Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2024

# Supporting Information

# Lewis functional nanodiamonds for efficient metal-free photocatalytic CO<sub>2</sub> reduction

Xiaowu Gao<sup>a,b,#</sup>, Xinyue Han<sup>a,#</sup>, Ziwei Zhao<sup>a,b,#</sup>, Ning-Yu Huang<sup>c</sup>, Keran Jiao<sup>a,d</sup>, Pengfei Song<sup>e</sup>, Jiaqi Zhu<sup>b,\*</sup>, and Yongjie Wang<sup>a,b,\*</sup>

<sup>a</sup> Guangdong Provincial Key Laboratory of Semiconductor Optoelectronic Materials and Intelligent Photonic Systems, School of Science, Harbin Institute of Technology, Shenzhen 518055, China

<sup>b</sup> National Key Laboratory of Science and Technology on Advanced Composites in Special Environments, Harbin Institute of Technology, Harbin 150080, China

<sup>c</sup> Shenzhen Key Laboratory of Micro/Nano-Porous Functional Materials (SKLPM),

Department of Chemistry, SUSTech-Kyoto University Advanced Energy Materials Joint Innovation Laboratory (SKAEM-JIL), Southern University of Science and Technology (SUSTech), Shenzhen 518055, China

<sup>d</sup> Department of Chemical Engineering, The University of Manchester, Oxford Road, Manchester M13 9PL, UK

<sup>e</sup> School of Advanced Technology, Xi'an Jiaotong-Liverpool University, Suzhou 215000, China

<sup>#</sup> These authors contributed equally to this work.
\*Corresponding authors: Yongjie Wang (<u>yjwang@hit.edu.cn</u>) and Jiaqi Zhu
(zhujq@hit.edu.cn)

# **Experimental Section**

# 1. Chemicals and reagents

The dispersible ND (noted as p-ND) with a median size range of 5–10 nm was purchased from Nanjing Xianfeng NANO Material Tech Co. Ltd. And the aminemodified ND (noted as ND-NH<sub>2</sub>) with <10 nm diameter nanoscale was purchased from Shanghai TCI chemical Co. Ltd. Ruthenium-tris(2,2'-bipyridyl) dichloride ([Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O, 98%), triethanolamine (C<sub>6</sub>H<sub>15</sub>NO<sub>3</sub>, AR), acetonitrile (CH<sub>3</sub>CN, AR, >99%), melamine (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>, 99%), and cyanuric acid (C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>O<sub>3</sub>, 99%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. All chemicals were used without further purification.

#### 2 Material synthesis

## 2.1 Preparation of Carboxyl- modified ND nanodiamonds (ND-COOH)

Carboxyl- modified ND nanodiamonds (noted as ND-COOH) were prepared via thermal treatment: NDs were first dried in a vacuum dryer at 80 °C for 2 h to remove organic impurities, and then heated in a muffle furnace at 500 °C for 8 h to remove non-diamond carbons and form hydrophilic. oxygen-containing groups (carboxyl) on the ND surface.

# 2.2 Synthesis of bulk g-C<sub>3</sub>N<sub>4</sub> (B-CN)

2.5 g of melamine was ground for 10 min and placed in a crucible with a lid, then placed in a muffle furnace and raised to 550 °C at an elevated rate of 5 °C/min, held for 4 h, and cooled naturally to room temperature to obtain the B-CN sample.

#### 2.3 Synthesis of B-CN/ND-COOH

An appropriate amount of p-ND powder was uniformly ground with 2.5 g of melamine for 30 min in a crucible with a lid, and then placed in a muffle furnace, raised to 550 °C at an elevation rate of 5 °C/min, held for 4 h, and naturally cooled to room temperature to obtain the B-CN/ND-COOH sample.

#### 2.4 Synthesis of B-CN/ND-NH<sub>2</sub>

An appropriate amount of p-ND powder was uniformly ground with 2.5 g of melamine for 30 min in a crucible with a lid, and then placed in a tube furnace with exhaust air, and the temperature was raised to 550 °C under Ar atmosphere at an elevated rate of 5 °C/min, held for 4 h, and then naturally cooled to room temperature to obtain the B-CN/ND-NH<sub>2</sub> sample.

## 2.5 Synthesis of 3D CN/ND-COOH

0.05 mol melamine and 0.05 mol cyanuric acid were mixed in 300 mL deionized water and magnetic stirred for 12 h at room temperature. Subsequently, the white cyanuric acid-melamine (CM) supramoleculars were centrifuged and dried by vacuum freeze drying. Secondly, the resulting 2.5g of CM supramolecular precursor and appropriate amount of ND-COOH were placed in a mortar and ground for 30 mins to form a homogeneous mixture. And then the mixture was placed in a covered alumina crucible and thermally treated at 550 °C for 4 h in a quartz tube furnace with a heating rate of 2 °C/min under Argon atmosphere, Finally, after the reaction was cooled to room temperature, the light-yellow sample was obtained, denoted as 3D CN/ND-COOH.

#### **3** Characterizations and measurements

## 3.1. Characterizations of the photocatalysts

The analyses of surface microstructures and chemical compositions of the catalysts were carried out on a FEI Quanta 200 F scanning electron microscopy (SEM) and JEOL JEM 2100 transmission electron microscopy (TEM). The phase structure of the photocatalysts was performed on a powder X-ray diffractometer (XRD, Shimadzu XRD 6000). The chemical bonds or functional information were obtained by using the attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) method. To study on the absorption property of the ultraviolet and visible range, UV–visible spectra were carried out on a Shimadzu UV-2600 UV–vis spectrophotometer in

the range of 200-800 nm. The Brunauer-Emmett-Teller (BET) method was carried out to calculated the specific surface area of the samples. The isotopic tracing test was carried out on 5977B GC/MS (Agilent) by using <sup>13</sup>CO<sub>2</sub> as reactants under the same as test condition of photocatalytic CO<sub>2</sub> reduction. Fluorescence luminescence (PL) spectroscopy was tested using the FLS1000 fluorescence luminescence spectrometer (Hitachi, Japan). The excitation source was monochromatic light with a wavelength of 340 nm, and the receiving fluorescence range was from 400 nm to 700 nm. X-ray photoelectron spectroscopy (XPS) with Auger electron spectroscopy (AES) and valence band-XPS (VB-XPS) measurements were obtained on the PerkinElmer PHI-1600 ESCA spectrometer equipped with the multi-channel detector. The spectra were excited by using the Mg Ka X-ray source (hv = 1253.6 eV,  $1 \text{ eV} = 1.603 \times 10^{-19} \text{ J}$ ). The binding energy of all elements in the photocatalysts was calibrated by the binding energy of C 1 s at 284.8 eV. Atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) measurements were both completed at SPM-9700 surface probe system (Shimadzu, Japan). Before the test, the probe is calibrated with the iron plate, which was the base for the test. The light source for in-situ KPFM is a 365-nm LED light (10 W). And in-situ Electron paramagnetic resonance (EPR) spectroscopy was collected on Bruker EMXnano, 10 mg catalysts were dissolved in 1mL H<sub>2</sub>O or CH<sub>3</sub>OH and 100 mM dimethyl-1-pyrroline N-oxide (DMPO) was added to it for the trapping of and with/without UV-vis light illumination under a 100W mercury lamp. CO2 temperature-programmed desorption (CO<sub>2</sub>-TPD) experiments were carried out using a Micromeritics AutoChem II 2920 automated characterization system with a quartz Utube reactor and detected by a TCD. For the pretreatment, the sample was heated under N<sub>2</sub> flow at 200 °C for 1 h and then it was cooled to room temperature. After saturation adsorption of CO<sub>2</sub>, the TPD analysis was performed under N<sub>2</sub> flow (30 mL/min) by heating the sample to 650 °C.

The density functional theory (DFT) calculation was performed by the Vienna Ab initio Simulation package (VASP) <sup>S1</sup>, and the exchange-correlation energy was approximately described by the Perdew, Burke and Ernzerhof (PBE) functional based

on the generalized gradient approximation (GGA) <sup>S2</sup>. The plane wave basis sets with projector-augmented wave (PAW) pseudopotentials were applied in structure optimization  $^{S3}$ . The structure of diamond (111) was built based on a 3×3 supercell, on this basis, the surface modification modifies the same number of amino and carboxyl groups on the principle of lowest energy by utilizing the covalent bonds missing from the carbon atoms fixed in the two layers at the bottom of the pseudohydrogen atom saturation. For g-C<sub>3</sub>N<sub>4</sub>/ND, the computed g-C<sub>3</sub>N<sub>4</sub> monolayer was connected with functional group modification ND (111) surface through interstorey van der Waals, as shown in Fig. S30, S31. The convergence tolerance of geometry optimization was set as  $1.0 \times 10^{-5}$  eV for energy, and all the forces on each atom were smaller than 0.01 eV·Å<sup>-1</sup>. The plane-wave cutoff energy was set to 520 eV. The Gamma-centered Monkhorst-Pack k-points grids was set to 3×3×1. The van der Waals interaction (Grimme's DFT-D3 method) was adopted for the whole DFT calculations. Dipole corrections were included in all surface calculations in the surface normal direction (LDIPOL = TRUE, IDIPOL = 3)<sup>S4</sup>. In order to avoid interactions between periodic images, a vacuum space of 25 Å was applied to all calculations. All the structures discussed in this study were visualized in the Visualization for Electronic and Structural Analysis (VESTA)  $^{S5}$ . The adsorption energy (E<sub>ads</sub>) between the catalyst slab and CO<sub>2</sub> molecules was calculated by the following equation (1):

$$E_{ads} = E_{total} - E_{CO2} - E_{slab}$$
(1)

where  $E_{total}$ ,  $E_{CO2}$  and  $E_{slab}$  are the total energy of the optimized CO<sub>2</sub> adsorbate on catalyst surface. The formation Gibbs free energy ( $\Delta G$ ) of the NRR intermediates is calculated as:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S \qquad (2)$$

where  $\Delta E$  is the electronic energy difference directly obtained from DFT calculations,  $\Delta ZPE$  is the change of zero-point energies, T is the temperature (T = 298.15 K), and  $\Delta S$  is the entropy changes. The entropy of gas molecules is taken from standard values.

# 3.2. Photoelectrochemical (PEC) measurements

Photoelectrochemical (PEC) measurements were performed by a three-electrode system using an electrochemical workstation (CHI 760E) in an H-type electrolytic cell with a transparent quartz window. Typically, Pt sheet was employed as the counter electrode, an Ag/AgCl electrode was the reference electrode, and the as-prepared samples covered FTO glass were used as the working electrodes. For the working electrodes, as-prepared materials (1 mg) were dispersed in isopropanol (1 ml) to obtain a slurry. Then the slurry (100  $\mu$ L) was deposited on the surface of the FTO glass (the area was 1 cm<sup>2</sup>) and dried in an oven overnight. Subsequently, the working electrodes were exposed to UV light for 1 h to eliminate isopropanol and calcined at 120 °C for 2 h. The Na<sub>2</sub>SO<sub>4</sub> solution (0.1 mol L<sup>-1</sup>) was acted as the electrolyte. The test environment of transient photocurrent in this system was to switch the lights on and off by 10 s, and the catalysts were excited by the Xe lamp (300 W). Mott-Schottky experiments was performed with three different frequencies (1200, 800 and 400 Hz), and the test frequency of electrochemical impedance spectra (EIS) ranges from 0.1 to 100,000 Hz at open circuit potential.

# 3.3. Tests on photocatalytic CO<sub>2</sub> reduction with H<sub>2</sub>O

In the typical photocatalytic CO<sub>2</sub> reduction reaction, 60 mg of photocatalysts, 10 mL of triethanolamine (TEOA), 10 mL of H<sub>2</sub>O and 30 mL of acetonitrile (MeCN) were added into a gas-closed glass reactor (420 mL in capacity). The mixed sample was uniformly ultrasound 15 mins and put into the photoreaction system. Before introduction of light irradiation, the photoreaction system was thoroughly vacuum-treated (3 times), and then high purity CO<sub>2</sub> was injected into the internal circulation reactor until the pressure reached 1 atm. Then, high purity CO<sub>2</sub> was introduced into the reactor with a partial pressure of 1 atm. A 300W Xe lamp (Beijing Perfectlight Inc., China) with a 420 nm cut-off filter was used as the light source. The temperature of the reaction system was kept at 10 °C. During the photocatalytic process, the reaction system was vigorously stirred with a magnetic stirrer. After the reaction, the generated

products were quantified by an GC-9790Plus (Zhejiang Fuli Analytical Instruments Inc, China) gas chromatograph. For the cyclic stability test, the samples were collected after the reaction, centrifuged and washed 3 times each with ethanol and deionized water, dried under vacuum at 60°C overnight, and tested in the same solution system.

The photon efficiency is an important standard to measure the efficiency of the photocatalytic reaction to convert light energy. The number of photons can be effectively measured and calculated by using a single-wavelength light source of  $\lambda$  (420, 450, 475, 500, 520, 550 and 600 nm, respectively). The number of photons converted by the reaction is converted by the molar amount of the product and the corresponding number of photons required. The ratio of the two is the efficiency of tourism, and the specific formula is as follows <sup>S6</sup>:

$$AQY = \frac{2 \times \text{Number of evolved CO molecules}}{\text{Number of incident photons}} \times 100\%$$
(3)





Fig. S1. XRD patterns of p-ND, ND-COOH and ND-NH<sub>2</sub>.

As shown in **Fig. S1**, the characteristic peaks of ND-based materials powder diffraction shown almost the same despite of the differences in the surface functional groups, indicating that the surface functional groups have almost no effect on the structure of ND.



Fig. S2. Electrochemical impedance spectra (EIS) of p-ND, ND-COOH and ND-NH<sub>2</sub>.



Fig. S3. (a) Tauc plots of p-ND, ND-COOH and ND-NH<sub>2</sub>. XPS valence band spectra for (b) p-DN, (c) ND-COOH and (d) ND-NH<sub>2</sub>.



Fig. S4. Motto-Schottky plots of (a) p-DN, (b) ND-COOH and (c) ND-NH<sub>2</sub>.



**Fig. S5.** Linear scanning voltammetry (LSV) tests were conducted in H-cells using a 0.5 M KHCO<sub>3</sub> solution of p-DN, ND-COOH and ND-NH<sub>2</sub> under saturated Ar and CO<sub>2</sub> atmospheres.



Fig. S6. (a) (b) SEM images of B-CN and (c) ND-NH<sub>2</sub> particles; (d) (e) TEM images and (f) HRTEM image of B-C<sub>3</sub>N<sub>4</sub>/ND-NH<sub>2</sub> sample.

As shown in **Fig. S6**, the bulk  $g-C_3N_4$  exhibits lamellar stacking in SEM images, and the individual ND nanoparticles are also clearly agglomerated on a large scale, however, in TEM images, because of the prolonged ultrasonic stripping treatment, the bulk g- $C_3N_4$  exhibits thin monolayers, and a more homogeneous loading of ND nanoparticles on the lamellae can also be observed.



Fig. S7. (a) SEM image and (b) (c) TEM images of 3D CN sample; (d) SEM image,(b) TEM image and (c) HRTEM image of 3D CN/ND-NH<sub>2</sub> sample.

The SEM images of 3D CN alone and ND loaded in 3D CN in **Fig. S7** show a threedimensional porous monolayer lamellar structure different from that of bulk  $g-C_3N_4$ , and it is also demonstrated in the TEM images that this structure is not a single monolayer but monolayers of lamellae cross-coupled with each other.



**Fig. S8.** (a) The calculating FWHM for XRD peaks of B-CN, 3D CN and 3D CN /ND-NH<sub>2</sub>. (b) XRD patterns of B-CN, B-CN/ND-COOH and B-CN/ND-NH<sub>2</sub>. (c) XRD characteristic peaks of 3D CN loaded with different contents of ND-NH<sub>2</sub>.

As shown in **Fig. S8**, relative to B-CN, the characteristic peaks of 3D CN-based materials at around 27.6° all have only a small offset, and the FWHM are all smaller than that of B-CN samples. The different types and contents of ND have almost no influence on the structure of ND in the B-CN sample. CN and 3D CN, the characteristic peaks of ND were observed, indicating that the composites were successfully synthesized.



Fig. S9. Photographs of the same volume for samples 3D CN and B-CN.

Samples	B-CN	3D CN	ND-NH2	3D CN/ND- NH <sub>2</sub>
BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )	8.46	112.00	310.65	125.69
Average Pore Diameter (nm)	16.11	13.09	14.44	13.45



Fig. S10. Raman spectra of 3D CN/ND-COOH.



Fig. S11. FT-IR spectra of 3D CN/ND-COOH.



Fig. S12. XPS survey pattern of p-ND, ND-COOH, ND-NH<sub>2</sub>, B-CN, 3D CN, 3D

CN/ND-NH<sub>2</sub>, and 3D CN/ND-COOH.

Table S2. Surface elemental content of ND, CN and composite samples with different

surface functional groups, N/C ratio.					
Sampla	Α	Atomic %		FWHM of sp <sup>3</sup>	N/C ratio
Sample	С	Ν	0	C (eV)	
p-ND	88.31	1.66	10.02	3.44	0.018

ND-COOH	86.83	1.96	11.2	3.7	0.022
ND-NH <sub>2</sub>	90.36	4.01	5.62	2.78	0.714
B-CN	46.57	50.01	3.42	1.15	1.073
3D CN	41.32	55.7	2.61	1.11	1.348
3D CN/ND-NH <sub>2</sub>	41.07	56.4	2.53	1.19	1.373
3D CN/ND-COOH	44.52	51.9	2.74	1.17	1.165



Figure S13. High resolution XPS spectra of B-CN and B-CN/ND-NH<sub>2</sub>: (c) C 1s, and (d) N 1s.

High-resolution XPS of the B-CN and B-CN/ND-NH<sub>2</sub> samples shown in **Fig. S13** revealed that the ND-NH<sub>2</sub> loaded B-CN was significantly altered in terms of peak intensities at C1s and N1s as well as their positions compared with pure B-CN, probably because the bulk g-C<sub>3</sub>N<sub>4</sub> encapsulates the ND material more than there is enough surface area for it to be loaded on, as in the case of 3D CN.



Figure S14. GG spectra of standard gases.

**Fig. S14** shows the gas product curves on FID and TCD for 1 ml of standard gas used with concentrations of CO, methane and hydrogen of 990, 994 and 1000 ppm, respectively, and the data were taken from the median values of multiple injections under the same conditions.



**Figure S15.** The GC spectra of gaseous products of 3D CN/9%wt ND-NH<sub>2</sub> sample during 1 h reaction process.

As shown in **Fig. S15**, the rate of CO generation from 3D CN/NH<sub>2</sub> increased almost linearly over the hour and almost no hydrogen generation was observed, indicating the high selectivity and competitiveness of 3D CN/NH<sub>2</sub> for CO<sub>2</sub> reduction.



**Figure S16.** The comparison of CO and H<sub>2</sub> production rate for B-CN, 3D CN, B-CN/ND-COOH, B-CN/ND-NH<sub>2</sub>, 3D CN/ND-COOH and 3D CN/ND-NH<sub>2</sub>.

		5			
Catalyst	Light source	Solvents	Major products	AQY	Ref.
Pores g-C <sub>3</sub> N <sub>4</sub>	300 W Xe arc lamp	H <sub>2</sub> O	CO: 11.2 µmol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S7]
			$CH_4: 0.45 \ \mu mol \cdot g^{-1} \cdot h^{-1}$		
Hollow fusiform	Xenon lamp (300	H <sub>2</sub> O/TEOA	CO: 0.32 µmol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S8]
g-C <sub>3</sub> N <sub>4</sub>	W) with 420nm		CH <sub>4</sub> : 1.63 µmol·g <sup>-1</sup> ·h <sup>-1</sup>		
	cutoff filter				
Quasi-	Xenon lamp (500	H <sub>2</sub> O	CO: 1.83 µmol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S9]
hexagonal	W) with a filter of		CH <sub>4</sub> : 3.42 µmol·g <sup>-1</sup> ·h <sup>-1</sup>		
prism g-C <sub>3</sub> N <sub>4</sub>	cut-off 400 nm				
HPW/g-C <sub>3</sub> N <sub>4</sub>	Xenon lamp (500	H <sub>2</sub> O	CO: 3.83 $\mu$ mol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S10]
nanosheet	W)				
Hexagonal	Xenon lamp (300	H <sub>2</sub> O/MeCN/TEO	CO: 2.93 $\mu$ mol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S11]
tubes g-C <sub>3</sub> N <sub>4</sub>	W) with 420nm	А	CH <sub>4</sub> : 0.17 µmol·g <sup>-1</sup> ·h <sup>-1</sup>		
	cutoff filter				
Hollow spheres	Xenon lamp (300	H <sub>2</sub> O	CO: 4.2 μmol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S12]
g-C <sub>3</sub> N <sub>4</sub> /CeO <sub>2</sub>	W) with 420nm		CH <sub>4</sub> : 0.83 µmol·g <sup>-1</sup> ·h <sup>-1</sup>		
	cutoff filter				

**Table S3.** Comparison of photocatalytic  $CO_2$  reduction performance based on g- $C_3N_4$ catalysts.

Ti <sub>3</sub> C <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Xenon lamp (300	H <sub>2</sub> O/TEOA	CO: 5.19 μmol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S13]
nanosheet	W) with 420nm		$CH_4{:}0.04\ \mu mol^{\cdot}g^{\text{-1}}{\cdot}h^{\text{-1}}$		
	cutoff filter				
Foam g-	Xenon lamp (300	H <sub>2</sub> O	CO: 8.18 μmol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S14]
C <sub>3</sub> N <sub>4</sub> /Cu <sub>2</sub> O QDs	W)		$CH_4:0.08 \ \mu mol \cdot g^{-1} \cdot h^{-1}$		
Porous tubular	Xenon lamp (300	H <sub>2</sub> O	CO: 10.07 µmol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S15]
yolk-shell g-	W)				
$C_3N_4$					
g-	Xenon lamp (300	H <sub>2</sub> O/TEOA	CO: 1.39 $\mu$ mol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S16]
C <sub>3</sub> N <sub>4</sub> /Ag/CeO <sub>2</sub>	W) with 420nm		CH <sub>4</sub> :0.74 µmol·g <sup>-</sup>		
	cutoff filter		<sup>1</sup> ·h <sup>-1</sup>		
Cu/S doped g-	500 W Xe arc lamp	H <sub>2</sub> O/TEOA	CO: 4.4 µmol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S17]
$C_3N_4$			$CH_4{:}0.57\ \mu mol\cdot g^{\text{-}1}{\cdot}h^{\text{-}1}$		
Pd nano-	Xenon lamp (300	H <sub>2</sub> O	CO: 4.4 µmol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S18]
icosahedrons /g-	W) with 420nm		$CH_4:0.57 \ \mu mol \cdot g^{-1} \cdot h^{-1}$		
$C_3N_4$	cutoff filter				
Pd-Ag/g-C <sub>3</sub> N <sub>4</sub>	Xenon lamp (100 W,	H <sub>2</sub> O/TEOA	CO: 5.42 $\mu$ mol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S19]
	AM 1.5)		$CH_4:4.03 \ \mu mol \cdot g^{-1} \cdot h^{-1}$		
Au/g-C <sub>3</sub> N <sub>4</sub>	8 W Hg lamp	H <sub>2</sub> O/TEOA	CO: 8.61 µmol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S20]
			CH <sub>4</sub> :4.81 $\mu$ mol $\cdot$ g <sup>-1</sup> $\cdot$ h <sup>-1</sup>		
Single-atom	Xenon lamp (300 W,	H <sub>2</sub> O	CO: 11.21 µmol·g <sup>-1</sup> ·h <sup>-1</sup>	N/A	[S21]
$Cu/g-C_3N_4$	AM 1.5)		CH4:0.61 $\mu$ mol $\cdot$ g <sup>-1</sup> ·h <sup>-1</sup>		
3D CN/ND-NH <sub>2</sub>	Xenon lamp (300	H <sub>2</sub> O/MeCN/TEO	CO: 13.81 µmol·g <sup>-1</sup> ·h <sup>-1</sup>	1.40%	This
	W) with 420nm	А			work
	cutoff filter				



**Fig. S17**. High-resolution XPS spectra of (a) C 1s for ND-COOH and ND-NH<sub>2</sub>, (b) O 1s for ND-COOH and (c) N 1s for ND-NH<sub>2</sub> after 4 h photocatalytic testing.



Fig. S18. High-resolution XPS spectra of (a) C 1s, and (b) N 1s for D CN/9%wt ND-

NH<sub>2</sub> sample after cyclic photocatalytic testing.



Fig. S19. Photoluminescence (PL) spectra of B-CN, 3D CN, and 3D CN/ND-NH<sub>2</sub>.



Fig. S20. AFM image of 3D CN/ND-NH<sub>2</sub> in darkness.



**Fig. S21.** Refractive index and extinction coefficient of (a) g-C<sub>3</sub>N<sub>4</sub> and (b) diamond; Behavior of light when propagating through (c) g-C<sub>3</sub>N<sub>4</sub> and diamond loaded g-C<sub>3</sub>N<sub>4</sub> interface by FDTD simulation.

As shown in Fig. S21, the results of the FDTD light absorption simulations carried

out indicate that the intrinsic photon absorption at the  $g-C_3N_4$  interface alone is rather limited, and when combined with the ND, a strong scattering effect of photons occurs at the resulting interface, which contributes to the enhancement of the overall light absorption properties.



Fig. S22. Photocurrent response of B-CN, B-CN/COOH, and B-CN/ND-NH<sub>2</sub>.

As shown in **Fig. S22**, when ND-based nanoparticles are introduced into B-CN, the photocurrents of the composites are all elevated, but their decay rates are also stronger than that of B-CN alone, suggesting that there are more defects in the composite of B-CN with the ND-based material, which receives a constraint on the carrier migration.



**Fig. S23.** UV–VIS diffuse reflectance spectra (DRS) and band gap energies (inset image) of B-CN, 3D CN, 3D CN/ND-NH<sub>2</sub>, and 3D CN/ND-COOH.

As shown in **Fig. S23**, a significant blue shift of absorption band appears in 3D CN owing to the well-known quantum confinement effect, and the bandgap of 3D CN is calculated as 2.96 eV by Kubelka-Munk function, albeit larger than that of B-CN, which generally means a stronger redox ability of 3D CN. Meanwhile, the band gap of ND-NH<sub>2</sub>-modified 3D CN was slightly smaller than that of ND-COOH-modified 3D CN, indicating that ND-NH<sub>2</sub> increased its light-absorbing ability while retaining the strong reducing ability of 3D CN/NH<sub>2</sub>.



**Fig. S24.** (a) Photograph of B-CN, B-CN/ND-COOH and B-CN/ND-NH<sub>2</sub>. (b) Photograph of p-ND, ND-COOH and ND-NH<sub>2</sub>.

As shown in **Fig. S24**, the appearance of pure p-ND and ND-COOH is similar, while the powder of pure ND-NH<sub>2</sub> exhibits a dark black color, indicating stronger lightabsorbing properties, and B-CN compounded with three different ND-based materials also transforms B-CN/ND-NH<sub>2</sub> from a light-yellow color to a gray-yellow color, indicating enhanced light-trapping ability.



Fig. S25. (a) UV-Vis diffuse reflectance spectra and (b) corresponding Tauc plots of B-CN, B-CN/ND-COOH and B-CN/ND-NH<sub>2</sub>.

The UV-vis curves and Tauc curves shown in the **Fig. S25** verify the above statement that the introduction of ND-NH<sub>2</sub> into both 3D CN and B-CN materials shows the most excellent light-absorbing properties, which is attributed to the almost full-spectrum absorption in the UV-visible range of ND-NH<sub>2</sub>.



Fig. S26. XPS valence band spectra of B-CN and 3D CN.



Fig. S27. Motto-Schottky plots of (a) B-CN, (b) 3D CN, (c) ND-NH<sub>2</sub>, and (d) ND-

$\boldsymbol{\cap}$	റ	റ	L	г
U	U	U	Г	1

Samples	band gap (eV)	Flat band (V vs. Ag/AgCl)	Conduction band (V vs. NHE pH=7.0)	Valence band (V vs. NHE pH=7.0)
B-CN	2.73	-1.17	-0.91	1.82
3D CN	2.96	-1.38	-1.07	1.79
p-ND	2.93	-0.52	-0.58	2.35
ND-NH <sub>2</sub>	2.38	-0.65	-1.28	1.10
ND-COOH	2.73	-0.43	-0.50	2.23

Table S4. Band gap and energy band potentials of all samples.



Fig. S28. Band structures of B-CN, 3D CN, p-ND, ND-NH<sub>2</sub>, and ND-COOH.



Fig. S29. EPR spectra of B-CN,3D CN and 3D CN/ND-NH<sub>2</sub> samples at room

temperature.



**Fig. S30.** Initial computed of crystal cells of (a) (b) bulk nanodiamond and (c) (d) graphitic carbon nitride model (mp-66, mp-971648, respectively).



**Fig. S31.** Top view and Top oblique view of the geometric structure of (a) g-C<sub>3</sub>N<sub>4</sub>/ND, (b)g-C<sub>3</sub>N<sub>4</sub>/ND-NH<sub>2</sub> and (c) g-C<sub>3</sub>N<sub>4</sub>/ND-COOH model.

As shown in **Fig. S30**, based on the computed cells in **Fig. S31** above, the (111) crystalline surface of the bulk nanodiamond was first cut out, and after cell expansion, different functional groups were modified on one layer of the modified surface, and the other side was saturated with pseudo-hydrogen, whereas, for the graphitic carbon nitride, one layer was deleted, and the nearest surface atoms to the nanodiamond were made to be 3 Å after entering into the school and expanding the cell, and at the same time, the van der Waals heterojunction was ensured to be formed with the lattice aberration of no more than 5%.



**Fig. S32.** The macroscopic average and planar average of the electrostatic potential for the (a) g-C<sub>3</sub>N<sub>4</sub>/ND and (b) g-C<sub>3</sub>N<sub>4</sub>/ND-COOH.

As shown in **Fig. S32**, the work function of the g-C<sub>3</sub>N<sub>4</sub>/ND-COOH model, although higher than that of g-C<sub>3</sub>N<sub>4</sub>/ND-NH<sub>2</sub>, is still lower than that of the g-C<sub>3</sub>N<sub>4</sub>/ND model, suggesting that different types of functional groups have easy electron escape from the surface of the heterojunction to participate in the reaction.



Fig. S33. (a) The charge density difference  $(0.001 \text{ e} \cdot \text{Å}^{-3})$  and (b) planar-averaged electron density difference  $\Delta \rho(z)$  for g-C<sub>3</sub>N<sub>4</sub>/ND; (c) The charge density difference  $(0.001 \text{ e} \cdot \text{Å}^{-3})$  and (b) planar-averaged electron density difference  $\Delta \rho(z)$  for g-C<sub>3</sub>N<sub>4</sub>/ND-COOH. The yellow and cyan areas indicate electron accumulation and depletion, respectively.

As shown in **Fig. S33**, the differential charge on the g-C<sub>3</sub>N<sub>4</sub>/ND surface is mostly concentrated on the nanodiamond surface despite a more pronounced charge transfer, and the charge distribution on the carbon nitride surface of the graphite phase is very sparse, whereas g-C<sub>3</sub>N<sub>4</sub>/ND-COOH exhibits a similar surface charge distribution to that of g-C<sub>3</sub>N<sub>4</sub>/ND-NH<sub>2</sub>.



Fig. S34. PDOS of layer (a) g-C<sub>3</sub>N<sub>4</sub>/ND and (b) g-C<sub>3</sub>N<sub>4</sub>/ND-COOH heterostructure.

It can be observed in **Fig. S34** that the CBM in the  $g-C_3N_4/ND$ -COOH model is mainly contributed by the N 2p orbitals, whereas after composite the VBM undergoes a more pronounced change due to the introduction of a large number of C atoms in the surface carboxylate group, which is mainly contributed by the C 2p orbitals.



**Fig. S35.** CO<sub>2</sub> molecules adsorbed at top and side views of (a) g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>/ND, g-C<sub>3</sub>N<sub>4</sub>/ND-COOH, and g-C<sub>3</sub>N<sub>4</sub>/ND-NH<sub>2</sub> of the constructed model.



Fig. S36. CO<sub>2</sub>-TPD profiles of B-CN, 3D CN, 3D CN/ND-NH<sub>2</sub>, and 3D CN/ND-CO

# **References:**

[S1] Kresse, G.; Furthmuller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys Rev B Condens Matter*. **1996**, *54* (16), 11169-11186.

[S2] John P. Perdew, K. B. M. E. Generalized Gradient Approximation Made Simple. *Phys Rev Lett.* **1996**, *18* (77).

[S3] Blochl, P. E. Projector Augmented-Wave Method. Phys Rev B. 1994, 24 (50).

[S4] Moellmann, J.; Grimme, S. DFT-D3 Study of some Molecular Crystals. J. Phys Chem C. 2014, 118 (14), 7615-7621.

[S5] Momma, K.; Izumi, F. Vesta 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. *J. Appl Crystallogr.* **2011**, *44* (6), 1272-1276.

[S6] Wang, Y.; Fan, G.; Wang, S.; Li, Y.; Guo, Y.; Luan, D.; Gu, X.; Lou, X. W. D. Implanting CoO<sub>x</sub> Clusters on Ordered Macroporous ZnO Nanoreactors for Efficient CO<sub>2</sub> Photoreduction. *Adv Mater.* **2022**, *34* (42), 2204865.

[S7] Liu, M.; Wageh, S.; Al-Ghamdi, A. A.; Xia, P.; Cheng, B.; Zhang, L.; Yu, J. Quenching Induced Hierarchical 3D Porous g-C<sub>3</sub>N<sub>4</sub> with Enhanced Photocatalytic CO<sub>2</sub> Reduction Activity. *Chem Commun.* **2019**, *55* (93), 14023-14026.

[S8] Jiang, Z.; Zhang, X.; Chen, H. S.; Yang, P.; Jiang, S. P. Fusiform-Shaped g-C<sub>3</sub>N<sub>4</sub> Capsules with Superior Photocatalytic Activity. *Small.* **2020**, *16* (42), 2003910. [S9] He, Z.; Wang, D.; Tang, J.; Song, S.; Chen, J.; Tao, X. A Quasi-Hexagonal Prism-Shaped Carbon Nitride for Photoreduction of Carbon Dioxide Under Visible Light. *Environ Sci Pollut R.* **2017**, *24* (9), 8219-8229.

[S10] Jiang, X.; Zhang, Z.; Sun, M.; Liu, W.; Huang, J.; Xu, H. Self-Assembly of Highly-Dispersed Phosphotungstic Acid Clusters onto Graphitic Carbon Nitride Nanosheets as Fascinating Molecular-Scale Z-Scheme Heterojunctions for Photocatalytic Solar-to-Fuels Conversion. *Appl Catal B*. **2021**, *281*, 119473.

[S11] Wan, S.; Ou, M.; Zhong, Q.; Cai, W. Haloid Acid Induced Carbon Nitride Semiconductors for Enhanced Photocatalytic H<sub>2</sub> Evolution and Reduction of CO<sub>2</sub> Under Visible Light. *Carbon.* 2018, *138*, 465-474.

[S12] Liang, M.; Borjigin, T.; Zhang, Y.; Liu, B.; Liu, H.; Guo, H. Controlled Assemble of Hollow Heterostructured g-C<sub>3</sub>N<sub>4</sub>@CeO<sub>2</sub> with Rich Oxygen Vacancies for Enhanced Photocatalytic CO<sub>2</sub> Reduction. *Appl Catal B.* **2019**, *243*, 566-575.

[S13] Yang, C.; Tan, Q.; Li, Q.; Zhou, J.; Fan, J.; Li, B.; Sun, J.; Lv, K. 2D/2D Ti<sub>3</sub>C<sub>2</sub>
Mxene/g-C<sub>3</sub>N<sub>4</sub> Nanosheets Heterojunction for high Efficient CO<sub>2</sub> Reduction
Photocatalyst: Dual Effects of Urea. *Appl Catal B.* 2020, *268*, 118738.

[S14] Sun, Z.; Fang, W.; Zhao, L.; Chen, H.; He, X.; Li, W.; Tian, P.; Huang, Z. g-C<sub>3</sub>N<sub>4</sub> Foam/Cu<sub>2</sub>O Qds with Excellent CO<sub>2</sub> Adsorption and Synergistic Catalytic Effect for Photocatalytic CO<sub>2</sub> Reduction. *Environ Int.* **2019**, *130*, 104898.

[S15] Tian, N.; Xiao, K.; Zhang, Y.; Lu, X.; Ye, L.; Gao, P.; Ma, T.; Huang, H. Reactive Sites Rich Porous Tubular Yolk-Shell g-C<sub>3</sub>N<sub>4</sub> Via Precursor Recrystallization Mediated Microstructure Engineering for Photoreduction. *Appl Catal B.* 2019, 253, 196-205.

[S16] Wang, H.; Guan, J.; Li, J.; Li, X.; Ma, C.; Huo, P.; Yan, Y. Fabricated g-C<sub>3</sub>N<sub>4</sub>/Ag/M-CeO<sub>2</sub> Composite Photocatalyst for Enhanced Photoconversion of CO<sub>2</sub>. *Appl Surf Sci.* 2020, *506*, 144931.

[S17] Ojha, N.; Bajpai, A.; Kumar, S. Visible Light-Driven Enhanced CO<sub>2</sub> Reduction by Water Over Cu Modified S-Doped g-C<sub>3</sub>N<sub>4</sub>. *Catal Sci Technol.* 2019, *9* (17), 4598-4613.

[S18] Lang, Q.; Hu, W.; Zhou, P.; Huang, T.; Zhong, S.; Yang, L.; Chen, J.; Bai, S.

Twin Defects Engineered Pd Cocatalyst on  $C_3N_4$  Nanosheets for Enhanced Photocatalytic Performance in CO<sub>2</sub> Reduction Reaction. *Nanotechnology*. **2017**, *28* (48), 484003-484003.

[S19] Wang, Z.; Lee, H.; Chen, J.; Wu, M.; Leung, D. Y. C.; Grimes, C. A.; Lu, Z.; Xu, Z.; Feng, S. Synergistic Effects of Pd–Ag Bimetals and g-C<sub>3</sub>N<sub>4</sub> Photocatalysts for Selective and Efficient Conversion of Gaseous CO<sub>2</sub>. *J Power Sources*. **2020**, *466*, 228306.

[S20] Li, X.; Liu, C.; Wu, D.; Li, J.; Huo, P.; Wang, H. Improved Charge Transfer by Size-Dependent Plasmonic Au on g-C<sub>3</sub>N<sub>4</sub> for Efficient Photocatalytic Oxidation of Rhb and CO<sub>2</sub> Reduction. *Chinese Journal of Catalysis*. **2019**, *40* (6), 928-939.

[S21] Wang, J.; Heil, T.; Zhu, B.; Tung, C.; Yu, J.; Chen, H. M.; Antonietti, M.; Cao,
S. A Single Cu-Center Containing Enzyme-Mimic Enabling Full Photosynthesis Under
CO<sub>2</sub> Reduction. *Acs Nano.* 2020, *14* (7), 8584-8593.