Supporting Information for

Nanoengineering Construction of Cu₂O Nanowire Arrays Encapsulated with g-C₃N₄ as 3D Spatial Reticulation All-Solid-State Direct Z-scheme Photocatalysts for Photocatalytic Reduction of Carbon Dioxide

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1. Experimental section

1.1 Materials

Copper gauze (100 mesh, 0.11 mm (0.0045 in) of the wire diameter), Cyanuric acid ($C_3H_3N_3O_3$, >99%) and Nafion (5%) were obtained from Alfa Aesar. Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Nitric acid (HNO₃), Ethanol (C_2H_5OH), Acetone (CH₃COCH₃), Barium sulfate (BaSO₄), Ferric sulfate (Fe₂(SO₄)₃), Potassium oxalate (K₂C₂O₄), 1,10-Phenanthrolin (C₁₂H₉N₃), Sodium acetate monohydrate (CH₃COONa·H₂O), Sulfuric acid (H₂SO₄) and Sodium sulfate (Na₂SO₄) were gained from Beijing Chemical Reagent Co., Ltd. 2,4-Diamino-6-phenyl-1,3,5-triazine (C₉H₉N₅, >98%) were purchased from Shanghai Macklin Biochemical Co., Ltd. D₂O were purchased from Shanghai Energy Chemical Co., Ltd. All chemicals were used directly as received without further purification. All aqueous solutions were manufactured using deionized water (DIW, 18.25 MΩ cm). All glassware and porcelain were soaked and washed with aqua regia (3 : 1 HCl : HNO₃) and then rinsed several times with DIW.

1.2 Experimental procedure

1.2.1 Preparation of 3D Cu(OH)₂ nanowire arrays/Cu mesh (Cu(OH)₂ NAs/CM)

Prior to the synthesis, Copper gauze was continuously sonicated in soap water, Acetone, Ethanol and DIW for 25 min, respectively. Then, the clean Copper gauze was anodized in 3 M NaOH by chronopotentiometry (10 mA cm⁻²) for 700 s to prepare Cu(OH)₂ NAs/CM¹.



Figure S1. (a) Digital photograph and (b) SEM image of the Cu mesh.



Figure S2. Galvanostatic (10 mA cm⁻²) anodization curve forming Cu(OH)₂

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NAs/CM.
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1.2.2 Preparation of 3D Cu₂O nanowire arrays/Cu mesh (Cu₂O NAs/CM)

The Cu(OH)₂ NAs/CM was annealed at 520 °C in an Ar atmosphere for 3 h, which leads to form 3D Cu₂O NAs/CM.

1.2.3 Preparation of 3D g-C₃N₄/Cu₂O nanowire arrays/Cu mesh (g-C₃N₄/Cu₂O NAs/CM)

First, 2,4-Diamino-6-phenyl-1,3,5-triazine (9.0 g) and Cyanuric acid (6.5 g) were dissolved in DIW (200 mL) and magnetically stirred for 24 h at ambient temperature. Secondly, the mixed suspension was subjected to suction filtration to achieve

solid-liquid separation and the white solid was placed in a oven at 60 °C for 8 h. Then, the dried white solid was placed in a mortar and ground to white powder. Finally, a piece of prepared Cu₂O NAs/CM was placed at the bottom of a 30 mL crucible, and the white powder (1.5 g, $g-C_3N_4$ precursor) was uniformly spread on the surface of the Cu₂O NAs/CM. The crucible was put into a tube furnace and the tube furnace passed nitrogen gas, heated to 500 °C at a heating rate of 2.5 °C min⁻¹, and maintained for 4 h. After the tube furnace was cooled to room temperature, the sample was taken out and placed in DIW for sonication (30 min) to make the surface unstable g-C₃N₄ fall off the surface and we obtained g-C₃N₄/Cu₂O NAs/CM-1.5. Similarity, 0.5 g, 2.5 g and 3.5 g $g-C_3N_4$ precursor white powder were applied in other conditions and the resulting photocatalysts were recorded as g-C₃N₄/Cu₂O NAs/CM-0.5, g-C₃N₄/Cu₂O NAs/CM-2.5 and g-C₃N₄/Cu₂O NAs/CM-3.5. Although the accurate content of g-C₃N₄ was hard to measure in the composite, the distinct amounts of precursor introduced were considered to effectively adjust the ratio of two semiconductors. The purpose of this is to form a gradient load g-C₃N₄ in Cu₂O NAs.

1.3 Material characterization

Field emission scanning electron microscope (FE-SEM) images were obtained on FE-SEM (Philips XL 30 ESEM FEG field emission system, acceleration voltage: 15.0 kV). Spray a layer of Au film on the surface of the samples before the SEM test to increase the conductivity of the samples and protect the surface morphology of the samples from being destroyed by high-energy electron beams. Then, SEM characterizations were performed to observe the morphology and structure of the prepared specimens. The morphology, lattice fringe spacing and material composition of the samples were executed by Transmission electron microscopy (TEM), High-resolution transmission electron microscopy (HR-TEM), Scanning transmission electron microscopy-High-angle annular dark field (STEM--HAADF) and elemental mapping on Tecnai G² microscope at 200.0 kV. The sample powder for TEM characterizations was ultrasonically dispersed in an Ethanol solution (ca. 0.1 mg mL⁻¹) for 30 min, and subsequent dispersion was dropwise added to a carbon-covered copper grid and was dried at ambient temperature. Powder X-ray diffraction (XRD) was carried out on a D8 Advance (Bruker) diffractometer (Cu K α , $\lambda = 1.54$ Å) to study the composition of the material, the structure or morphology of the atoms or molecules inside the material, etc. The instrument sweep speed is 0.2 °C min⁻¹ in the 20 range from 10 to 80 degrees. X-ray photoelectron spectroscopy (XPS) was recorded using VG ESCALABMK II X-ray photoelectron spectrometer with Al Ka (1486.6 eV) as the X-ray excitation source to analyze the chemical composition or elemental composition of the samples surface and provide information on chemical bonds and charge distribution. Ultraviolet-visible (UV-vis) diffuse reflectance spectra (DRS) (BaSO₄ as the reference) were in progress by Hitachi U-3900 UV-vis spectrophotometer. According to DRS, the Tauc plots can be derived to calculate the band gap ((αhv)^{1/n} = A(hv-E_g)), where α , h, v, A and E_g mean absorptivity, Plank constant, frequency, proportionality constant and band gap, respectively. The index n is directly related to the semiconductor type: direct bandgap semiconductor (n = 0.5); indirect bandgap semiconductor (n = 2). The nitrogen absorption and desorption isothermal curve measurements and CO₂ adsorption tests were applied on a Quantachrome ASiQwin-Autosorb Station 1. The specific surface areas and pore size distributions were calculated by multipoint BET method and Barret–Joyner–Halenda (BJH) method using desorption data. Photoluminescence spectroscopy was measured using a fluorescence spectrophotometer (Hitachi, F-4600) with a xenon lamp as an excitation source (excitation wavelength: 420 nm). The photocatalytic reaction products were detected by gas chromatography (GC-2014, Shimadzu, Japan). Methanol labeled by ¹³C and ¹²C was detected with gas chromatography-mass spectrometer (GC-MS Agilent Technologies 7890B GC system with 5977B MSD, USA). ¹H NMR was detected on a Bruker AV-400 in D₂O. In-situ Fourier transform infrared (in-situ FTIR) spectroscopy was detected on a Nicolet IS-50 FT-IR spectrometer (Thermo fisher, USA).

1.4 Photocatalytic CO₂ reduction Measurement

The photocatalytic activity and selectivity of the prepared samples were appraised by photocatalytic reduction of CO_2 to solar energy under simulated sunlight. As shown in **Figure S3**², the photocatalytic CO_2 reduction reaction evaluation device is a airtight vacuum glass reaction system, which is composed of a reaction chamber, a constant temperature condensed water cooling reaction system and a circulation pump. Before the photocatalytic reaction, it is necessary to extract all the gas in the photocatalytic evaluation device to the vacuum, which is achieved by a vacuum pump and an exhaust valve, and the connected barometer displays the relative vacuum. During the reaction, the internal temperature of the reaction device rises, and a condensed water cooling system is required to maintain a constant temperature (0 °C).



The circulation pump makes the gas circulation in the reaction system uniform.



The photocatalytic CO_2 reduction is a gas-solid phase reaction, which is carried out under the 300 W xenon lamp (as the light source) in a ~230 mL reaction system. In brief, a piece of 4 cm² Copper mesh loaded with photocatalyst (ca. 10 mg) was placed in the center of a 5 mL reaction chamber. Although operations and tests were strictly controlled during the experimental process, it is very hard to accurately control exact 10 mg catalyst loading actually. Typically, the quality of the photocatalyst was calculated as following: First, the quality of the clean Copper mesh was tested and recorded as M1. After several procedures of different treatment techniques, the Copper mesh covered with catalyst was tested and recorded as M2. By calculating the difference value of the Copper mesh, M2-M1 was deemed as the true amount of photocatalyst. After the experiment tests with various samples, the resulting catalytic products were unified and proportioned with 10 mg catalyst as equivalent. Here are 3 examples for determining the amount of photocatalyst (**Figure S4**). Before the reaction, all the air in the reaction device was withdrawn, and then the processing of evacuation and Ar pumping was repeated for three times. Subsequently, high purity CO_2 gas (99.999%) was passed into the reaction chamber and the pressure of the reaction device reached the atmosphere. 0.5 mL DIW was injected into the reaction system. Finally, after dark saturation adsorption (10 h), the reactor was irradiated under xenon lamp. The gas products were detected by a gas chromatograph (GC-2014, Shimadzu, Japan) and calibrated with a standard gas mixture. All gas components were identified by retention time and the concentrations of gas components were calculated by the external standard method of peak areas.



Figure S4. (a) Weighing of clean Copper gauze and copper mesh loaded with

catalyst.

The photocatalyst quality: M2 - M1 = 0.3082 - 0.2977 = 0.0105 (g) (1)



Figure S4. (b) Weighing of clean Copper gauze and copper mesh loaded with

catalyst.

The photocatalyst quality: M2 - M1 = 0.2991 - 0.2879 = 0.0112 (g) (2)



Figure S4. (c) Weighing of clean Copper gauze and copper mesh loaded with

catalyst.

The photocatalyst quality: M2 - M1 = 0.2780 - 0.2662 = 0.0118 (g) (3)

1.5 The calculation of apparent quantum efficiency (AQE)

Considering the influence of the mass, time, light source and reaction system of the catalyst etc., the apparent quantum efficiency (AQE), that is, the ratio of the number of photogenerated electrons required to generate the reduced products to the number of photons of incident light is an important parameter for evaluating the efficiency of photocatalytic conversion. The CO_2 photocatalysis of the reaction system involves two types of reactions, as follows:

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \tag{4}$$

$$\mathrm{CO}_2 + 8\mathrm{H}^+ + 8\mathrm{e}^- \to \mathrm{CH}_4 + 2\mathrm{H}_2\mathrm{O} \tag{5}$$

Therefore, the apparent quantum efficiency can be expressed as the following equation,

$$AQE(\%) = \frac{N_e}{N_p} \times 100\% = \frac{N_{methanol} \times 6 + N_{methane} \times 8}{N_p} \times 100\%$$
(6)

Where N_e , N_p , $N_{methanol}$ and $N_{methane}$ signify the number of electrons required for the reaction products, the number of incident photons, the number of molecules that produce methanol, and the number of molecules that generate methane, respectively. The number of incident photons was measured by the ferrioxalate actinometer method ³. Fe₂(SO₄)₃ solution (5 mL, 0.2 M) was added to K₂C₂O₄ solution (5 mL, 1.2 M) and then the mixed solution was diluted to 100 mL with DIW. The above solution was irradiated for 15 s. The photochemical reaction performed as:

$$2Fe^{3+} + C_2O_4^2 \xrightarrow{hv} 2Fe^{2+} + 2CO_2 \tag{7}$$

The Fe²⁺ concentration was determined by spectrophotometric determination of the Phenanthroline complex at 510 nm.

1 mL of the photochemical reaction solution, 2 ml of an aqueous solution of 1,10-Phenanthrolin (0.2 wt %) and 0.5 ml of a buffer solution (pH = 4.5) were added and diluted to 100 mL with DIW. The buffer solution was prepared by dissolving 8.20 g of CH₃COONa·H₂O to 10 mL of H₂SO₄ (1.84 M) and diluting to 1 L with DIW. Finally, the absorbance of the solution at 510 nm was measured by using a UV-Vis

spectrophotometer. The blank value was studied using the same process but without light irradiation. The number of incident photons was calculated as the following equation (8),

$$N_p = \frac{(A_t - A_0) \times V \times N_A}{\varepsilon \times L \times \Phi \times t}$$
(8)

Where A_{b} A_{0} and V represent the absorbance at 510 nm (experimental value: 0.0294 and blank value: 0.00574) and related volume of the solution (1 L), respectively. N_A = 6.02×10^{23} , $\varepsilon = 1.1 \times 10^{4}$ L mol⁻¹ cm⁻¹, L = 1 cm, $\Phi = 1.2$, t = 15 s. Thus, the number of incident photons was 7.195×10^{16} photons s⁻¹.

1.6 Photoelectrochemical characterizations

1.6.1Transient photocurrent

Transient photocurrent experiments were measured by an electrochemical workstation (CHI 660C, Chenhua Instrument, China) using a home-made three-electrode system in light (3W, PerfectLight-LED100B, China) with an ultraviolet (UV) cutoff filter (λ = 450 nm) and 100 mW cm⁻² power density ⁴. The transient photocurrent response testing device and its structural composition diagram are presented as **Figure S5a** and **Figure S5b**, severally. In brief, the slurry was prepared by adding 20 mg of a sample (g-C₃N₄/Cu₂O, prepared by gently scraping the debris falling from the surface of the g-C₃N₄/Cu₂O NAs/CM with a knife) to a mortar, grinding with 100 µL of Nafion (5%) and 1.5 mL of Ethanol. The Indium doped tin oxide (ITO) with the area of 1.5 cm⁻² was consecutively sonicated in NaOH (1 M), Acetone, Ethanol and DIW for 30 min, respectively and ITO was blown dry with N₂.

tin foil at 60 ° C for 12 h. The g-C₃N₄/Cu₂O catalyst was attached tightly onto the surface of ITO to form working electrode. Cu₂O/ITO and Cu(OH)₂/ITO were used the same method as above. A platinum wire was as counter electrode, Ag/AgCl (3M KCl) was as reference electrode and Na₂SO₄ (0.5 M, pH = 7) was as electrolyte.



Figure S5. (a) Transient photocurrent response testing device. (b) Structural composition diagram of transient photocurrent response testing device.

1.6.2 Electrochemical impedance spectroscopy (EIS)

The Nyquist plots were measured on a frequency response analyzer (Solartron 1255 B, UK). g-C₃N₄/Cu₂O NAs/CM was directly as a working electrode (Cu₂O NAs/CM and Cu(OH)₂ NAs/CM were similar.). A platinum gauze was as counter electrode and Ag/AgCl (3M KCl) was as reference electrode. Na₂SO₄ (0.5 M, pH = 7) was as electrolyte. EIS measurements were carried out at open circuit potential from 10^5 to 0.01 Hz.

1.6.3 Mott-Schottky experiment

A Mott–Schottky experiment was in progress in $0.5 \text{ M Na}_2\text{SO}_4$ using 500 Hz at an applied potential ranging from -0.4 to 0.5 V, maintaining an AC amplitude of 10 mV at each of the potentials.

2. Supplementary Results and Discussion



Figure S6. XRD pattern of Cu(OH)₂ NAs/CM.

The crystal type and related parameters of $Cu(OH)_2$ NAs/CM were examined by XRD analysis ⁵. The XRD pattern of $Cu(OH)_2$ NAs and Cu mesh can be indexed for the peak of 23.86°, 34.10°, 38.30°, 53.46° and 43.34°, 50.46°, 74.16°, respectively in the sample of $Cu(OH)_2$ NAs/CM according to PDF no. 13-0420 and PDF no. 04-0836. Specifically, the peaks at 23.86°, 34.10°, 38.30°, 53.46° and 43.34°, 50.46°, 74.16° can be assigned to the (021) plane, (002) plane, (111) plane, (130) plane, (132) plane of $Cu(OH)_2$ NAs and (111) plane, (200) plane, (220) plane of Cu mesh, separately.



Figure S7. XRD pattern of Cu₂O NAs/CM.

The XRD pattern of Cu₂O NAs/CM reveals that the diffraction peaks of the Cu₂O (crystal system: Cubic; space group: Pn-3m (224); JCPDS. 05-0667) and Cu (crystal system: Cubic; space group: Fm-3m (225); JCPDS. 04-0836) ⁶. The Cu₂O NAs demonstrates an angle of 29.46° for the (110) plane, an angle of 36.38° for the (111) plane, an angle of 42.24° for the (200) plane, an angle of 61.30° for the (220) plane and an angle of 73.48° for the (311) plane. Besides, the Cu mesh displays three distinct diffraction peaks at 43.18°, 50.40° and 74.08°, corresponding to (111), (200) and (220) crystal phases, respectively.



Figure S8. XPS data of Cu(OH)₂ NAs/CM: (a) survey spectrum, high-resolution spectra of (b) Cu 2p and (c) O 1s.

The main element types and valence states of $Cu(OH)_2$ NAs/CM were determined by XPS analysis ⁷. The survey XPS spectrum of $Cu(OH)_2$ NAs/CM via galvanostatic anodization demonstrates the main elemental peaks of Cu and O. The inevitable C 1s peak comes from adventitious carbon species. As for the Cu 2p high-resolution spectrum, the two main peaks at 954.2 and 934.5 eV can be indexed to Cu $2p_{1/2}$ and Cu $2p_{3/2}$, respectively. The energy gap between the main peaks and the satellite peaks of Cu 2p is very important in determining the oxidation state of Cu. The energy gap is ~20 eV, which is characteristic of $Cu^{2+ 8}$. The O 1s spectrum is divided into two peaks, which are assigned to the oxygen on hydroxyl groups (HO-Cu(OH)₂) and oxygen on hydroxide (Cu(OH)₂).



Figure S9. XPS data of Cu₂O NAs/CM: (a) survey spectrum, high-resolution spectra of (b) Cu 2p and (c) O 1s.

The survey XPS spectrum includes three elements of Cu, O and C, which correspond to the XRD data ⁹. For the high resolution of Cu 2p spectrum, besides the two satellite peaks, it contains four deconvoluted peaks, the Cu species at 951.3 eV and 931.7 eV are assigned to the Cu⁺ $2p_{1/2}$ and Cu⁺ $2p_{3/2}$, respectively. In addition, two peaks of about 953.6 eV and 933.9 eV are observed corresponding to the Cu²⁺ $2p_{1/2}$ and Cu²⁺ $2p_{3/2}$ peaks, respectively. The above result manifests that the formed Cu₂O is unstable and oxidizes in the air to form CuO ¹⁰. For the high resolution of O 1s spectrum, the O species at 531.4 eV and 530.1 eV are assigned to O adsorbed on the surface of Cu₂O and O²⁻ in Cu₂O. It can be seen that O-Cu₂O peak is higher than O²⁻-Cu₂O peak, which evidences much oxygen is adsorbed on the surface and it is consistent with the analysis of the Cu 2p spectrum.



Figure S10. Transmission electron microscopy images of the Cu(OH)₂ NAs/CM.

It clearly observes that the $Cu(OH)_2$ nanowire has smooth surface with no obvious wrinkle-like structure, which is a structural feature of $Cu(OH)_2$. It is consistent with the results obtained by the SEM. Under high-resolution conditions, the sample has the 0.251 nm and 0.285 nm interlayer spacing of the lattice fringes, which correspond to the (111) plane and (110) plane of $Cu(OH)_2^{11}$.



Figure S11. Transmission electron microscopy images of the Cu₂O NAs/CM.

It presents the structure of independent 1D Cu₂O nanowire with anomalistic rough surface. This irregular rough surface is because of the dehydration and deoxygenation processes of the smooth Cu(OH)₂ nanowire. In the high-magnification TEM image, the Cu₂O nanowire exists the typical (111) crystal facet (interlayer spacing: 0.261 nm) 12 .



Figure S12. Transmission electron microscopy images of the $g-C_3N_4/Cu_2O$ NAs/CM.

The TEM image of the g-C₃N₄/Cu₂O NAs/CM shows that there are significant morphological changes, which stands in a sharp contrast with the Cu₂O NAs/CM and Cu(OH)₂ NAs/CM whose images show abundant presence of nanowires separated from each other. The g-C₃N₄/Cu₂O NAs/CM has 1D nanowire cross-linking and further forms 3D network structure. In addition, it obviously shows that the g-C₃N₄ layers are well coated onto the surface of the Cu₂O nanowires. The high-resolution TEM (HR-TEM) image of g-C₃N₄/Cu₂O NAs/CM provides the lattice spacings of 0.263 nm, which attributes to (111) plane of Cu₂O nanowires ¹³.



Figure S13. (a), (b) Transmission electron microscopy images of g-C₃N₄/Cu₂O NAs/CM. (c) STEM-HAADF and elemental mapping images of Cu, O, C, and N of g-C₃N₄/Cu₂O NAs/CM.

As shown in **Figure S13a**, through careful observation of the TEM image, the composite system is found to exhibit a 3D cross-linked network structure after loading g-C₃N₄ on the cuprous oxide nanowire array. In a zoom-in image (**Figure S13b**), it can be observed that the cuprous oxide nanowires serve as the inner axis, and the outer side is tightly coated with g-C₃N₄ to form a heterojunction. In order to further explore the interface and distribution of g-C₃N₄ on Cu₂O NAs, STEM-HAADF and elemental mapping were used to study the distribution of different components in the composite (**Figure S13c**). It can be seen that the core structure is composed of Cu and O (Cu₂O), and the shell is composed of C and N (g-C₃N₄) to form a g-C₃N₄/Cu₂O NW composite structure. It is observed that the distribution width of Cu and O is narrower than that of C and N, which reflects that g-C₃N₄ tightly encapsulates Cu₂O and they form an effective heterojunction. Such a cohesive structure will greatly reduce the

resistance at the interface of the $g-C_3N_4/Cu_2O$ NAs composite material and facilitate the separation and transmission of photo-generated carriers.



Figure S14. (a) UV–vis DRS. (b) Tauc plot of (Ahv)² versus energy (hv).

The band structure and light absorption performance of all the samples $Cu(OH)_2$ NAs/CM, Cu_2O NAs/CM, g-C₃N₄/Cu₂O NAs/CM and g-C₃N₄ were determined by UV-vis DRS analysis. For Cu(OH)₂ NAs/CM, a dramatic increase in wavelength of absorption less than 560 nm is attribute to inherent band gap of Cu(OH)₂. After annealing and reduction, the absorbance threshold of Cu₂O NAs/CM is further increased to ~640 nm, which reveals that the material has preferable light absorption properties in the ultraviolet and visible bands. Finally, after combining Cu₂O NAs with g-C₃N₄, although the wavelength of the composite material is blue-shifted compared to Cu₂O NAs/CM, the absorption range for visible light is still decent. In the light of Kubelka-Munk bandgap theory, the energy bandgaps of Cu(OH)₂ NAs/CM, Cu₂O NAs/CM, g-C₃N₄/Cu₂O NAs/CM and g-C₃N₄ derived from Tauc plots are calculated to be 2.4 eV, 2.0 eV, 2.1 eV and 2.7 eV, respectively. All the above DRS characterizations and bandgap deductions strongly illustrate the doping effect during the synthetic process of the hybrids ¹⁴.



Figure S15. (a) N₂ adsorption-desorption isotherms, pore size distributions (inset

of (a)) and (b) CO₂ adsorption curves of as-prepared samples.

Table S1 The physicochemical properties of Cu(OH)₂ NAs, Cu₂O NAs and

| Sample | S _{BET} | Pore volume | Average pore size | CO ₂ adsorption |
|--|------------------|------------------------------------|-------------------|----------------------------|
| | $(m^2 g^{-1})$ | (cm ³ g ⁻¹) | (nm) | (mmol g ⁻¹) |
| Cu(OH) ₂ | 25.12 | 0.062 | 17.12 | 0.019 |
| Cu ₂ O | 38.97 | 0.073 | 18.29 | 0.035 |
| g-C ₃ N ₄ /Cu ₂ O | 31.01 | 0.068 | 13.86 | 0.070 |

 $g-C_3N_4/Cu_2O$ NAs materials.

The Brunauer-Emmet-Teller (BET) specific surface (S_{BET}) area and Barrett-Joiner-Halenda (BJH) pore structure of Cu(OH)₂ NAs/CM, Cu₂O NAs/CM and g-C_3N_4/Cu_2O NAs/CM materials were investigated by N_2 adsorption-desorption isotherm analysis. Three samples are provided with type IV isotherms suggesting the existence of mesopores (2-50 nm)¹⁵. In addition, the type H3 hysteresis loops are at high pressure ¹⁶, which demonstrates the existence of slit-like mesopores as a result of the particles aggregation and g-C₃N₄ layer stacking. The S_{BET} of Cu(OH)₂ NAs/CM, Cu₂O NAs/CM and g-C₃N₄/Cu₂O NAs/CM samples was calculated to be 25.12, 38.97, and 31.01 m² g⁻¹, respectively (Table S1). In comparison with pure Cu₂O NAs/CM,

the S_{BET} of sample g-C₃N₄/Cu₂O NAs/CM decreases due to the introduction of g-C₃N₄. The pore size distributions declare that samples present wide pore size distribution from 3 to >100 nm suggesting that there are indeed micropores and macropores in the three samples. The large S_{BET} and rich pore structure of the photocatalysts increase the surface active sites for adsorption and interface reaction.

The CO₂ adsorption performance of the photocatalysts is an important parameter determining the photocatalytic CO₂ reduction. It can be seen that among the three catalysts, g-C₃N₄/Cu₂O NAs/CM has the highest adsorption capacity. In particular, the trend of g-C₃N₄/Cu₂O NAs/Cu curve growth is obviously higher than other catalysts due to the existence of suitable pore structure and attachment sites. At P/P_0 = 1.0, the maximum CO₂ adsorption values at atmosphere pressure of Cu(OH)₂ NAs/CM, Cu₂O NAs/CM and g-C₃N₄/Cu₂O NAs/CM are 0.019, 0.035 and 0.070 mmol g⁻¹ (**Table S1**). The surface amino groups into hydrazine groups of g-C₃N₄ provide effective Lewis base adsorption sites, which further promote the interface transport and surface reaction kinetics ¹⁷.



Figure S16. The GC–MS patterns of the produced CH_3OH over g- C_3N_4/Cu_2O

NAs/CM using ¹²CO₂ and ¹³CO₂ as the carbon source, respectively.

In order to detect the carbon source of the reaction products, gas chromatography-mass spectrometer (GC-MS) analysis was underway to trace the source of methanol by isotope labeling (12 C and 13 C). It can be seen from the **Figure S16** that the retention time of methanol produced by CO₂ marked by 12 C and 13 C is basically the same. Further testing through MS, it shows that 12 CH₃OH (m/z = 32) is the foremost product with 12 CO₂ as the carbon source and 13 CH₃OH (m/z = 33) is the foremost product with 13 CO₂ as the carbon source. In summary, the product produced by the photocatalyst is derived from CO₂.



Figure S17. (a) Gas chromatography and (b) ¹H NMR for detection after 6 h of

g-C₃N₄/Cu₂O NAs/CM photocatalytic reduction of carbon dioxide.

During the experimental process, when the photocatalytic reduction of carbon dioxide proceeded for 6 h, gas chromatography and ¹H NMR techniques were employed for detection of the catalytic products. Here only methanol and methane could be detected by these instruments, but CO, H₂, HCOOH and other species were not recorded. The above case indicates that CH₃OH and CH₄ were the most dominant resultants in this photocatalytic system. While the other products are inexistent, or they should be in a very trace amount which can be hardly detected via the current instrument.



Figure S18. Yields of oxygen as a function of time.

The water acted as a reducing agent during the CO_2 photoconversion process and was oxidized to oxygen by the generated photogenerated holes.

Under the condition that the photocatalytic reduction of carbon dioxide test system unchanged, we studied the type of catalytic system mechanism by testing the photo-oxidized water process (half reaction relative to photocatalytic reduction). It can be seen that if the g-C₃N₄/Cu₂O NAs/CM structure is of type II, the band gap range of the composite does not include the oxidation potential of water, thus the photocatalytic oxidation product does not include oxygen. Only when the complex system is Z-scheme, it can generate oxygen (the potential range of the composite structure covers the oxidation potential of water). To further confirm our speculation, the photo-oxidized water via g-C₃N₄ and Cu₂O NAs/CM catalysts was investigated. The results show that since the band gap of g-C₃N₄ covers the oxidation potential of water, oxygen can be generated, but the amount of oxygen generated is significantly less than that of g-C₃N₄/Cu₂O NAs/CM nanostructure. In sharp contrast, Cu₂O NAs/CM does not produce oxygen. Overall, the above experimental results prove that our composite catalyst has a Z-scheme structure.



Figure S19. (a) Yields of methanol as a function of time. (b) Hydrocarbon generation of different ratios of $g-C_3N_4$ composite samples.

In addition to $g-C_3N_4/Cu_2O$ NAs/CM-0.5, $g-C_3N_4/Cu_2O$ NAs/CM-1.5, $g-C_3N_4/Cu_2O$ NAs/CM-2.5 and $g-C_3N_4/Cu_2O$ NAs/CM-3.5, samples of Cu₂O NAs/CM (unloaded $g-C_3N_4$) and pristine $g-C_3N_4$ were also employed as candidate for control experiments. Through systematic testing of the samples, we carefully studied the effect of different $g-C_3N_4$ loadings on the photocatalyst.

As shown in **Figure S19a**, it reveals that the pristine $g-C_3N_4$ basically has no catalytic activity. In contrast, Cu₂O NAs/CM shows a certain catalytic activity for methanol production. With the continuous increase of $g-C_3N_4$ loading, the performance of methanol production via the composite catalyst gradually increased, among which $g-C_3N_4/Cu_2O$ NAs/CM-2.5 demonstrates the crest value. However, when $g-C_3N_4$ continues to increase, the methanol production decreases. It might be ascribed to the active sites blocking after excessive loading of $g-C_3N_4$, which further reduces the catalytic efficiency of the composite. **Figure S19b** also reflects that the catalytic capability towards $g-C_3N_4$ loading depicts a volcanic distribution for the

production of methanol, among which the methanol production rate of $g-C_3N_4/Cu_2O$ NAs/CM-2.5 is the highest. While for the by-product methane, the yields of all the samples are low. It also indicates that the selectivity of the $g-C_3N_4/Cu_2O$ NAs/CM samples is advisable.



Figure S20. SEM image and XRD of g-C₃N₄/Cu₂O NAs/CM after 60 hours

photocatalytic CO₂ reduction.

Typically, when 60 hours photocatalytic reaction accomplished, the composite was first washed 5 times with DIW, then heated to at 200 °C and maintained for 5 h in a vacuum oven to remove the residue adsorbed on the surface of the material. Finally, the catalyst was cooled to room temperature and took to SEM and XRD characterization. The surface topography and crystal structures of the g-C₃N₄/Cu₂O NAs/CM after the 60 hours photocatalytic reactions are presented. It can be seen that the surface structure does not change significantly compared to the fresh catalyst before the photocatalytic reaction and the used g-C₃N₄/Cu₂O NAs/CM displays similar diffraction peaks, which shows that the crystal structure of the material has not changed, which further proves that the material has good stability.



Figure S21. XPS data of $g-C_3N_4/Cu_2O$ NAs/CM before and after 60 hours photocatalytic CO₂ reduction: (a) survey spectrum, high-resolution spectra of (b) Cu

Typically, when 60 hours photocatalytic reaction accomplished, the composite was first washed 5 times with DIW, then heated to at 200 °C and maintained for 5 h in a vacuum oven to remove the residue adsorbed on the surface of the material. Finally,

the catalyst was cooled to room temperature and took to XPS characterization. **Figure S21** reveals that the element valence, the chemical composition and elemental composition of the catalyst composite have not changed substantially before and after the reaction, indicating that the catalyst has advisable stability.

Table S2 The products of methanol and methane apparent quantum efficiency (AQE)
 of samples under solar light.

| Sample | Cu(OH) ₂ | Cu ₂ O | g-C ₃ N ₄ /Cu ₂ O |
|--|---------------------|-------------------|--|
| Methanol (ppm cm ⁻² h ⁻¹) | 4.42 | 9.44 | 22.60 |
| Methane (ppm cm ⁻² h ⁻¹) | 0.38 | 0.45 | 0.60 |
| AQE (%) | 0.95 | 1.85 | 4.23 |

Apparent quantum efficiency is an important way to evaluate the efficiency of photocatalytic reactions. For the three photocatalysts, the selectivity to methanol is very high, and the yield of CH_3OH and CH_4 differs by an order of magnitude. By calculating the AQE, it is shown that the composite catalyst (g- C_3N_4/Cu_2O) has the highest light conversion efficiency to reach 4.23%.



Figure S22. Transient photocurrent of the Cu(OH)₂ NAs/CM, Cu₂O NAs/CM, and

g-C₃N₄/Cu₂O NAs/CM.

For the stability of the material, it needs to determine whether the transient photocurrent value is constant under open circuit voltage (the applied potential is 0 V). As shown in **Figure S22**, for g-C₃N₄/Cu₂O NAs/CM sample, it is observed that the on-off cycles are almost reversible and carry on via fast and stable photocurrent signals (-4.5 mA cm⁻²), indicating an excellent sensitivity to light for the catalyst. The transient photocurrent decays to -2.0 mA cm⁻² and -1.3 mA cm⁻² in Cu₂O NAs/CM and Cu(OH)₂ NAs/CM, respectively. Thus, it is a powerful explanation that the g-C₃N₄/Cu₂O NAs/CM has excellent stability.



Figure S23. In situ FTIR spectra of g-C₃N₄/Cu₂O NAs/CM over CO₂ and H₂O in

the dark for 60 min and with light for another 60 min.

Table S3 The products of CO₂ reduction and corresponding reduction potentials with

reference to NHE at pH = 7.

| Product | Reaction | E (V vs. NHE) |
|--------------------|---|---------------|
| CH ₄ | $\rm CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ | -0.24 |
| CH ₃ OH | $CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$ | -0.38 |
| НСООН | $\rm CO_2 + 2H^+ + 2e^- \rightarrow \rm HCOOH$ | -0.61 |

The CO₂ photocatalysis intermediates on the g-C₃N₄/Cu₂O NAs were detected on the in situ FTIR. Before the experiment, the sample was placed in a vacuum oven at 160 ° C for 5 h to remove the residue adsorbed on the surface of the material. First of all, the in situ FTIR spectrum in the dark was collected as the blank. Then, introduce CO₂ into the test system and use subtraction the blank to obtain in situ FTIR spectra. The in situ FTIR analysis was conducted in two consequent steps. (1) CO₂ adsorption on the g-C₃N₄/Cu₂O NAs was executed in the dark under continuous flow of a mixture of CO₂ and H₂O (vapor) for 1 h. (2) The reactor was illuminated with a lamp (LED, $\lambda = 420$ nm) for 1 h.

When the g-C₃N₄/Cu₂O NAs was under CO₂ and H₂O in the atmosphere in the dark, carbonate (CO₃²⁻, 1299, 1315, 1345, 1363, 1465, 1584 and 1652 cm⁻¹) and bicarbonate (HCO₃⁻, 1235, 1398 and 1422 cm⁻¹) generated ¹⁸⁻²¹. When a LED light source was added for illumination (1 h), the peaks of carbonate and bicarbonate basically did not change. Two new peaks (1352 and 1520 cm⁻¹) appeared, which attributed to COO^{- 22}. The peak at 1640 cm⁻¹ assigned to H₂O can also be observed. This result manifested that HCOOH acted as the intermediate and photocatalytic reaction had H₂O generation during the photocatalytic CO₂ reduction. According to **Table S2**, the formation of HCOOH from CO₂ is a two-electron reaction at -0.61 V vs. NHE (pH = 7).

3. References

(1) Hou, J.; Cheng, H.; Takeda, O.; Zhu, H., Three-dimensional bimetal-graphene-semiconductor Coaxial Nanowire Arrays to Harness Charge Flow for the Photochemical Reduction of Carbon Dioxide. *Angew. Chem. Int. Ed.* **2015**, *54*, 8480-8484.

(2) Li, P.; Zhou, Y.; Zhao, Z.; Xu, Q.; Wang, X.; Xiao, M.; Zou, Z., Hexahedron
Prism-anchored Octahedronal CeO₂: Crystal Facet-based Homojunction Promoting
Efficient Solar Fuel Synthesis. J. Am. Chem. Soc. 2015, 137, 9547-9550.

(3) Schiavello, M.; Augugliaro, V.; Loddo, V.; López-Muñoz, M. J.; Palmisano, L., Quantum Yield of Heterogeneous Photocatalytic Systems: Further Application of an Experimental Method for Determining the Absorbed Photon Flow. Res. Chem. Intermed. **1999**, *25*, 213-227.

(4) Zhao, X.; Zhang, X.; Han, D.; Niu, L. Ag Supported Z-scheme WO_{2.9}/g-C₃N₄
Composite Photocatalyst for Photocatalytic Degradation under Visible Light. *Appl. Surf. Sci.* 2020, *501*, 144258.

(5) Zhang, Z.; Dua, R.; Zhang, L.; Zhu, H.; Zhang, H.; Wang, P., Carbon-layer-protected Cuprous Oxide Nanowire Arrays for Efficient Water Reduction. *ACS Nano* **2013**, *7*, 1709-1717.

(6) Kim, C.; Cho, K. M.; Al-Saggaf, A.; Gereige, I.; Jung, H.-T., Z-scheme Photocatalytic CO₂ Conversion on Three-dimensional BiVO₄/Carbon-coated Cu₂O Nanowire Arrays under Visible Light. *ACS Catal.* **2018**, *8*, 4170-4177. (7) Yu, J.; Ran, J., Facile Preparation and Enhanced Photocatalytic H₂-production Activity of Cu(OH)₂ Cluster Modified TiO₂. *Energy Environ. Sci.* **2011**, *4*, 1364-1371.

 (8) Akhavan, O.; Azimirad, R.; Safa, S.; Hasani, E., CuO/Cu(OH)₂ Hierarchical Nanostructures as Bactericidal Photocatalysts. *J. Mater. Chem.* 2011, *21*, 4170-4177.

(9) Wang, W. Z.; Wang, G. H.; Wang, X. S.; Zhan, Y. J.; Zheng, C. L., Synthesis and Characterization of Cu₂O Nanowires by a Novel Reduction Route. *Adv. Mater.* 2002, 14, 67-69.

(10) Musa, A. O.; Akomolafe, T.; Carter, M. J., Production of Cuprous Oxide, a Solar Cell Material, by Thermal Oxidation and a Study of Its Physical and Electrical Properties. *Sol. Energy Mater. Sol. Cells* **1998**, *51*, 305-316.

(11) Li, Y.; Yang, X. Y.; Rooke, J.; Van Tendeloo, G.; Su, B. L., Ultralong Cu(OH)₂
and CuO Nanowire Bundles: PEG200-directed Crystal Growth for Enhanced
Photocatalytic Performance. *J. Colloid Interface Sci.* 2010, *348*, 303-312.

(12) Shang, Y.; Guo, L., Facet-controlled Synthetic Strategy of Cu₂O-based Crystals for Catalysis and Sensing. *Adv. Sci.* **2015**, *2*, 1500140.

(13) Yuan, G. Z.; Hsia, C. F.; Lin, Z. W.; Chiang, C.; Chiang, Y. W.; Huang, M. H., Highly Facet-dependent Photocatalytic Properties of Cu₂O Crystals Established through the Formation of Au-decorated Cu₂O Heterostructures. *Chem.* **2016**, *22*, 12548-12556.

(14) Wei, Z.; Wang, J.; Mao, S.; Su, D.; Jin, H.; Wang, Y.; Xu, F.; Li, H.; Wang, Y.,
In Situ-generated Co⁰-Co₃O₄/N-Doped Carbon Nanotubes Hybrids as Efficient and

Chemoselective Catalysts for Hydrogenation of Nitroarenes. ACS Catal. 2015, 5, 4783-4789.

(15) Jin, J.; Yu, J.; Guo, D.; Cui, C.; Ho, W., A Hierarchical Z-scheme CdS-WO₃ Photocatalyst with Enhanced CO₂ Reduction Activity. *Small* **2015**, *11*, 5262-5271.

(16) Jin, J.; Yu, J.; Liu, G.; Wong, P. K., Single Crystal CdS Nanowires with High Visible-light Photocatalytic H₂-production Performance. *J. Mater. Chem. A* **2013**, *1*, 10927-10934.

(17) Cao, S.; Shen, B.; Tong, T.; Fu, J.; Yu, J. 2D/2D Heterojunction of Ultrathin MXene/Bi₂WO₆ Nanosheets for Improved Photocatalytic CO₂ Reduction. *Adv. Funct. Mater.* 2018, *28*, 1800136.

(18) Liu, L.; Zhao, C.; Xu, J.; Li, Y., Integrated CO₂ Capture and Photocatalytic Conversion by a Hybrid Adsorbent/Photocatalyst Material. *Appl. Catal., B* **2015**, *179*, 489-499.

(19) Li, K.; Peng, T.; Ying, Z.; Song, S.; Zhang, J., Ag-loading on Brookite TiO₂ Quasi Nanocubes with Exposed {210} and {001} Facets: Activity and selectivity of CO₂ Photoreduction to CO/CH₄. *Appl. Catal., B* **2016**, *180*, 130-138.

(20) Liu, L.; Jiang, Y.; Zhao, H.; Chen, J.; Cheng, J.; Yang, K.; Li, Y., Engineering Coexposed {001} and {101} Facets in Oxygen-deficient TiO₂ Nanocrystals for Enhanced CO₂ Photoreduction under Visible Light. *ACS Catal.* **2016**, *6*, 1097-1108.

(21) Liu, L.; Zhao, H.; Andino, J. M.; Li, Y., Photocatalytic CO₂ Reduction with H₂O on TiO₂ Nanocrystals: Comparison of Anatase, Rutile, and Brookite Polymorphs and Exploration of Surface Chemistry. *ACS Catal.* **2012**, *2*, 1817-1828.

(22) Wilfong, W. C.; Srikanth, C. S.; Chuang, S. S., In Situ ATR and DRIFTS Studies of the Nature of Adsorbed CO₂ on Tetraethylenepentamine Films. *ACS Appl. Mater. Interfaces* **2014**, *6*, 13617-13626.