## Supplementary Information

## Enhanced Photochemical CO<sub>2</sub> Reduction in the Gas Phase by Graphdiyne

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## **Experimental Section**

**Sample preparation.** CdS/GDY (CdGDY) and CdS/graphene (CdG) were prepared by a solvothermal method. GO was synthesized from natural graphite powder by a modified Hummers' method.<sup>1</sup> Graphdiyne (GDY) was synthesized on the surface of copper via a cross-coupling reaction using hexaethynylbenzene as the precursor.<sup>2</sup> 1 mmol of Cd(Ac)<sub>2</sub>·2H<sub>2</sub>O and a known amount of GDY were dispersed in 60 mL of dimethyl sulfoxide (DMSO). After ultrasonic treatment for 30 min, the homogeneous solution was transferred into a 100 mL Teflon-lined autoclave and kept at 180 °C for 12 h. The obtained precipitates were then washed with acetone and ethanol several times to remove residual DMSO, and dried in an oven at 60 °C for 12 h. The nominal mass ratios of GDY to CdS were set as 0, 0.5% and 1.0%, and the samples were labeled as CdS, CdGDY-0.5 and CdGDY-1, respectively. CdG samples were prepared under similar experimental conditions except that graphdiyne was replaced by graphene oxide. These were denoted as CdG-0.5 and CdG-1.

**Material characterization.** The morphology of the samples was observed by transmission electron microscopy (TEM, Titan G<sup>2</sup>, FEI, USA). Field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDS) mapping images of samples were taken on a scanning electron microscope (7500F, JEOL, Japan). X-ray diffraction (XRD) patterns were collected on a D/Max-RB X-ray diffractometer (Rigaku, Japan). Raman spectra were collected on a micro-Raman spectrometer (InVia, Renishaw, England) with a 514 nm Ar<sup>+</sup> laser as the excitation source. X-ray photoelectron spectroscopy (XPS) measurements were performed using an electron spectrometer (ESCALAB 210, VG Scientific, UK) with Mg K $\alpha$  radiation. The XPS binding-energy range was calibrated by shifting the main C–C peak to 284.8 eV and all data processing was performed using XPSPEAK41 software. Electron paramagnetic resonance (EPR) spectroscopy was performed on a benchtop EPR spectrometer (EMX-Nano, Bruker, Germany) equipped with a variable-temperature cryostat (Oxford). Nitrogen adsorption-desorption experiments

were performed at 77K using a surface area and porosity analyser (ASAP 3020, Micromeritics Instrument, USA). Specific surface area was determined by the multipoint Brunauer–Emmett–Teller (BET) method using adsorption data in the relative pressure ( $P/P_0$ ) range from 0.05 to 0.3, and pore size distributions were calculated from desorption data by the Barrett–Joyner–Halenda (BJH) method. UV-visible diffuse reflectance spectra were obtained using a UV-2600 spectrophotometer (Shimadzu, Japan) with BaSO<sub>4</sub> as reference. Steady-state photoluminescence (PL) spectra were acquired on a fluorescence spectrophotometer (F-7000, Hitachi, Japan) with 425 nm excitation light source. Nicolet iS50 spectrometer (Instrument, US) was used to record the in-situ infrared Fourier transform spectra (in-situ FTIR) during the photocatalytic reaction.

Time-resolved photoluminescence (TRPL) spectra were collected on a customized time-correlated single photon counting apparatus. The second harmonic (395 nm) of the output of a Spectra Physics 1 kHz amplified femtosecond Ti:sapphire laser was used as the excitation source. The emission was collected with the help of a Princeton Instruments SP2358 monochromator and using a Hamamatsu R3809U-50 MCP-PMT detector. The detected signal was then amplified by a preamplifier (Becher & Hickl GmbH HFAC-26). The output of the preamplifier and that from a fast PicoQuant TDA 200 photodiode were then connected to a Becher & Hickl GmbH SPC-130 module as the start and stop pulses, respectively. The instrumental response function (IRF) of this setup was ~70 ps.

Data were fitted to biexponential decay kinetics as shown in the following equation:

$$y(t) = A_1 \times \exp\left(\frac{-t}{\tau_1}\right) + A_2 \times \exp\left(\frac{-t}{\tau_2}\right) + y_0 \qquad (1)$$

Where  $A_1$  and  $A_2$  denote pre-exponentials related to the concentration of emitting species,  $\tau_1$  and  $\tau_2$  are the corresponding lifetimes, *t* is the measurement time, and *y*(*t*) is the number of photon counts at time *t*.

The average lifetime  $(\tau_m)$  is calculated by the following equation:

$$\tau_m = \frac{\sum_{i=1}^n A_i \tau_i^2}{\sum_{i=1}^n A_i \tau_i} \qquad (2)$$

**Photocatalytic CO<sub>2</sub> reduction activity tests.** Photocatalytic CO<sub>2</sub> reduction tests were carried out in a two-necked 200 mL Pyrex glass reactor. A 350 W Xe arc lamp with an AM1.5 filter (light intensity =  $100 \text{ mW/cm}^2$ ) was used as the light source and positioned 10 cm above the reactor. In a typical photocatalytic experiment, 20 mg of the sample was dispersed in 10 mL of deionized water, and dried at 80 °C for 4 h to

form a uniform film on the bottom surface of the reactor. NaHCO<sub>3</sub> (84 mg) was added into a groove at one of the necks. After purging with nitrogen for 30 min, 0.3 mL of  $H_2SO_4$  (2 mol L<sup>-1</sup>) was injected into the groove and allowed to react with NaHCO<sub>3</sub> to produce CO<sub>2</sub> and H<sub>2</sub>O. The reactor was then irradiated using a Xe lamp and the gaseous products were detected by a gas chromatograph equipped with a FID and TCD detectors, and a methanizer (PGC-80, PANNA, CHINA). The concentrations of the different gases in the mixture were calculated using the external standard method with respect to peak areas; isotope tracer experiments were performed under identical conditions and the produced gases were detected using a gas chromatography–mass spectrometer (6890N–5975, Agilent, American).

**Photoelectrochemical characterization.** Photoelectrochemical tests were performed on a three-electrode electrochemical workstation (CHI660C, Chenhua Instrument, China), with a Pt sheet as the counter electrode, Ag/AgCl electrode as the reference electrode, fluorine-doped tin oxide (FTO) glass with a sample film on the conductive surface as the working electrode, and 0.1 M sodium phosphate buffer (pH = 7) as electrolyte. The light source was a Xenon arc lamp (CHF-XM-500W, Beijing Changtuo Co., Ltd., China). Open circuit voltages were set as the initial bias voltages in transient photocurrent response and electrochemical impedance spectroscopic (EIS) tests. EIS spectra were analyzed based on the corresponding analog equivalent circuit with  $R_s$ ,  $R_t$ , representing, respectively, resistance of the electrolyte solution, and the charge-transfer resistance of the working electrode, and CPE is the constant phase element in parallel with a double capacitance.

Mott–Schottky curves were scanned at 5 mV/s from -1.0 V to 1.0 V (vs. Ag/AgCl, pH = 7) at 500 Hz. The correlation between the density of charge carriers ( $N_d$ ) and Mott–Schottky curves can be determined using the following equation:

$$\frac{1}{C_{sc}^{-2}} = \frac{2}{\epsilon\epsilon_0 e N_d A^2} \left( E - E_{fb} - \frac{kT}{e} \right)$$

where  $C_{sc}$  represents the space-charge capacitance,  $E_{fb}$  denotes the flat band potential,  $\varepsilon$  is the dielectric constant, A is the contacting area between the sample and the solution, E is the applied voltage and T is the thermodynamic temperature.  $\varepsilon_0$ , e and k are, respectively, the permittivity of vacuum (8.854 × 10<sup>-12</sup> F m<sup>-1</sup>), electronic charge unit (1.602 × 10<sup>-19</sup> C) and Boltzmann constant (1.38 × 10<sup>-23</sup> J k<sup>-1</sup>). Obviously,  $N_d$  is inversely proportional to the slope of the Mott–Schottky curves.

**Computation Methods.** The density functional theory (DFT) calculations were carried out by using the VASP code. The exchange-correlation interaction was described by generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional. The energy cutoff was set as 400 eV. The Monkhorst–Pack k-point mesh was set as  $2 \times 2 \times 1$  and  $3 \times 3 \times 1$  for geometry optimization and

calculation of electronic property, respectively. During the geometry optimization, the convergence tolerance was set as  $1.0 \times 10^{-5}$  eV for energy. For the construction of surface models, a vacuum of 20 Å was used to eliminate interactions between periodic structures. The DFT-D2 method of Grimme was employed to treat the van der Waals (vdW) interaction.

Samples	$S_{\rm BET}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{\rm pore}~({\rm cm}^3~{\rm g}^{-1})$
CdS	75.8	0.11
CdG	100.6	0.17
CdGDY	112.4	0.16

**Table S1.** BET specific surface area ( $S_{\text{BET}}$ ), pore volume ( $V_{\text{pore}}$ ) of pure CdS, CdG and CdGDY.

**Table S2.** The average lifetimes and the relative contributions (%) of PL decay data determined from biexponential fitting.

 Samples	τ <sub>1</sub> (ns) (rel.%)	τ <sub>2</sub> (ns) (rel.%)	$\tau_{m}$ (ns)	
 CdS	0.08 (80.1)	0.49 (19.9)	0.33	
CdG	0.06 (77.0)	0.43 (23.0)	0.31	
CdGDY	0.10 (72.6)	0.66 (27.4)	0.50	

Sample	CO	СН₃ОН	CH <sub>4</sub>	Total CO <sub>2</sub> conversion (Selectivity)	H <sub>2</sub> (Selectivity)
CdS	0.72	0.71	0	1.43 (64%)	1.63 (36%)
CdG-0.5	14.03	0.75	0.19	14.97 (82%)	3.67 (18%)
CdG-1	11.56	1.02	0.13	12.71 (77%)	4.48 (23%)
CdGDY-0.5	16.61	1.79	0.32	18.72 (89%)	2.85 (11%)
CdGDY-1	8.83	4.82	0.69	14.34 (83%)	5.31 (17%)

**Table S3.** The yield of gas products ( $\mu$ mol h<sup>-1</sup> g<sup>-1</sup>) of gas-phase CO<sub>2</sub> reduction over various photocatalysts without any sacrificial agent.

<sup>a</sup>Selectivity is calculated based on the number of consumed electrons of the products.

Table S4. Comparison of gas-phase  $CO_2$  reduction over typical graphene-based

Photocatalysts and total mass	Light source	Products and yield (μmol g <sup>-1</sup> h <sup>-1</sup> )	Ref.
Fe <sub>2</sub> V <sub>4</sub> O <sub>13</sub> /RGO/CdS (25 mg)	$300 \text{ W Xe lamp} \\ (\lambda > 420 \text{ nm})$	CH <sub>4</sub> (2.04)	3
Amine-functionalized graphene/CdS (50 mg)	300 W Xe lamp $(\lambda > 420 \text{ nm})$	CH <sub>4</sub> (2.84)	4
Cu/GO (100 mg)	300 W Xe lamp	CH <sub>3</sub> OH (2.94) CH <sub>3</sub> CHO (3.88)	5
1,1'-bi(2-naphthalene) functionalized graphene quantum dots (100 mg)	300  W Xe lamp ( $\lambda > 420 \text{ nm}$ )	CH <sub>3</sub> OH (0.695)	6
CdS/rGO (100 mg)	300 W Xe lamp $(\lambda > 420 \text{ nm})$	CH <sub>4</sub> (2.51)	7
TiO <sub>2</sub> /graphene (10 mg)	300 W Xe lamp	CO (8.91) CH <sub>4</sub> (1.14)	8
$\begin{array}{llllllllllllllllllllllllllllllllllll$	300 W Xe lamp	CO+CH <sub>4</sub> (0.35)	9
WO <sub>3</sub> /graphene (100 mg)	300 W Xe lamp $(\lambda > 400 \text{ nm})$	CH <sub>4</sub> (1.11)	10

photocatalysts in the absence of any sacrificial agent reported in literatures.



Fig. S1. Schematic diagrams of the structure of graphdiyne and graphene.



Fig. S2. Raman spectra of GDY, CdGDY, CdS, CdG, and GO.



**Fig. S3.** (a) TEM image of GDY; (b) TEM image of CdS; TEM (c) and HRTEM (d) images of CdGDY; TEM (e) and HRTEM (f) images of CdG. HRTEM images in Fig. S3d and f show lattice fringes of 0.341 and 0.205 nm corresponding to the (111) and (220) lattice planes of cubic CdS.



**Fig. S4.** XRD patterns of CdS, CdGDY, and CdG. Peaks at 26.4°, 43.9°, 52.0°, and 70.3° correspond, respectively, to diffraction from (111), (220), (311), and (331) facets of cubic CdS (JCPDS 65-2887). Characteristic diffraction peaks due to carbon species are absent because of the low amount of graphdiyne and graphene in the composites.



**Fig. S5.**  $N_2$  adsorption-desorption isotherms and the corresponding pore size distribution curves of pure CdS, CdGDY and CdG. All samples show type IV nitrogen adsorption-desorption isotherms characteristic of mesoporous adsorbents, based on the IUPAC classification. The shape of the hysteresis loops of CdGDY and CdG are characteristic of a combination of types H2 and H3, associated with inkbottle-like mesopores formed by CdS nanocrystals and slit-like pores formed by non-rigid aggregates of plate-like particles.



**Fig. S6.** FESEM and EDS mapping images of CdGDY (a) and CdG (b) after continuous sonication for 3 hours



Fig. S7. UV-vis diffuse reflectance spectra of CdS, CdGDY, CdG and GDY.



Fig. S8. Mott–Schottky curves of CdS, CdGDY and CdG.



Fig. S9. Steady-state PL spectra of CdS, CdG, and CdGDY.



**Fig. S10.** GC spectra of resulting  $O_2$  after photocatalytic  $CO_2$ -reduction reaction over CdGDY.



Fig. S11. GC–MS analysis of the reaction product CO over CdGDY when using  ${}^{12}CO_2$  and  ${}^{13}CO_2$  as carbon sources



Fig. S12. In-situ FTIR spectra over CdGDY photocatalytic system in the dark (a) and under 365 nm light irradiation (b) for  $CO_2$  reduction.



Fig. S13. Schematic diagram of photocatalytic  $CO_2$  reduction illustrating reaction mechanism.

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