## Electronic Supplementary Information

# N-CNDs modified NH<sub>2</sub>-UiO-66 for photocatalytic CO<sub>2</sub> conversion under visible light by a photo-induced electron transfer process

Liyong Chen,\*a Fengyang Yua, Xiaoshuang Shen,<sup>b</sup> and Chunying Duan\*a

#### **Experimental section**

### Materials and characterization methods

All chemical reagents were used as received and were commercially available. Copper specimen grids (300 mesh) were purchased from Beijing XXBR Technology Co. Transmission electron microscopy (TEM), and scanning electron microscopy (SEM) were performed for structural and morphological characterization on Tecnai F30, and HITACHI

performed for structural and morphological characterization on Tecnai F30, and HITACHI UHR FE-SEM SU8220, respectively. X-ray diffraction (XRD) was carried out with a Rigaku D/Max 2400 automatic powder X-ray diffractometer with Cu- $K\alpha$  radiation ( $\lambda = 1.5418$  Å). X-ray photoelectron spectroscopy was conducted on Thermo ESCALAB 250Xi with Al-K $\alpha$  radiation (hv = 1486.6 eV). Electron spin resonance (ESR) spectra were carried out on Bruker A200 upon irradiation at room temperature. UV-vis absorption spectra and photoluminescence (PL) emission spectra/time-resolved PL spectra were measured on HITACHI U-4100 spectrometer and FLS 920 fluorescence spectrometer, respectively. N<sub>2</sub> sorption isotherm at 77 K and CO<sub>2</sub> adsorption isotherm at 273 K were carried out Micromeritics 3Flex Surface Characterization Analyzer after being degassed in vacuum at 200 °C for 12 h. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Optima 2000DV was used to estimate the amount of Zr in aqueous solution. Electrochemical/photoelectrochemical measurements were conducted on a CHI760E electrochemical workstation with a typical three-electrode cell. Electrochemical impedance spectroscopy (EIS) was performed on a ZAHNER ENNIUM electrochemical workstation.

#### Synthesis of nitrogen-doped carbon nanodots (N-CNDs)

Citric acid monohydrate (2.1 g, 10 mmol) and triethanolamine (1.49 g, 10 mmol) were added into a 20 mL Teflon-lined stainless autoclave and heated at 180 °C for 6 h. The resulting mixture was dispersed in 50 mL deionized water and then dialysed four times in 1 L deionized water. Finally, the reddish brown powder was separated by a freeze-drying treatment process.

#### Synthesis of NH<sub>2</sub>-UiO-66 nanocrystals

In a typical synthetic procedure,  $ZrCl_4$  (0.087 mmol) and 2-aminoterephthalate acid (ATA) (0.065 mmol) were dissolved in DMF (15 mL) including HAc (1.2 mL) and sonicated for 20 min. The resulting solution was transferred into a 20 mL Teflon-lined stainless autoclave and heated at 120 °C for 24 h. The final sample was cooled down to room temperature naturally, collected by centrifugation at 5000 *g* for 5 min, washed several times with ethanol, and dried under vacuum at 100 °C for 12 h before it was subjected to characterization.

UiO-66 octahedra were prepared while terephthalic acid (0.065 mmol) was used to replace ATA under otherwise identical condition.

#### Synthesis of N-CNDs/NH<sub>2</sub>-UiO-66 composites

ZrCl<sub>4</sub> (0.087 mmol) and 2-aminoterephthalate acid (ATA) (0.065 mmol) were dissolved in DMF (15 mL) containing HAc (1.2 mL). Afterwards, N-CNDs (0.1 mg) dissolved in DMF (1 mL) was introduced into the aforementioned mixture with sonication for 20 min. The resulting solution was

transferred into a 20 mL Teflon-lined stainless autoclave and heated at 120 °C for 24 h. The final sample was cooled down to room temperature naturally, collected by centrifugation at 5000 g for 5 min, washed several times with ethanol, and dried under vacuum at 100 °C for 12 h.

N-CNDs/UiO-66 composites were prepared while terephthalic acid (0.065 mmol) was used to replace ATA under otherwise identical condition.

#### Photocatalytic CO<sub>2</sub> reduction measurements

N-CNDs/NH<sub>2</sub>-UiO-66 powders were incubated in ethanol for 24 h to remove residual DMF and other guest species adsorbing on internal pores following drying under vacuum at 120 °C for 12 h before being used as photocatalysts for CO<sub>2</sub> reduction. The photocatalyst powder (2 mg) was dispersed into a 20 mL quartz glass reactor containing 4 mL of acetonitrile and 1 mL of ethanol. Before light irradiation, the reactor was sealed with a rubber septum after being bubbled carefully with CO<sub>2</sub> for 30 min. The photocatalytic system was irradiated using a xenon lamp (300 W, Beijing Perfectlight Technology Co. Ltd) with a UV-cutoff filter for 2 h under magnetic stirring and kept at room temperature with a condensation water system. The final mixture was treated by centrifugation to remove the photocatalysts and by rotary evaporation to remove solvent. After adding deionized water (10 mL), the liquid product was analyzed by ion chromatograph (Dionex ICS-5000). The gas product taken from the reactor by a syring was analysed using a gas chromatograph (GC7900 Techcomp) equipped with a flame ionized detector and methanizer; liquid product was analysed by nuclear magnetic resonance spectroscopy (Varian INOVA 400MHz).

The collected photocatalysts were repeatedly used without further treatment.



Fig. S1 N-CNDs: (a) TEM image (inset is HRTEM image, and scale bar is 2 nm), (b) UV-vis absorption spectrum and (c) PL spectra with different excitation wavelength.



Fig. 3 Raman spectrum of N-CNDs.



Fig. S3 High resolution XPS spectra of C1s and N1s: (a, d) N-CNDs, (b, e) NH<sub>2</sub>-UiO-66, and (c, f) N-CNDs/NH<sub>2</sub>-UiO-66.



Fig. S4 Time-resolved PL spectra of N-CNDs, NH2-UiO-66, and N-CNDs/NH2-UiO-66



Fig. S5  $N_2$  physisorption isotherms at 77 K: (a) NH<sub>2</sub>-UiO-66 and (b) N-CNDs/NH<sub>2</sub>-UiO-66. (c) CO<sub>2</sub> adsorption isotherms of NH<sub>2</sub>-UiO-66 and N-CNDs/NH<sub>2</sub>-UiO-66 at 273 K, respectively.

Nitrogen sorption isotherm measured at 77 K was used to analyse the specific surface area, and pore size distribution of both samples. Type I isotherms of NH<sub>2</sub>-UiO-66 and N-CNDs/NH<sub>2</sub>-UiO-66 composites reveals their microporous structures. The Brunauer-Emmett-Teller (BET) surface areas of 983  $m^2/g$  for NH<sub>2</sub>-UiO-66 and 835  $m^2/g$  for N-CNDs/NH<sub>2</sub>-UiO-66 were calculated.



Fig. S6 pore size distribution of (a) NH<sub>2</sub>-UiO-66 and (b) N-CNDs/NH<sub>2</sub>-UiO-66.

Albeit N-CNDs implanted in MOF matrices led to decrease of surface area, pore width of  $\sim$ 0.61 nm for N-CNDs/NH<sub>2</sub>-UiO-66 was almost kept unchanged as compared to pure NH<sub>2</sub>-UiO-66.



Fig. S7  $CO_2$  adsorption isotherm of UiO-66 at 273 K.



Fig. S8 Photocatalytic activity of N-CNDs/NH<sub>2</sub>-UiO-66 composites with different amount of N-CNDs added in synthetic system of NH<sub>2</sub>-UiO-66.



Fig. S9 Photocatalytic activity of N-CNDs/NH $_2$ -UiO-66 upon different wavelength light illumination.



Fig. S10 (a) TEM and (b) SEM images and (c) XRD pattern of N-CNDs/NH<sub>2</sub>-UiO-66 composites used repeatedly for all stability tests. Inset is the HRTEM image of N-CNDs in the composites (scale bar is 2 nm).



Fig. S11 (a) Transient photocurrent response, and (b) Nyquist plots of N-CNDs/ $NH_2$ -UiO-66 and N-CNDs; Mott-Schottky plots of (c)  $NH_2$ -UiO-66 and (d) N-CNDs.



Fig. S12 TEM images of (a) UiO-66 and (b) N-CNDs/UiO-66 composites; (c) UV-vis spectrum of UiO-66 and PL spectrum of N-CNDs, and (d) photocatalytic performance of UiO-66 and N-CNDs/UiO-66 towards  $CO_2$  reduction. Inset is the HRTEM image of N-CNDs in the composites (scale bar is 2 nm).



 $Fig. \ S13 \quad ESR \ spectra \ of \ NH_2-UiO-66 \ and \ N-CNDs/NH_2-UiO-66 \ upon \ visible-light \ irradiation.$ 



Fig. S14 Tauc plot of N-CNDs.

Photocatalyst	Light	Solvent Sacrificial agent	Rate of HCOOH (µmol g <sup>.1</sup> h <sup>.1</sup> )	Referenc e
NH <sub>2</sub> -MIL-125(Ti)	420-800 nm	MeCN TEOA	16.3	1
MOF-253-Ru(5,5'- dcbpy)(CO) <sub>2</sub> Cl <sub>2</sub>	420-800 nm	MeCN TEOA	16.8	2
PCN-222	420-800 nm	MeCN TEOA	60	3
Pt/NH2-MIL-125(Ti)	420-800 nm	MeCN TEOA	32.4	4
(NH <sub>2</sub> ) <sub>2</sub> -UiO-66(Zr/Ti)	420-800 nm	MeCN TEOA/BNAH	$1052.3 \pm 54.7$	5
$\label{eq:cd2} \begin{split} &\{Cd_2[Ru(4,4'\text{-}$$$ dcbpy)_3]\text{-}12H_2O\}_n \end{split}$	420-800 nm	MeCN TEOA	77.2	6
NH <sub>2</sub> -UiO-66/GR	>410 nm	DMF TEOA	418	7
NH <sub>2</sub> -UiO-66	420-800 nm	MeCN TEOA	26.4	8
O-ZnO/rGO/ NH <sub>2</sub> -UiO- 66	>420 nm	H <sub>2</sub> O no	6.4	9
N-CNDs/NH <sub>2</sub> -UiO-66	400-800 nm	MeCN EtOH	10.9	This work
N-CNDs/NH <sub>2</sub> -UiO-66	400-800 nm	MeCN TEOA	~80	This work

Table S1 Comparison of MOF-based photocatalysts towards CO<sub>2</sub> reduction.

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Photocatalyst	Product	Photosensitizer Sacrificial agent	AQY (%)	Reference
ZnS	НСООН	no Na <sub>2</sub> S	1.44 (330 nm)	1
UiO-67- Mn(bpy)(CO) <sub>3</sub> Br	НСООН	[Ru(dmb) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub> BNAH/TEOA	13.8 (470 nm)	2
fac-Mn(bpy)(CO) <sub>3</sub> Br	НСООН	[Ru(dmb) <sub>3</sub> ] <sup>2+</sup> TEOA	5.3 (480 nm)	3
Ni MOLs	СО	Ru(bpy)3 <sup>2+</sup> TEOA	2.2 (420 nm)	4
ZnS:Ni nanocrystals	НСООН	no K <sub>2</sub> SO <sub>3</sub>	59.1 (340 nm); 5.6 (420 nm)	5
Au/Pt/carbon	НСООН	Ru(bpy)3 <sup>2+</sup> EDTA	0.3 (visible)	6
RuReCl	НСООН	Ru(II) complex sodium ascorbate	0.2 (546 nm)	7
N-CNDs/NH <sub>2</sub> -UiO-66	НСООН	no ethanol	0.74 (420 nm)	This work
N-CNDs/NH <sub>2</sub> -UiO-66	НСООН	no TEOA	~6.8 (420 nm)	This work

Table S2 Comparison of AQY for different photocatalysts towards CO<sub>2</sub> reduction.

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