

Supporting Information

Synthesis of valence-mixed Cu phthalocyanine/Graphene/g-C₃N₄ ultrathin heterojunctions as efficient photocatalysts for CO₂ reduction

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Experimental Section

1. Synthesis of Ultrathin g-C₃N₄ (UCN):

g-C₃N₄ was synthesized by heating urea in a semi-covered ceramic crucible at 550 °C for 3 h with a rate of 0.5 °C min⁻¹. After that, the ceramic crucible was allowed to room temperature naturally. The obtained light-yellow product was grinded into fine powder for further experimental work.

The ultrathin g-C₃N₄ nanosheets were prepared as follows: 1 g of the g-C₃N₄ was heated at 550 °C for 4 h with a ramp rate of 5 °C min⁻¹ in an open ceramic container and. 2 g obtained powder was then placed into a three-necked bottle prefilled with 100 mL 5 M HNO₃ solution and refluxed at 120 °C for 2 h. After naturally cooling to room temperature, the refluxed product was centrifuged, washed at least five times with deionized water until the pH of the mixture reached to about 7, and then washed there times with ethanol. The obtained pale-yellow powder was determined to be UCN.

2. Synthesis of xCuPc/UCN nanocomposites:

Firstly, 0.5 g UCN nanosheets were dispersed in 100 mL of DMF under ultrasonication for 30 min. Secondly, a calculated volume of CuPc DMF solution was added into the UCN suspension followed by sonication and stirring for 30 min to obtain a well-mixed suspension.

The suspension was further stirred at room temperature for 24 h. Then the solid suspension was filtered and washed with ethanol. The as-obtained solid was dried overnight at 80 °C and then calcined at 200 °C for 1 h in a muffle furnace with a heating rate of 5 °C min⁻¹. These samples were represented by xCuPc/CN, where x indicates the mass ratio (0.25, 0.5 and 0.75%) of CuPc to UCN.

3. Synthesis of yG/UCN nanocomposites:

There are two primary steps in this procedure. The first step is to prepare G functionalized UCN nanosheets. G was prepared by an *in situ* self-generating template route as described before^{27,28}. It was treated by an acid-treatment process to induce more hydroxyl groups. Acid-treated graphene (G) was prepared as follows: 0.5 g of graphene, HNO₃ (65%, 10 mL) and H₂SO₄ (98%, 30 mL) were added into a flask under vigorous stirring. The flask was immersed in an ultrasonic bath for 30 min, and then stirred for 30 min under refluxing conditions at 80 °C. This process was repeated six times. After cooling down to room temperature naturally, the reaction mixture was centrifuged and washed with deionized water until the pH of the mixture reached to about 7. Then, the solid was dried under a vacuum at 60 °C for 24 h. Afterwards, a certain amount of G was dispersed in 100 mL of deionized water under ultrasonication for 1h. Then, UCN nanosheets (0.5 g) were dispersed in 100 mL of deionized water under ultrasonication for 30 min. Following that, a calculated volume of G solution with water as the solvent was added into the UCN suspension, followed by sonication and stirring for 30 min to obtain a well-mixed suspension. The suspension was further stirred at room temperature for 24 h. The as-obtained solid was filtered and dried overnight at 80 °C. These samples were represented by yG/UCN, where y indicates the mass ratio (0.5, 0.75, 1 and 1.25%) of G to UCN.

4. Hydroxyl radical measurement

0.02 g of the photocatalyst was placed in 50 mL of coumarin solution. The mixture was stirred for 30 min before the experiment to ensure that it reached the adsorption-desorption equilibrium. After 1 h irradiating, an appropriate amount of the suspension was centrifuged and the supernatant was transferred into a Pyrex glass cell for the fluorescence measurement of 7-hydroxycoumarin by a spectrofluorometer (Perkin-Elmer LS55). To cut off UV-light, a light filter of 420 nm was placed between the light source and the reactor.

5. CO₂ (CO) Temperature-programmed desorption measurements

Temperature-programmed desorption (TPD) of CO₂ was measured by a chemisorption analyzer equipped with a TCD detector. The typical method is as follows: 50 mg of sample powders were treated at 400 °C for 1 h with the rate of 30 mL min⁻¹ ultra-high-pure He gas flow. Then, highly pure CO₂ was introduced at a constant temperature of 30 °C under a flow rate of 30 mL min⁻¹ for 1 h. Subsequently, He gas was passed through the system at 30 °C for 1 h to remove the physically adsorbed CO₂. Finally, the temperature was increased to 400 °C with a heating rate of 10 °C min⁻¹ under the flow of He. The desorbed CO₂ was monitored by Chemisorption Analyzer (Tp 5080 Chemisorb). The CO-TPD test method was the same as the CO₂-TPD method, except CO replaced CO₂.

6. EPR measurements

The •O₂⁻ radicals can be trapped by 5,5-dimethyl-1-pyrroline N-oxide (DMPO), producing the EPR signals of their adducts. The sample (5 mg) was dissolved in DMPO solution with CH₃OH as the solvent to obtain the liquid mixture. After illumination for a certain time, the mixture was characterized using a Bruker EMX plus model spectrometer operating at room temperature.

7. Photoelectrochemical and electrochemical measurements

The film electrode was fabricated as follows: 10 mg of samples, 0.1 mL of Nafion and 0.9 mL of ethanol were mixed thoroughly into the slurry. Then the slurry was coated on the FTO glass electrode (1.0 cm × 1.0 cm). Finally, the coated electrode was dried at 60 °C for 30 min. Photoelectrochemical (PEC) and electrochemical (EC)

measurements were conducted on the IVIUM V13806 electrochemical workstation with a three-electrode system. The as-prepared film electrodes were used as working electrodes. The Pt plate (99.9%) and Ag/AgCl were used as the counter electrode and reference electrode, respectively. 0.2 M Na₂SO₄ solution was used as the electrolyte for all PEC and EC measurements. I-V curves were performed under the irradiation of a 300 W Xenon lamp with a cut-off filter ($\lambda > 420$ nm). EC experiments were performed in the high purity N₂ or CO₂ bubbled system.

8. In-situ diffuse reflectance infrared Fourier transform (DRIFTS)

In-situ DRIFTS measurements were performed using a Nicolet iS50 Fourier transform spectrometer equipped with a MCT diffuse reflectance accessory. Each spectrum was recorded by averaging 16 scans at a resolution of 4 cm⁻¹. The samples were compressed and held in a custom-fabricated IR reaction chamber which was sealed with ZnSe windows. Before measurement, the photocatalyst was purged with nitrogen at 120°C for 3 h to remove the impurity gas adsorbed on the surface. The samples were subsequently cooled down to room temperature and the background spectrum was collected. After that, the mixture of CO₂ and water vapor was introduced into the reaction chamber until the absorption reached equilibrium. Then, the samples were swept by the N₂ to remove the unabsorbed gas. Subsequently, the FT-IR spectra were collected at different irradiation intervals.

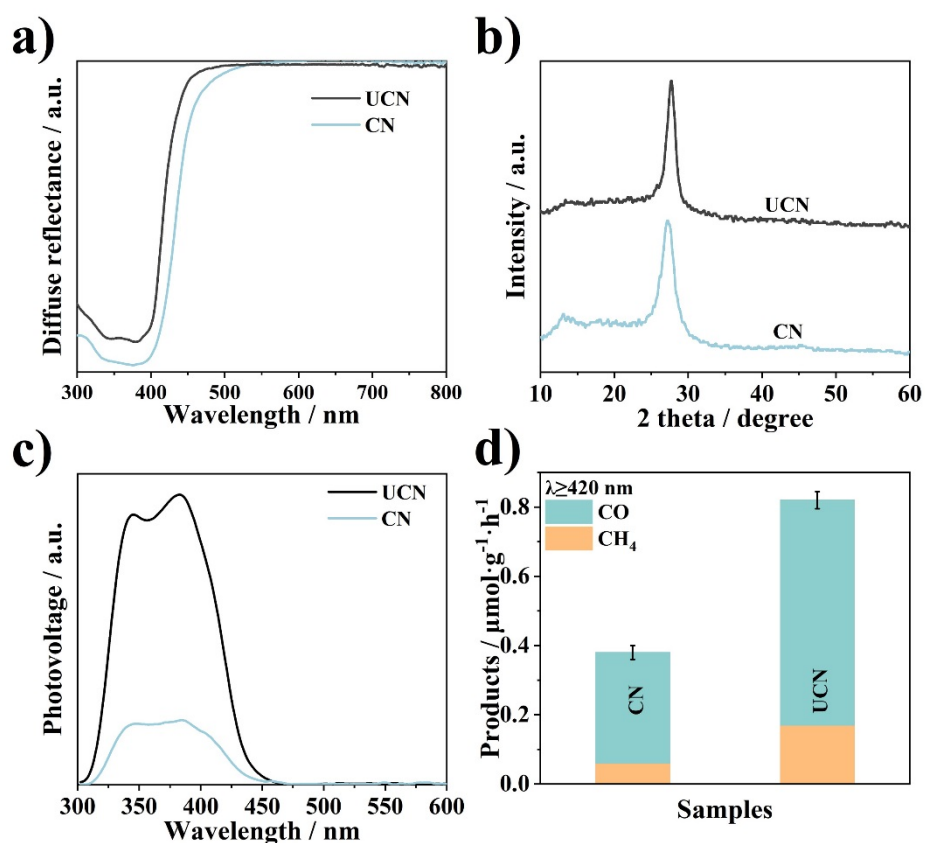


Fig. S1. a) UV-vis DRS, b) XRD patterns, c) SS-SPS and d) photocatalytic activities for CO₂ conversion under visible-light irradiation of CN and UCN.

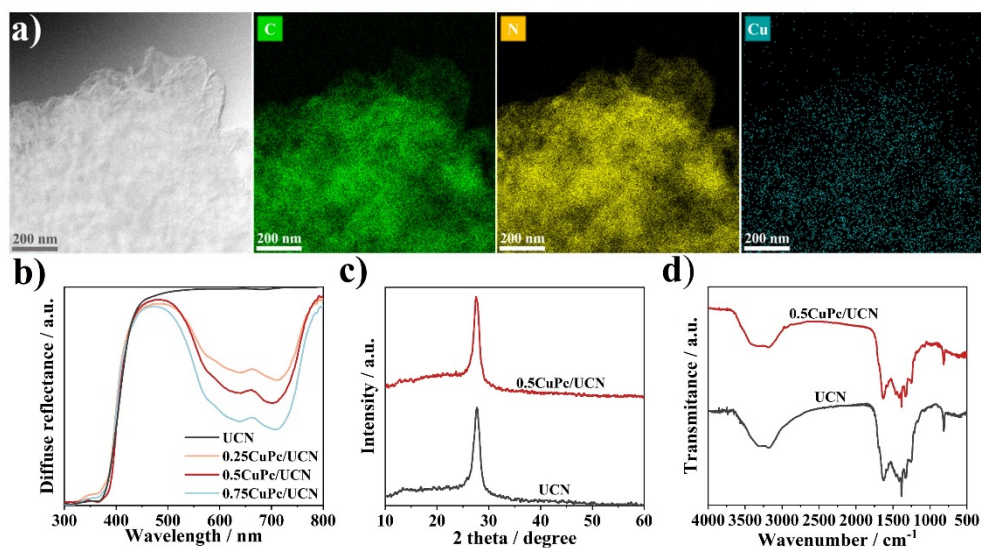


Fig. S2. a) HAADF-STEM image of 0.5CuPc/UCN with the corresponding EDS elemental mapping images of C, N and Cu. b) UV-vis DRS of UCN and xCuPc/UCN. c) XRD patterns d) FT-IR spectra of UCN and 0.5CuPc/UCN.

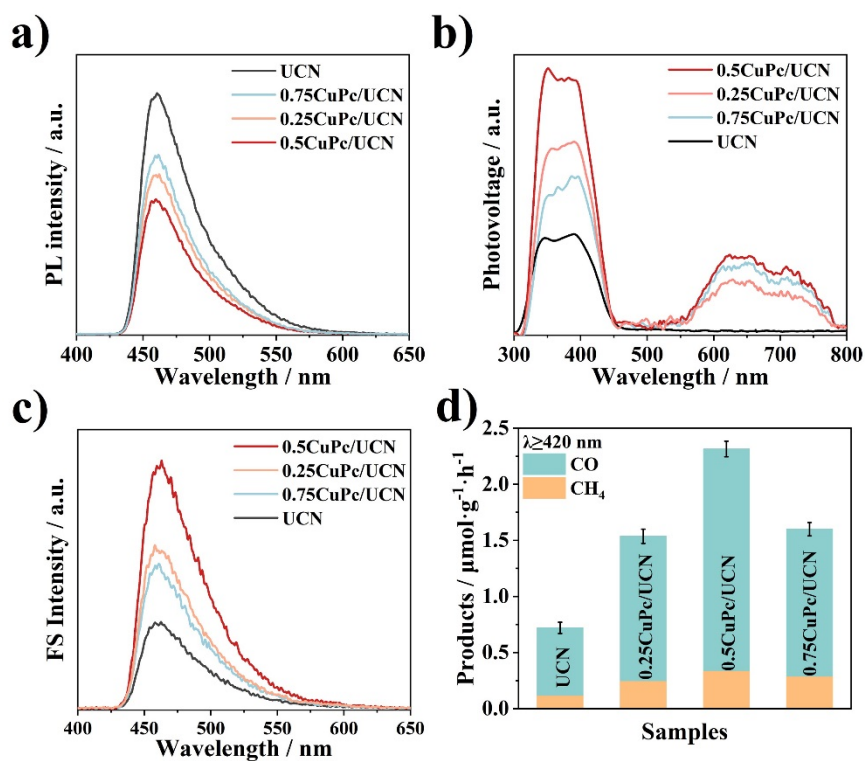


Fig. S3. a) PL spectra, b) SS-SPS, c) FS related to the formed hydroxyl radicals under visible-light irradiation and d) photocatalytic activities for CO₂ conversion under visible-light irradiation of UCN and xCuPc/UCN.

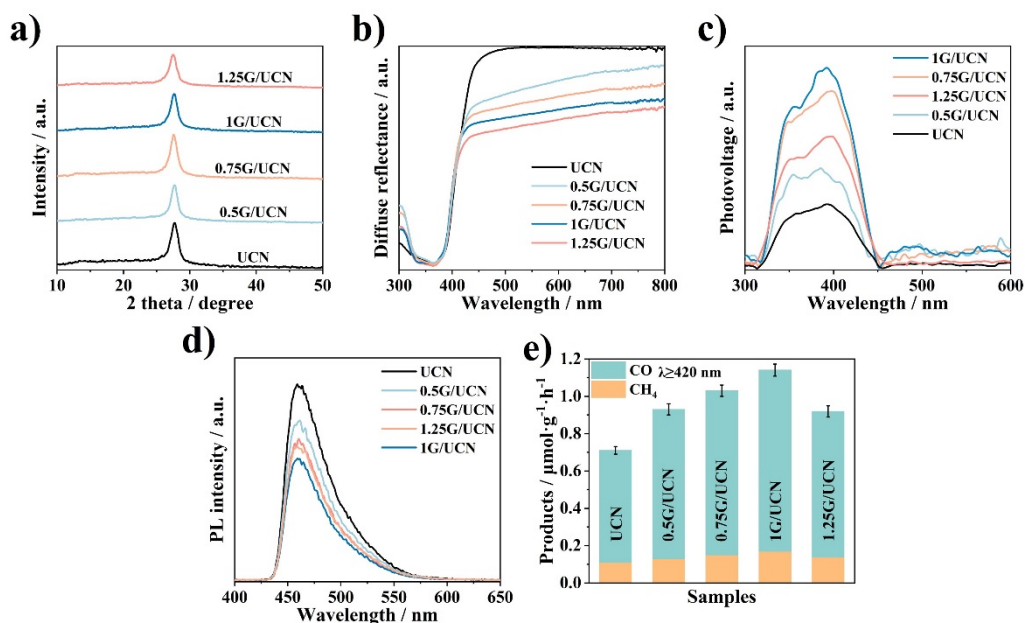


Fig. S4. a) XRD patterns, b) UV-vis DRS, c) SS-SPS, d) PL spectra and e) photocatalytic activities for CO₂ conversion under visible-light irradiation of UCN and yG/UCN.

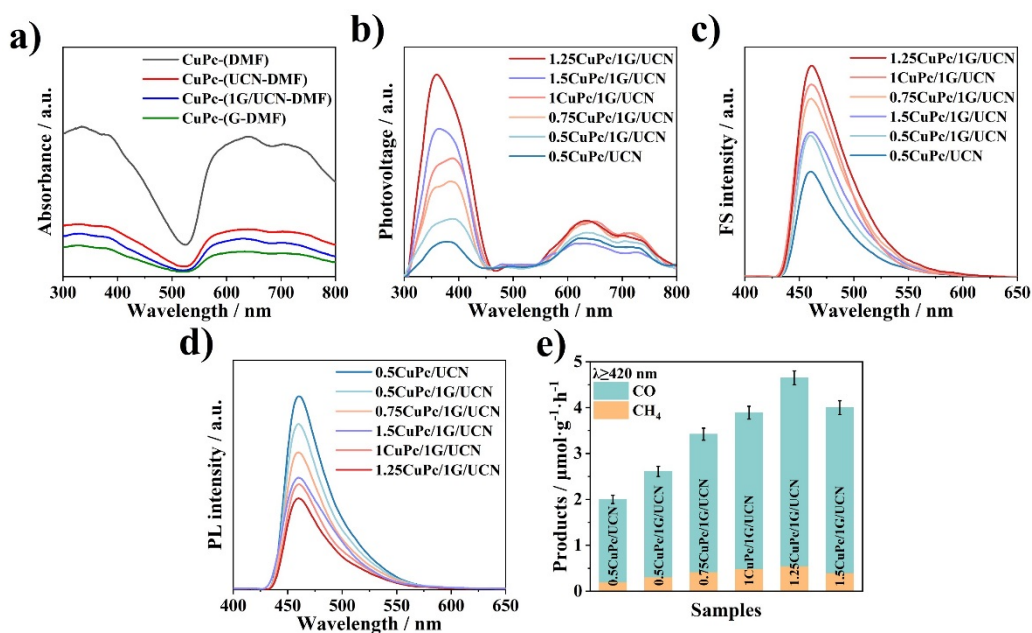


Fig. S5. a) UV-vis absorption spectra of CuPc scattered in the DMF, UCN-DMF, G-DMF and 1G/UCN-DMF. b) SPS, c) FS related to the formed hydroxyl radicals under visible-light irradiation, d) PL spectra and e) photocatalytic activities for CO₂ conversion under visible-light irradiation of 0.5CuPc/UCN and zCuPc/1G/UCN.

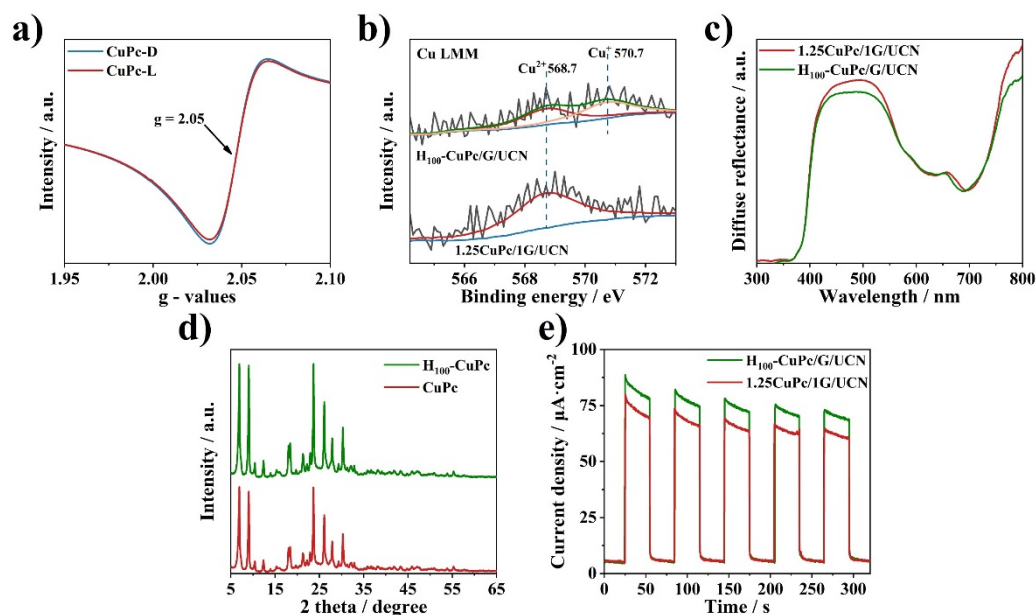


Fig. S6. a) EPR spectra of CuPc under visible-light irradiation and in dark under 98 K. b) Cu LMM XPS and c) UV-vis DRS of 1.25CuPc/1G/UCN and H₁₀₀-CuPc/G/UCN. d) XRD patterns of CuPc and H₁₀₀-CuPc. e) Electrochemical stability of 1.25CuPc/1G/UCN and H₁₀₀-CuPc/G/UCN.

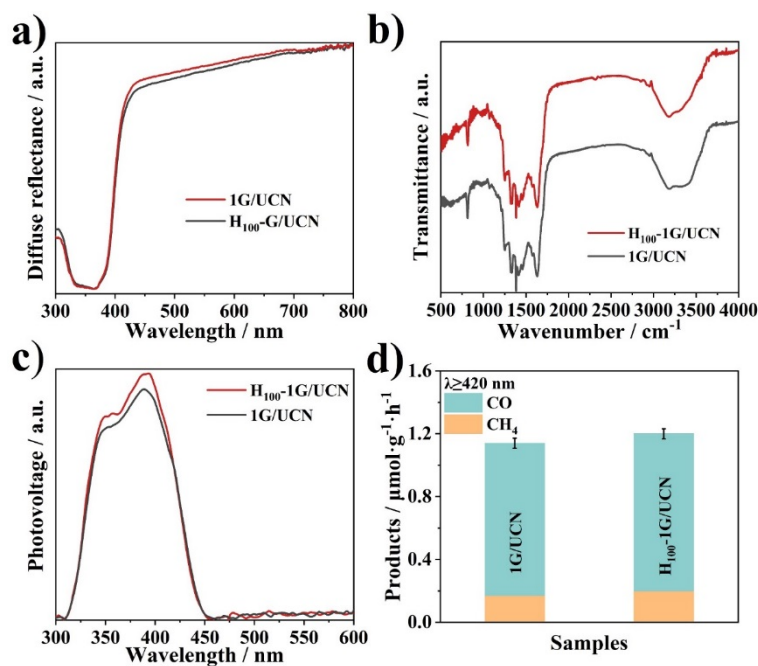


Fig. S7. a) DRS, b) FT-IR spectra c) SPS and d) photocatalytic activities for CO_2 conversion under visible-light irradiation of 1G/UCN and H_{100} -1G/UCN.

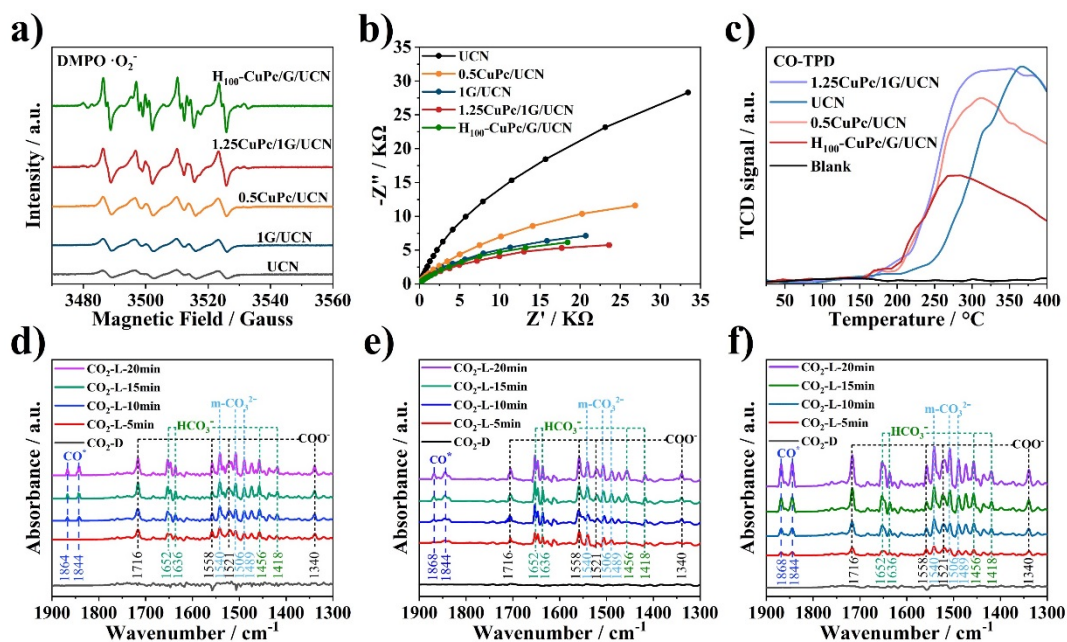


Fig. S8. a) EPR spectra of $\text{DMPO}\cdot\text{O}_2^-$ adducts, b) electrochemical impedance spectra (EIS) under visible-light irradiation and c) CO-TPD curves of UCN, 0.5CuPc/CN, 1.25CuPc/1G/UCN and H_{100} -CuPc/G/UCN, respectively. *In-situ* DRIFT spectra of d) 0.5CuPc/UCN, e) 1.25CuPc/1G/UCN and f) H_{100} -CuPc/G/UCN.

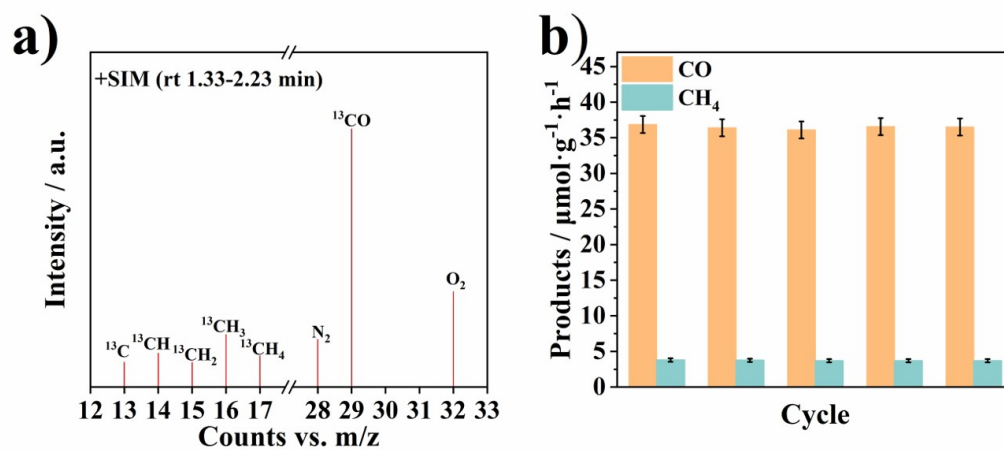


Fig. S9. a) m/z values for tested productions after photocatalytic reduction of isotopic $^{13}\text{CO}_2$ under visible-light irradiation for 4 h. b) Photocatalytic cycling test of $\text{H}_{100}\text{-CuPc/G/UCN}$.

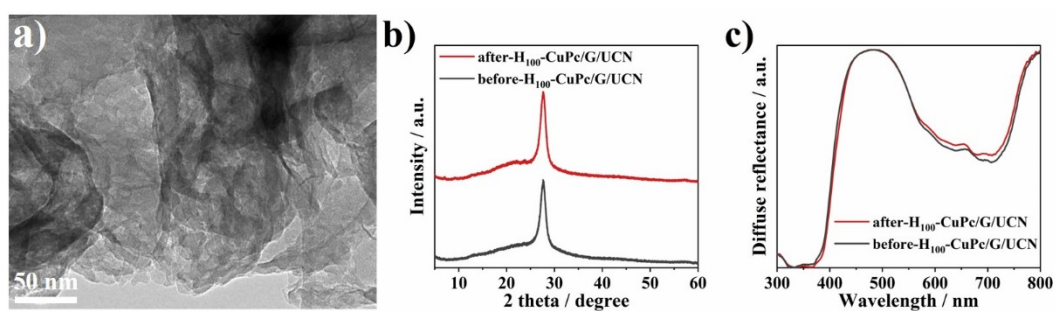


Fig. S10. TEM image (a) of $\text{H}_{100}\text{-CuPc/G/UCN}$ after 5 cycles. XRD patterns (b) and UV-vis DRS (c) of $\text{H}_{100}\text{-CuPc/G/UCN}$ before and after 5 cycles.

Table S1. Comparison between this work and the previous work of g-C₃N₄ based heterojunction for photocatalytic CO₂ conversion under similar conditions.

Photocatalyst	Products ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Light source	Solvent	References
g-C ₃ N ₄ /BiWO ₆	CO 5.19	300W Xe lamp ($\lambda > 420$)	H ₂ O	Ref. 1
CuPc/g-C ₃ N ₄	CO 1.5 CH ₄ 0.25	300W Xe lamp ($\lambda > 420$)	H ₂ O	Ref. 2
LaPO ₄ /g-C ₃ N ₄	CO 14.4	300W Xe lamp	H ₂ O	Ref. 3
g-C ₃ N ₄ foam/Cu ₂ O QDs	CO 8.128	300W Xe lamp ($350 < \lambda < 780$)	H ₂ O	Ref. 4
Ti ₃ C ₂ (OH) ₂ /g-C ₃ N ₄	CO 11.21 CH ₄ 0.203	300W Xe lamp ($\lambda > 420$)	H ₂ O	Ref. 5
Cu-NPs/g-C ₃ N ₄	CO 10.247	300W Xe lamp ($350 < \lambda < 780$)	H ₂ O	Ref. 6
g-C ₃ N ₄ /Bi ₂ O ₃ [BO ₂ (OH)]	CO 6.09	300W Xe lamp	H ₂ O	Ref. 7
H-CuPc/Graphene/g-C ₃ N ₄	CO 9.17 CH ₄ 0.91	300W Xe lamp ($\lambda > 420$)	H ₂ O	This work

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