 50 mL closed quartz reactor. Ten
19 mg of catalyst was dispersed in 10 mL of deionized water and sonicated for 20 min to make it uniformly
20 dispersed. Subsequently, high-purity CO₂ was introduced into the reaction system for 30 min to completely
21 exhaust the air and saturate the system with CO₂. The photocatalytic CO₂ reduction performance was then
22 tested using a 300 W xenon lamp (500 mW cm⁻²) as a light source. The gaseous products were qualitatively
23 and quantitatively detected by a gas chromatograph (GC 5890N) equipped with a hydrogen flame ionization
24 detector (FID) and using nitrogen (N₂) as carrier gas. In particular, the gas chromatograph was equipped with
25 a well-sealed gas injection needle, and samples were taken and injected into the chromatography every one
26 hour of light exposure, with four hours as a complete photocatalytic CO₂ reduction test. The inlet consists of
27 two signal channels, A and B. Channel A detects multi-carbon products (e.g., C₂H₄) in the reduction products,
28 while channel B detects one-carbon products (e.g., CO, CH₄).

29

30 **In situ FTIR investigation into photocatalytic CO₂ reduction**

31 In-situ diffuse reflectance infrared Fourier transform spectroscopy (In-situ Transmission) experiments were

1 carried out on a Thermo Scientific Nicolet Is10 (Thermo Fisher Scientific, USA) spectrometer fitted with a
2 photoconductive detector (mercury cadmium telluride, MCT). The catalyst samples were sealed in a reaction
3 chamber with two zinc selenide (ZnSe) windows. CO₂ gas was brought into the reaction chamber by means of
4 a gas path through a water bulb until equilibrium. A xenon lamp was used as a light source, which was reflected
5 into the ZnSe windows of the chamber through a reflector to carry out the in-situ photoresponse, and the
6 infrared spectral signals were recorded and saved on a monitor connected to it. All in situ infrared
7 spectroscopic measurements were performed at atmospheric pressure and room temperature.

8

9 **Calculation of Apparent Quantum Efficiency (AQY)**

10 The apparent quantum efficiency is given by the following equation :

$$11 \quad AQY = \frac{8 \times \text{the number of evolved } CH_4 \text{ molecules}}{N}$$

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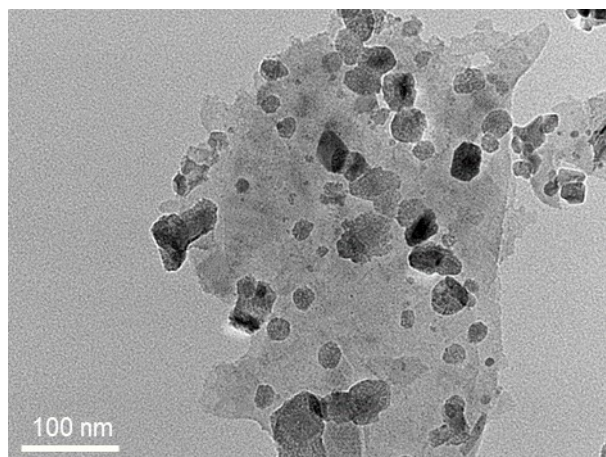
13 where E represents the electron charge; λ represents the wavelength of incident light; h represents Planck's
14 constant; c represents the speed of light; and N represents the number of incident photons.

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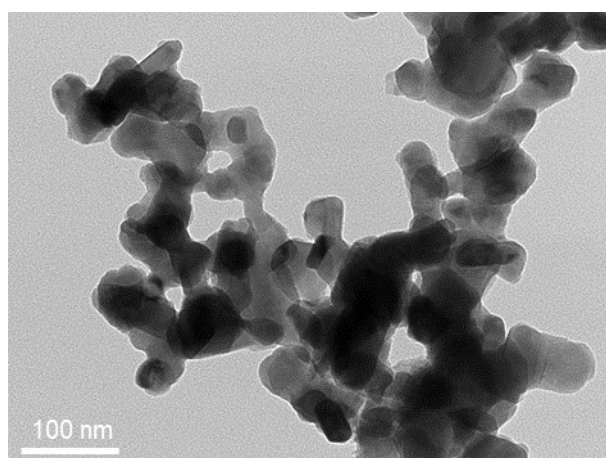
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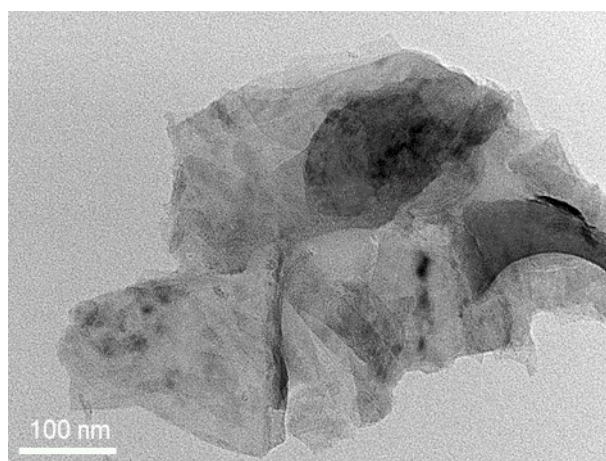
1 Supplementary Figures



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Figure S1. TEM of CuS/Ti₃C₂.



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Figure S2. TEM of CuS.



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Figure S3. TEM of Ti₃C₂.

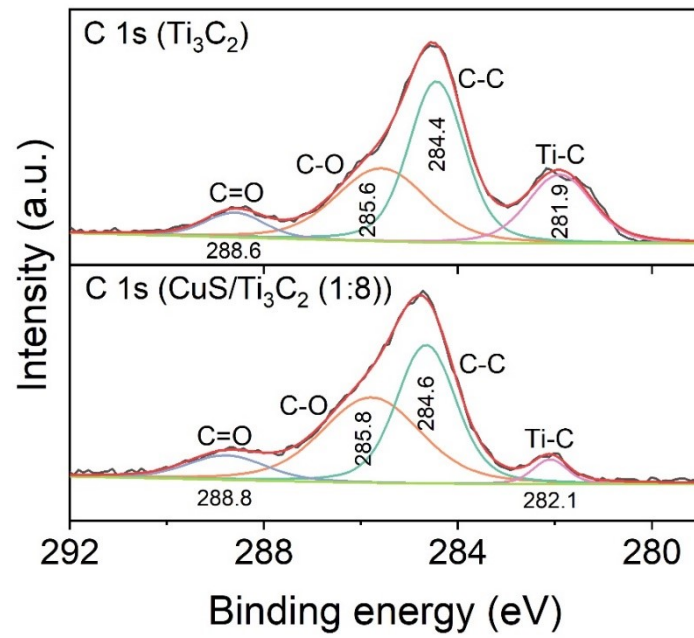


Figure S4. XPS spectra of C 1s for Ti_3C_2 and $\text{CuS}/\text{Ti}_3\text{C}_2$ (1:8).

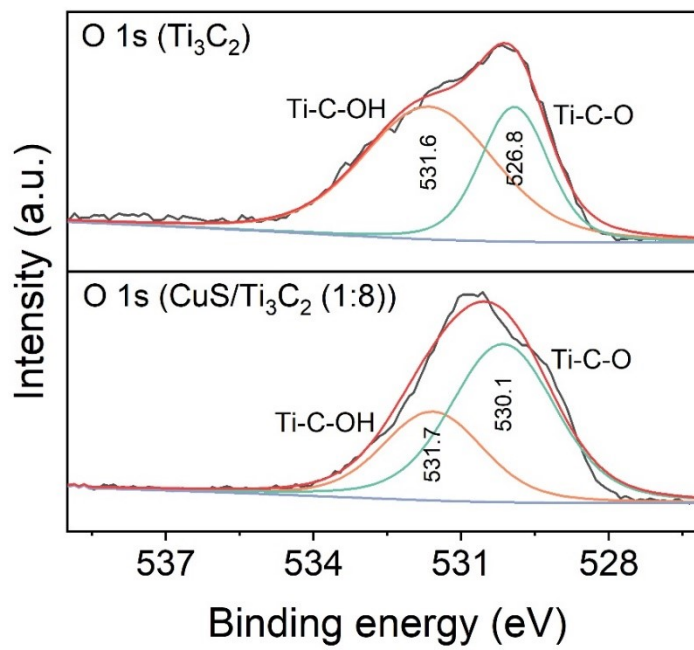


Figure S5. XPS spectra of O 1s for Ti_3C_2 and $\text{CuS}/\text{Ti}_3\text{C}_2$ (1:8).

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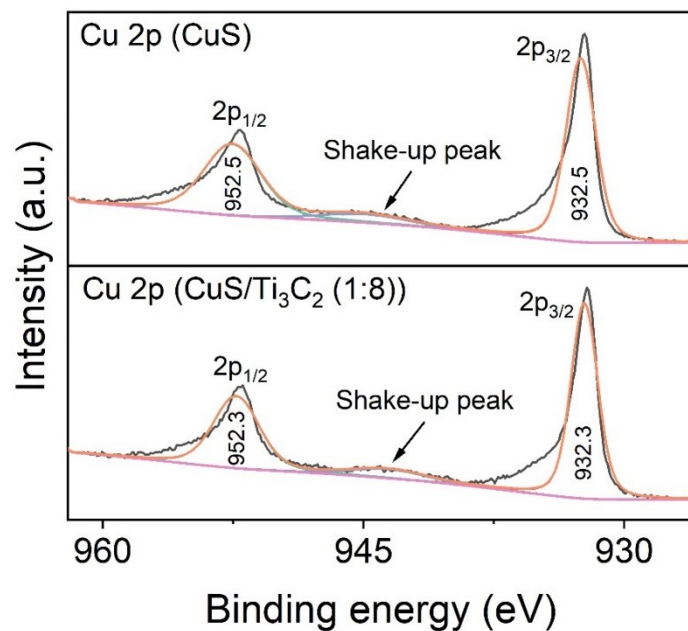


Figure S6. XPS spectra of Cu 2p for CuS and CuS/Ti₃C₂ (1:8).

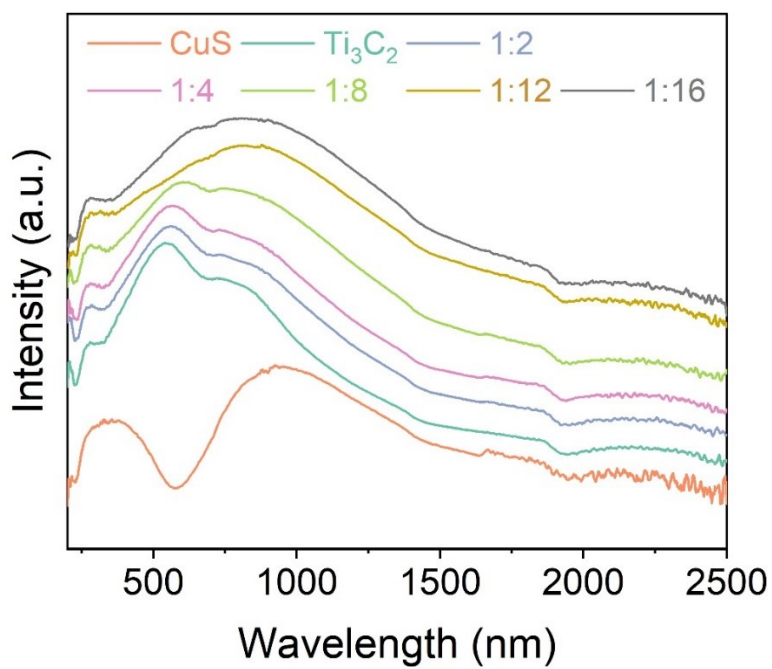
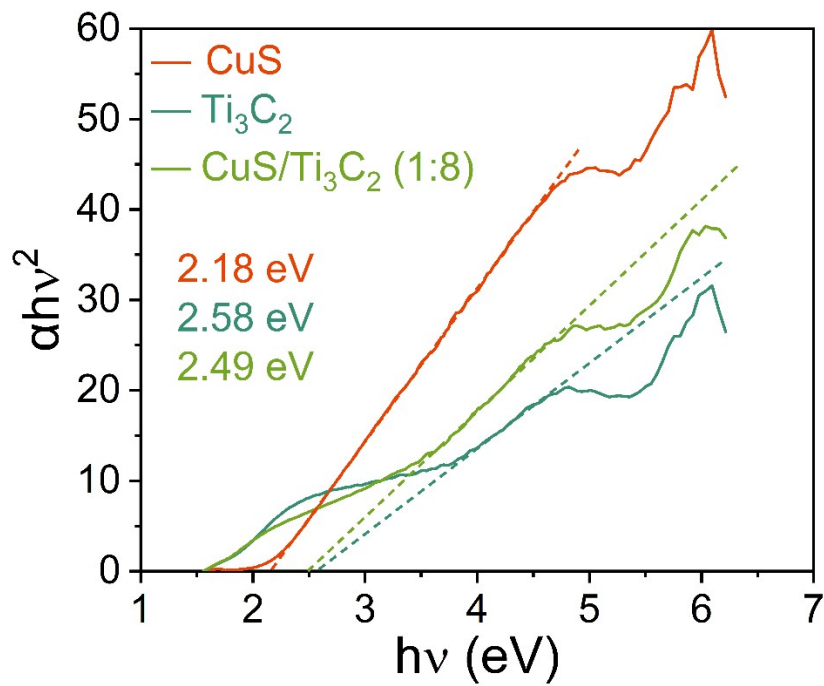


Figure S7. UV-vis DRS spectra of CuS, Ti₃C₂ and different CuS/Ti₃C₂ catalysts.

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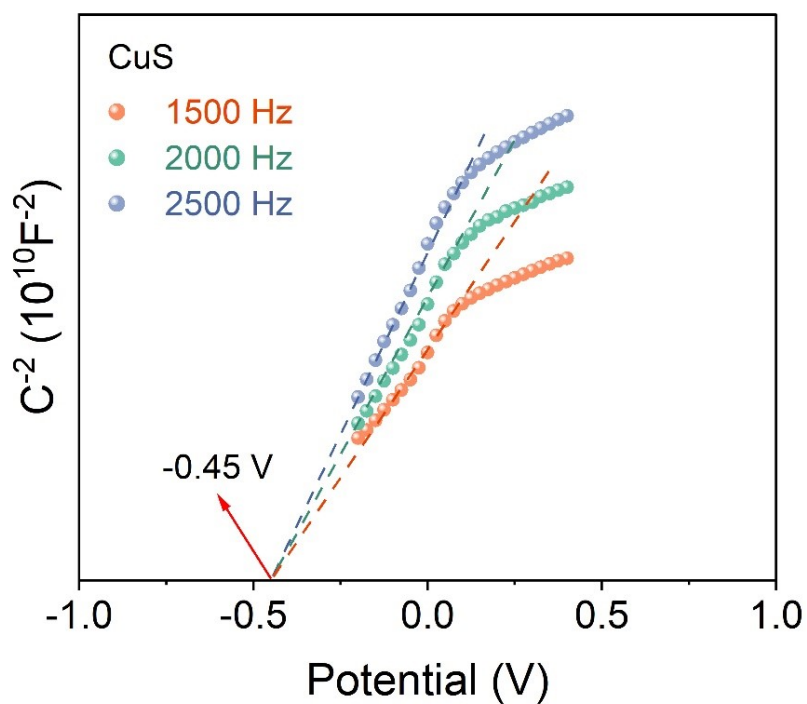
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2 **Figure S8.** (a) UV-vis DRS spectra of CuS, Ti₃C₂ and different CuS/Ti₃C₂ catalysts; (b) (ahv)²-hv curve of CuS, Ti₃C₂ and
 3 CuS/Ti₃C₂ (1:8) catalysts.

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Figure S9. M-S curves of CuS.

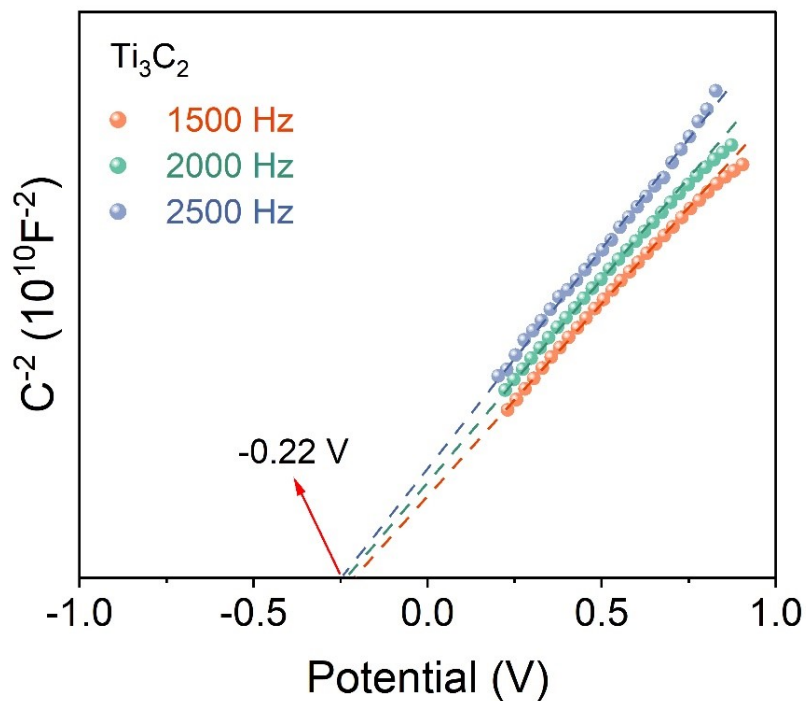


Figure S10. M-S curves of Ti_3C_2 .

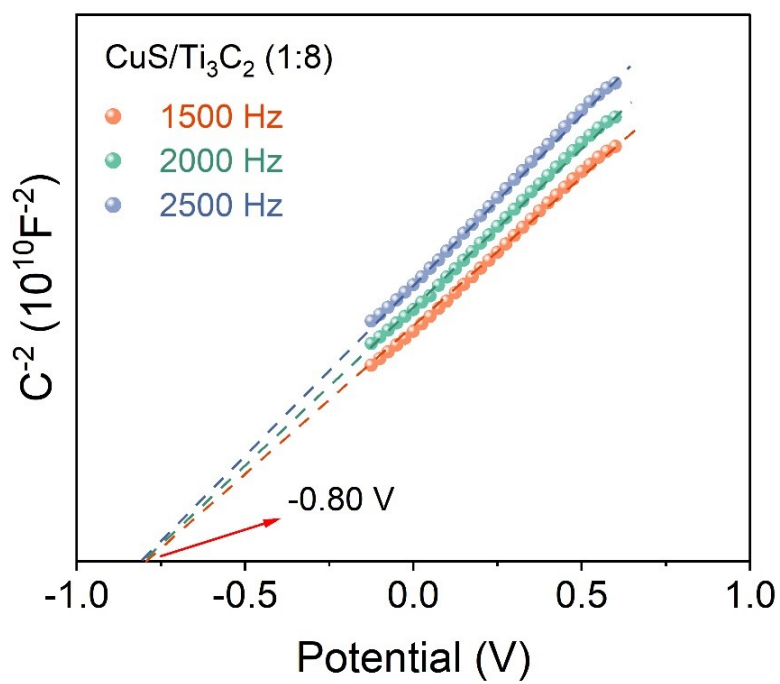
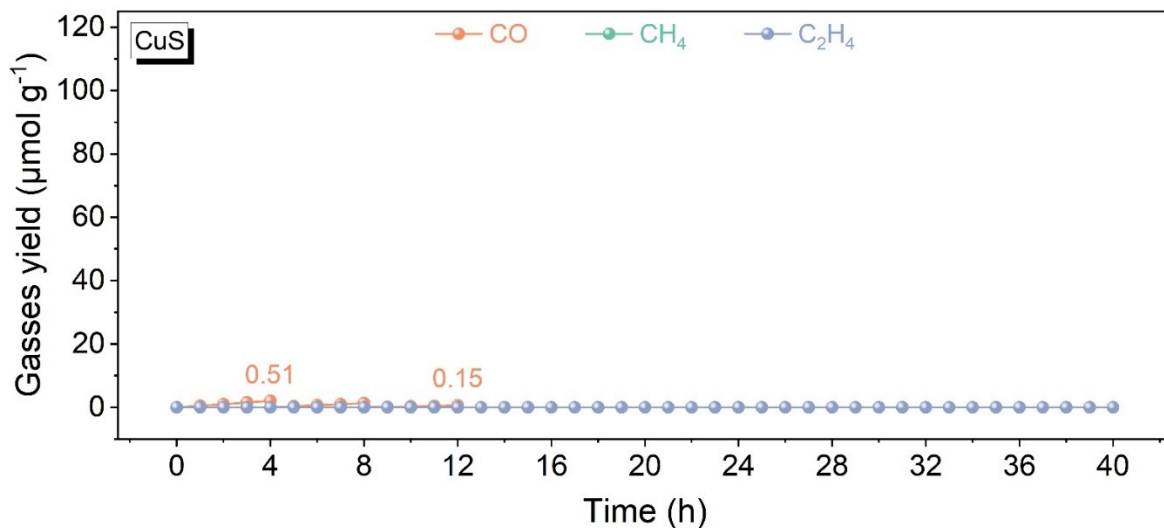


Figure S11. M-S curves of $\text{CuS}/\text{Ti}_3\text{C}_2$ (1:8).



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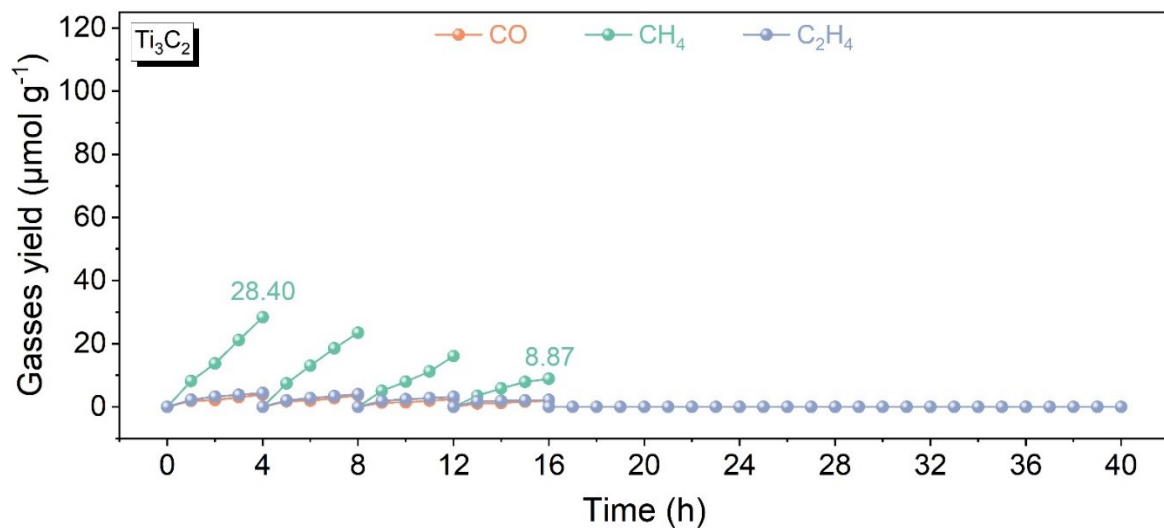
2 **Figure S12.** Long-term recycling gases production performances over CuS NFs under white light (Xe lamp, 500 mW·cm⁻²)

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in 40 h

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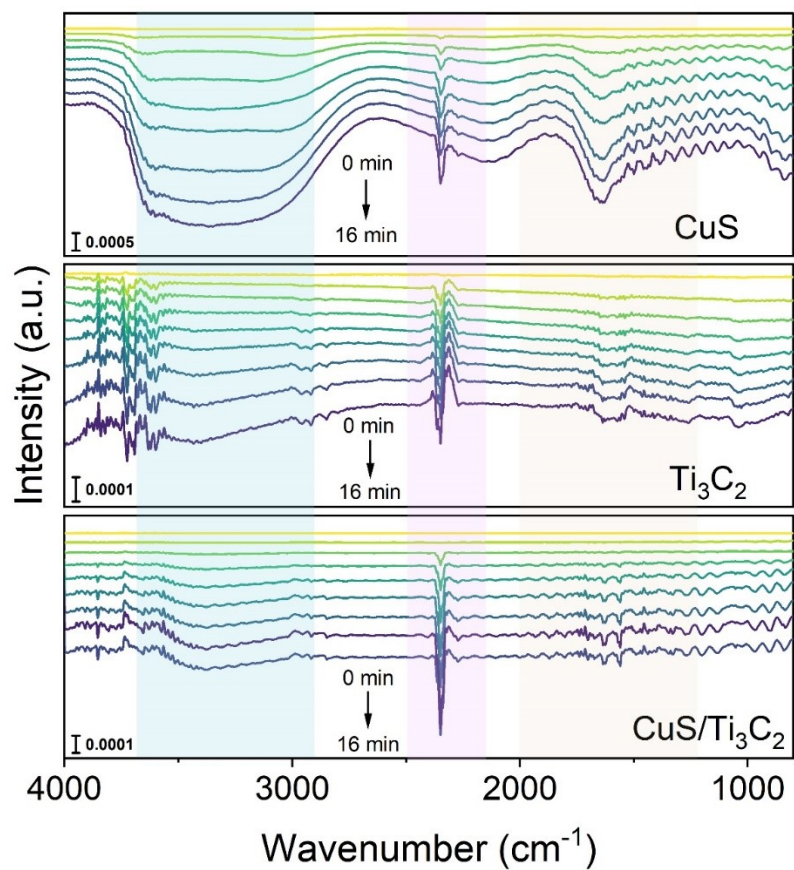
7 **Figure S13.** Long-term recycling gases production performances over Ti₃C₂ sample under white light (Xe lamp, 500

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mW·cm⁻²) in 40 h

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2 **Figure S14.** In-situ-FTIR spectra collected from the interface with co-adsorbed H_2O and CO_2 under white light (Xe
3 lamp, $100 \text{ mW} \cdot \text{cm}^{-2}$) irradiation in 16 min using CuS , Ti_3C_2 and $\text{CuS}/\text{Ti}_3\text{C}_2$ (1:8) catalysts.
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1 **Supplementary Tables**

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Table S1. Wavelength-dependent AQYs on CuS/Ti₃C₂ (1:8) catalyst.

CuS/Ti ₃ C ₂ (1:8)					
波长 (nm)	CH ₄ evolution ($\mu\text{mol g}^{-1}$)	Light intensity (mW cm^{-2})	Irradiation time (h)	Irradiation area (cm^2)	AQY (%)
365	0.120	10	1	4	0.211
420	0.078	20	1	4	0.061
450	0.119	20	1	4	0.087
475	0.153	20	1	4	0.109
500	0.183	20	1	4	0.122
535	0.214	20	1	4	0.131
578	0.200	20	1	4	0.117
600	0.119	20	1	4	0.065
650	0.065	20	1	4	0.033
670	0.040	20	1	4	0.018
730	0.021	20	1	4	0.016
765	0.008	20	1	4	0.014
850	0.001	20	1	4	0.011
940	0.001	20	1	4	0.011

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