Supporting Information

Efficient spatial charge separation and transfer in ultrathin g-C$_3$N$_4$ nanosheets modified with Cu$_2$MoS$_4$ as noble-metal-free co-catalyst for superior visible-light-driven photocatalytic water splitting

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1. Experimental section

Preparation of CuS/g-C$_3$N$_4$ nanosheets and MoS$_2$/g-C$_3$N$_4$ nanosheets

CuS/g-C$_3$N$_4$ nanosheets (CuS/CN) were prepared via a two-step route. Firstly, 0.48 g of Cu(NO$_3$)$_2$·3H$_2$O was dissolved in 30 mL of deionized water to form a blue solution. At the same time, 0.60 g of thioacetamide (TAA) was dissolved in 10 mL deionized water to form a colorless solution. Subsequently, the TAA solution was injected into the above blue solution, and the resultant mixed solution was then maintained at 60 °C for 10 min. The generated precipitate was collected by centrifugation and washed with deionized water and ethanol for several times, and then was dried in an oven at 60 °C overnight, resulting in the pure CuS. Secondly, 13 mg of CuS and 100 mg of g-C$_3$N$_4$ nanosheets were added to 20 mL of ethanol. The resultant suspension was ultrasonicated for 1 h and then stirred for 12 h. Subsequently, the precipitate was collected by centrifugation and washed with deionized water and ethanol for several times. After being dried in an oven at 60 °C overnight, the final CuS/CN product was obtained.

MoS$_2$/g-C$_3$N$_4$ nanosheets (MoS$_2$/CN) were synthesized via a two-step route. Firstly, 0.242 g of Na$_2$MoO$_4$·2H$_2$O and 0.381 g of thiourea were dissolved in 30 mL of deionized water. The resultant solution was transferred to a 50 mL Teflon-lined autoclave and maintained at 220 °C for 24 h. The resulting samples were separated by centrifuging and washed with deionized water and ethanol for several times, and then dried in an oven at 60 °C overnight, resulting in the pure MoS$_2$ sample. Secondly, 13 mg of MoS$_2$ and 100 mg of g-C$_3$N$_4$ nanosheets were added to 20 mL of ethanol and the suspension was ultrasonicated for 1 h and then stirred for 12 h. The precipitate was collected by centrifugation and washed with deionized water and ethanol for several times. After being dried in an oven at 60 °C overnight, the final MoS$_2$/CN product was obtained.

2. The calculation of apparent quantum efficiency

The apparent quantum efficiency (AQE) was analyzed at different wavelength (400, 450, 475, 500 and 550 nm, ± 10 nm) under the 300 W Xenon lamp irradiation. The other experimental conditions are similar to the photocatalytic hydrogen evolution measurement as described before. The light intensity was obtained with an optical power meter (CEL-NP2000, CEAULIGHT, Beijing). For example, if 400 nm is used, the average light intensity is 12.29 mW/cm². The irradiation area was 28.3 cm² (3 cm radius). The number of incident photons (N) is 7.56×10^{21} calculated by equation (1). The amount of H_2 molecules generated for 3 h are ~25.7 μmol. The AQE was then calculated in equation (2).

$$N = \frac{E\lambda}{hc} = \frac{12.29 \times 28.3 \times 10^{-3} \times 3 \times 3600 \times 400 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 7.56 \times 10^{21} \quad (1)$$

$$AQE = \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\%$$

$$= \frac{2 \times the\ number\ of\ evolved\ H_2\ molecules}{N} \times 100\% \quad (2)$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 25.7 \times 10^{-6}}{7.56 \times 10^{21}} \times 100\% = 0.41\%$$

3. The calculation of solar-to-hydrogen energy conversion efficiency

The solar-to-hydrogen energy conversion efficiencies (STH) under visible-light and full-spectrum-light illumination were evaluated respectively by using a 300 W Xenon arc lamp (PLS-SXE300) with or without a 420 nm cutoff filter as light source (25.8 and 70.0 mW/cm^2, respectively) and CNMS-2 sample as the catalyst (10 mg catalyst in 20 mL deionized water). The light intensity was obtained with an optical power meter (CEL-NP2000, CEAULIGHT, Beijing). After 4 h of visible-light illumination, the total incident power over the 28.3 cm^2 irradiation area (3 cm radius) was:

$$P_{Solar} = 25.8 \times 28.3 \times 10^{-3} = 0.73 \text{ W}$$

The total input energy in 4 hours was:

$$E_{Solar} = 0.73 \times 4 \times 3600 = 1.051 \times 10^4 \text{ J}$$

During the photocatalytic reaction under visible-light illumination, 89.97 μmol H$_2$ was detected by gas chromatography (GC), which indicated that the energy generated by water splitting was:

$$E_{Hydrogen} = 89.97 \times 10^{-6} \times 6.02 \times 10^{23} \times 2.46 \times 1.609 \times 10^{-19} = 21.4 \text{ J}; 2.46 \text{ eV is the free energy}$$

of water splitting.

The STH under visible-light illumination was determined to be:

$$STH = E_{Hydrogen}/E_{Solar} = 21.4/(1.051 \times 10^4) = 0.20\%$$

After 4 h of full-spectrum-light illumination, the total incident power over the 28.3 cm^2 irradiation area (3 cm radius) was:

$$P_{Solar} = 70.0 \times 28.3 \times 10^{-3} = 1.98 \text{ W}$$

The total input energy in 4 hours was:

$$E_{Solar} = 1.98 \times 4 \times 3600 = 2.85 \times 10^4 \text{ J}$$

During the photocatalytic reaction under full-spectrum-light illumination, 370.05 μmol H$_2$ was

detected by gas chromatography (GC), which indicated that the energy generated by water splitting was:

$E_{Hydrogen} = 370.05\times10^{-6}\times6.02\times10^{23}\times2.46\times1.609\times10^{-19} = 88.2$ J; 2.46 eV is the free energy of water splitting.

The STH under visible light was determined to be:

$STH = E_{Hydrogen}/E_{Solar} = 88.2/(2.85\times10^4) = 0.31\%$

4. Tables

Table S1 Structural parameters of the samples.

Samples	S_{BET} ($m^2 \cdot g^{-1}$)	Pore size (nm)	V_{pore} ($cm^3 \cdot g^{-1}$)
BCN	6.2	3.94	0.12
CN	273.6	3.71	3.05
Cu_2MoS_4/CN-2	228.2	2.22	2.38

Table S2 Photocatalytic H_2 evolution rates over some noble-metal-free co-catalysts modified g-C_3N_4 photocatalysts in reported work in contrast with this work.

Photocatalysts	Reactant solution and catalysts	Light source	Photocatalytic H_2 evolution rates ($\mu mol \cdot h^{-1}$)	Ref
NiS/g-C_3N_4	100 mg of catalyst in 100 mL of aqueous solution (15 vol% TEOA)	300 W Xe lamp, $\lambda > 420$ nm	48.2	74
CoP/ g-C_3N_4	100 mg of catalyst in 100 mL of aqueous solution (10 vol% TEOA)	300 W Xe lamp, $\lambda > 420$ nm	47.4	75
MoS$_2$/g-C_3N_4	20 mg of catalyst in 100 mL of aqueous solution (10 vol% lactic acid)	300 W Xe lamp, $\lambda > 420$ nm	26.8	76
Cu$_2$MoS$_4$/g-C_3N_4	10 mg of catalyst in 20 mL of aqueous solution (10 vol% TEOA)	300 W Xe lamp, $\lambda > 420$ nm	21.7	This work
NiCoP/g-C_3N_4	10 mg of catalyst in 100 mL of aqueous solution (10 vol% TEOA)	300 W Xe lamp	16.4	77
Ni$_3$C/g-C_3N_4	50 mg of catalyst in 80 mL of aqueous solution (15 vol% TEOA)	350 W Xe lamp, $\lambda > 420$ nm	15.2	78
Ag$_2$S/g-C_3N_4	50 mg of catalyst in 80 mL of aqueous solution (25 vol% methanol)	Four 3 W LEDs, $\lambda > 420$ nm	10.0	79
Ni(OH)$_2$/g-C_3N_4	50 mg of catalyst in 80 mL of aqueous solution (10 vol% TEOA)	350 W Xe lamp, $\lambda > 400$ nm	7.6	80
WC/g-C_3N_4	50 mg of catalyst in 100 mL of aqueous solution (15 vol% TEOA)	300 W Xe lamp, $\lambda > 420$ nm	7.3	81
WS$_2$/g-C_3N_4	50 mg of catalyst in 80 mL of aqueous solution (25 vol% methanol)	300 W Xe lamp, $\lambda > 420$ nm	5.1	71
Ni$_x$P$_y$/g-C_3N_4	2 mg of catalyst in 5 mL of aqueous solution (20 vol% TEOA)	Xe lamp, $\lambda > 420$ nm	0.3	82

5. Scheme and Figures
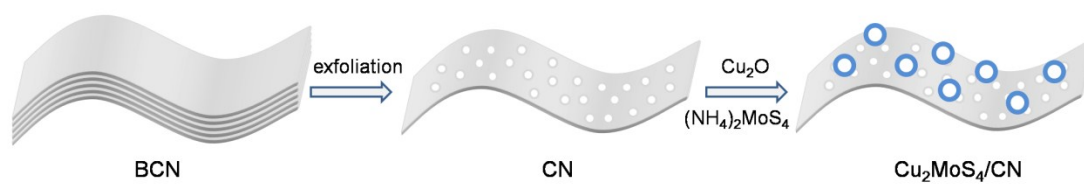
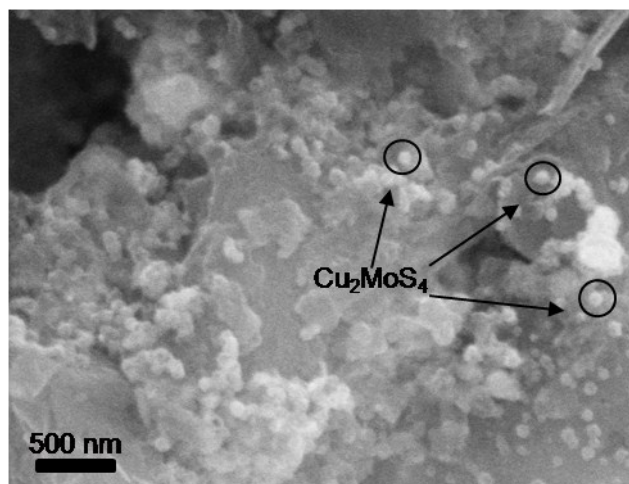**Scheme S1.** Schematic illustration of the formation of Cu_2MoS_4/CN composites

Fig. S1. SEM image of Cu_2MoS_4/BCN

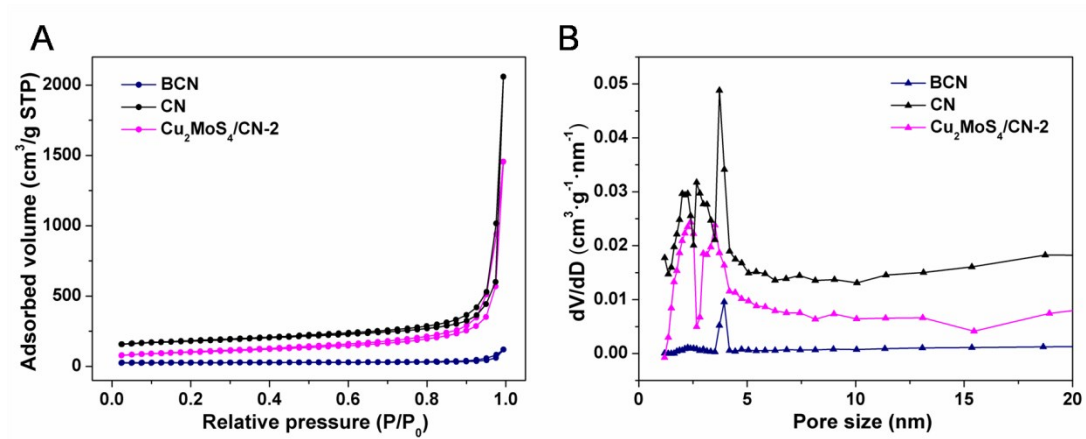**Fig. S2.** N_2 adsorption–desorption isotherms (A) and pore size distribution curves (B) of BCN,

CN, and Cu_2MoS_4/CN-2 samples.

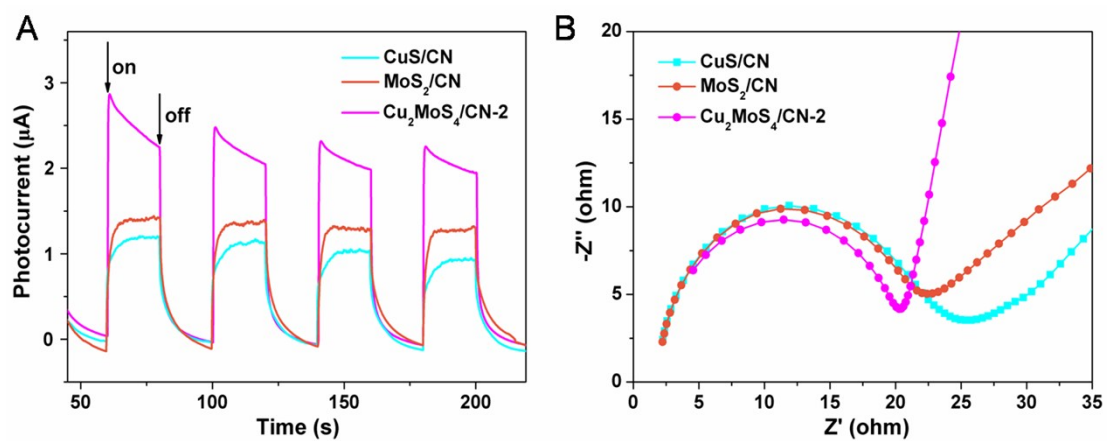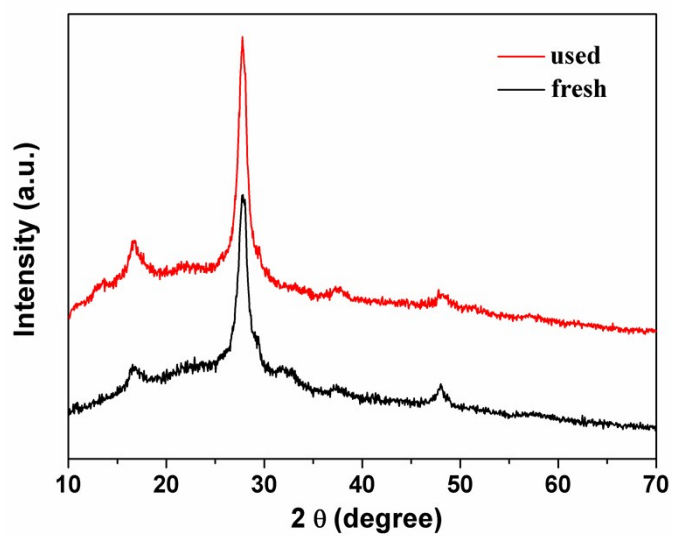**Fig. S3.** Photocurrent response (A) and EIS (B) of Cu_2MoS_4/CN-2, CuS/CN and MoS_2/CN samples.

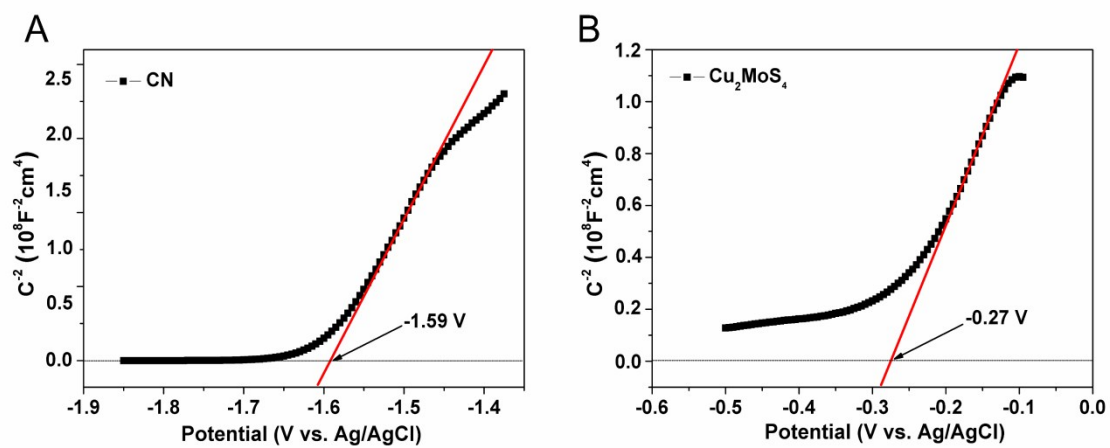**Fig. S4.** XRD patterns of fresh and used Cu_2MoS_4/CN-2 samples.

Fig. S5. Mott-Schottky plots of (A) CN with E_{fb} of about -1.59 V and (B) Cu_2MoS_4 with E_{fb} of about -0.27 V vs Ag/AgCl. These values can be converted into -1.39 V for CN and -0.07 V for Cu_2MoS_4, respectively.
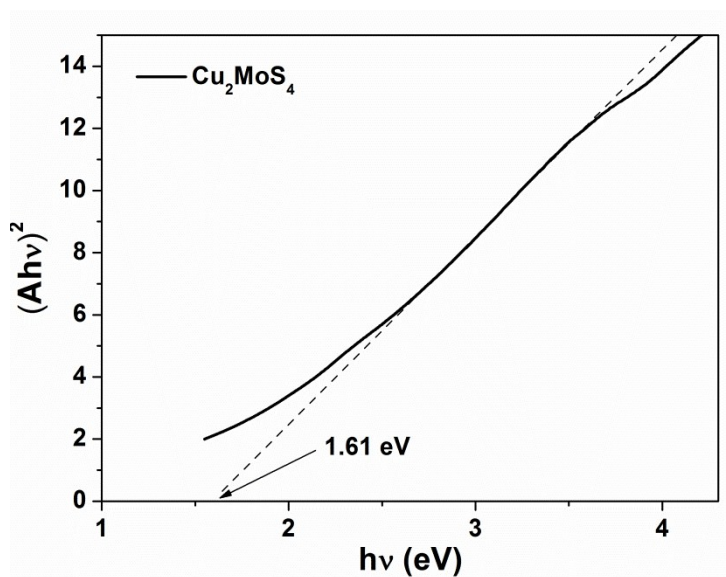

Fig. S6. Tauc plots of $(Ah\nu)^2$ versus $h\nu$ of Cu_2MoS_4.