

## Supporting Information

### **Highly effective photoreduction of CO<sub>2</sub> to CO promoted by integration of CdS with molecular redox catalysts through metal–organic frameworks**

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## Experimental Section

**Materials.** Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (A. R. grade), CoCl<sub>2</sub>·6H<sub>2</sub>O (A. R. grade), NiCl<sub>2</sub>·6H<sub>2</sub>O (A. R. grade), N,N-Dimethylformamide (DMF, A. R. grade), ethanol (A. R. grade), acetone (A. R. grade), dimethyl sulfoxide (A. R. grade), tetrahydrofuran (A. R. grade) were provided by Sinopharm Chemical Reagent Co., Ltd. 2,2'-Bipyridine-5,5'-dicarboxylate (purity>99%), tris(2-hydroxyethyl)amine (TEOA, purity>99%), biphenyl-4,4'-dicarboxylic acid (purity>99%), Zirconium tetrachloride (purity>99%) were obtained from J&K Scientific Ltd. Formic acid (purity>96%) was provided by Alfa Aesar China (Tianjin) Co., Ltd.

**Synthesis of UiO-bpy.** The method reported for synthesis of UiO-bpy was used.<sup>[s1]</sup> In the experiment, ZrCl<sub>4</sub> (73.5 mg, 0.318 mmol), 2,2-bipyridine-5,5-dicarboxylic acid (bpydc, 78 mg, 0.312 mmol), HCO<sub>2</sub>H (3 mL), and DMF (30 mL) were charged into a vial and heated at 120 °C for 24 h. The resulting solid was collected, washed with DMF and THF, and then dried overnight at 120 °C under vacuum to obtain white powdery product UiO-bpy. The UiO-67 was prepared using similar method except that the bpydc was replaced by the biphenyl-4, 4'-dicarboxylic acid (75 mg, 0.312 mmol).

**Synthesis of CdS/UiO-bpy.** 0.3 g of UiO-bpy, 30 mg of Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O and 80 ml of DMSO were introduced into a 100 mL flask and stirred for 1 h. Then the mixed solution was poured into a Teflon-lined stainless steel autoclave with 100 mL volume, and maintained at 180 °C for 10 h. After the system was naturally cooled down to room temperature, the obtained yellow suspension was washed by water and ethanol for 6 times and dried overnight at 60 °C under vacuum. The content of CdS nanoparticles was controlled by changing amount of Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O with fixed amount of UiO-bpy (0.3 g). Pure CdS was also prepared via a similar procedure but without the addition of UiO-bpy. The CdS/UiO-67 was also prepared via a similar procedure except that the UiO-bpy was replaced by the UiO-67.

**Synthesis of CdS/UiO-bpy/Co.** In a vial, CoCl<sub>2</sub>·6H<sub>2</sub>O (71.0 mg, 0.30 mmol) was dissolved in 20 mL of THF. CdS/UiO-bpy (100 mg) was added to the CoCl<sub>2</sub>

solution. The resulting suspension was slowly stirred overnight at room temperature. The green solid was then centrifuged and washed with THF for 6 times, and dried overnight at 60 °C under vacuum to obtain the CdS/UiO-bpy/Co. The CdS/UiO-68/Ni was also prepared via a similar procedure except that the  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was replaced by the  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ .

**Synthesis of Co-bpy.** In a vial, 2, 2'-bipyridine (156 mg) and  $\text{CoCl}_2$  (129 mg) were added to acetonitrile (30 mL), and the mixture was heated at 313 K in air. The green powder was collected by filtration and dried under vacuum.

**Materials characterizations.** The microstructures of the catalysts were characterized by scanning electron microscope (SEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL JEM-2100F) equipped with EDS. X-ray photoelectron spectroscopy (XPS) study was carried out on the Thermo Scientific ESCALab 250Xi using a 200W Al-K $\alpha$  radiation. In the analysis chamber, the base pressure was about  $3 \times 10^{-10}$  mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon was used for energy referencing. X-Ray diffraction (XRD) analysis of the samples were performed on a Rigaku D/max-2500 X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 0.15406$  nm) and the scan speed was 5 °/min. The  $\text{N}_2$  adsorption/desorption isotherms were determined using a Micromeritics ASAP 2020 sorptometer operated at 77 K, and then BET surface areas and pore volumes were obtained. The adsorption isotherms of  $\text{CO}_2$  were determined at 298 K in the pressure range of 0-1 atm on a TriStar II 3020 device. The CdS and Co loadings in the catalysts were determined by ICP-AES method (VISTA-MPX). The UV-Vis absorption was measured with a UV-visible spectrophotometer (Shimadzu, UV-2600) using  $\text{BaSO}_4$  as the reflectance standard reference. EPR measurements of sample were carried out at room temperature on a JEOL E-500 by addition of sample to  $\text{CH}_3\text{CN}$  and TEOA solution.

**The photoelectrochemical (PEC) properties.** The photoelectrochemical (PEC) properties of the samples were carried out on the electrochemical workstation (CHI 6005E). The experiment was conducted in a single cell with a three electrodes configuration, which was consisted of working electrode, a platinum foil as counter

electrode, and Ag/AgCl (saturated KCl solution) as reference electrode. The working electrode was fabricated by dropcasting an ethanol suspension of photocatalyst samples on indium-tin oxide (ITO) glasses slide within an active area of 1 cm<sup>2</sup>. Na<sub>2</sub>SO<sub>4</sub> aqueous solution (0.5 M) served as the electrolyte. The light illumination was supplied by a 300 W Xe arc lamp equipped with a 420 nm cut-off filter in the PEC measurements. An applied bias of 0.2 V was used to measure the transient photocurrent response.

**Apparent Quantum Yield (AQY) calculations.** The AQY for CO evolution for the CdS and CdS/UiO-bpy/Co composites was measured using the standard experimental setup. The system was irradiated by 300 W Xe lamp equipped with a 420 nm optical band-pass filter and subjected to react for 10 h. The amount of CO evolved in the duration of 10 h for CdS, CdS@Co-bpy and CdS/UiO-bpy/Co composites was 0.98, 4.7 and 10.1 μmol respectively. The average intensity of irradiation was determined to be 5 mW/cm<sup>2</sup> by a CEL-NP2000 spectrometer. The irradiation area was measured to be 4.91 cm<sup>2</sup>. Finally, the AQY was then estimated as follows:

$$QE = \frac{2 \times \text{the number of evolved CO molecules}}{\text{the number of incident photos}} \times 100\%$$

**For the CdS:**

$$\begin{aligned} QE &= \\ & \frac{2 \times 0.98 \times 10^{-6} \times 6.02 \times 10^{23}}{5 \times 10^{-3} \times 4.91 \times 420 \times 10 \times 3600 \times 10^{-9} / 6.626 \times 10^{-34} \times 3 \times 10^8} \times 100 \\ & = 0.063\% \end{aligned}$$

**For the CdS@Co-bpy:**

$$\begin{aligned} QE &= \\ & \frac{2 \times 4.7 \times 10^{-6} \times 6.02 \times 10^{23}}{5 \times 10^{-3} \times 4.91 \times 420 \times 10 \times 3600 \times 10^{-9} / 6.626 \times 10^{-34} \times 3 \times 10^8} \times 100 \\ & = 0.302\% \end{aligned}$$

**For the CdS@Co-bpy:**

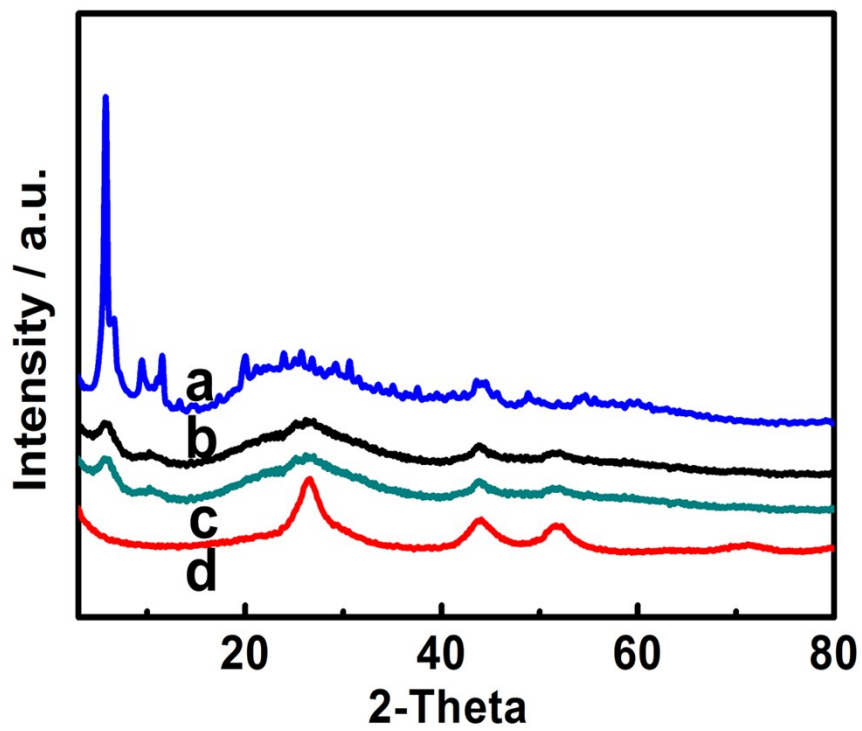
$$\begin{aligned}
 \text{QE} &= \frac{2 \times 10.1 \times 10^{-6} \times 6.02 \times 10^{23}}{5 \times 10^{-3} \times 4.91 \times 420 \times 10 \times 3600 \times 10^{-9} / 6.626 \times 10^{-34} \times 3 \times 10^8 \times 100} \\
 &= \mathbf{0.65\%}
 \end{aligned}$$

**The turnover number (TON) calculations.**

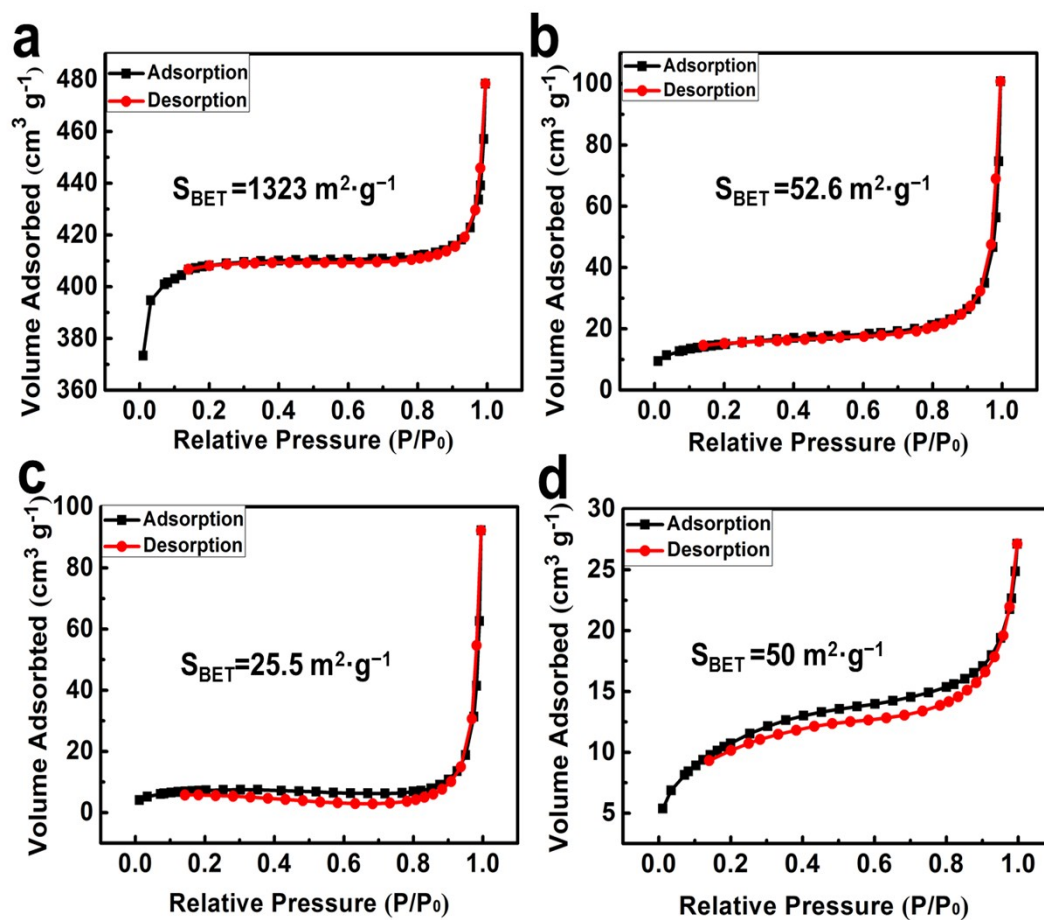
$$\begin{aligned}
 \text{TON} &= \frac{\text{the mole of evolved CO molecules}}{\text{the mole of the active sites}} \\
 &= \frac{2350 \times 10^{-6} \times 10 \times 10^{-3}}{10 \times 10^{-3} \times 0.0618 / 59} \\
 &= \mathbf{2.24}
 \end{aligned}$$

**Photoreduction of CO<sub>2</sub>.** Photoreduction of CO<sub>2</sub> was conducted in a gas-closed system with a side irradiation Pyrex cell. The 300 W Xe lamp (Aulight CEL-HX, Beijing) equipped with a 420 nm cut-off filter was used as the light source. Typically, 10 mg of catalysts were dispersed in 5 mL of CH<sub>3</sub>CN containing 1 mL of TEOA as sacrifice agent. The amounts of H<sub>2</sub> and CO gas were determined using a gas chromatograph (Agilent 4890D), and the liquid products were determined using a high performance liquid chromatography (LC-20AT). In the reuse experiments, the CdS/UiO-bpy/Co composites were washed by acetone for 6 times, and used for the next run directly after drying at 60 °C under vacuum. The isotope-labeled experiment was performed using <sup>13</sup>CO<sub>2</sub> instead of <sup>12</sup>CO<sub>2</sub>, and the gas products were analyzed using gas chromatography-mass spectrometry (GC-MS, 7890A and 294 5975C, Agilent).

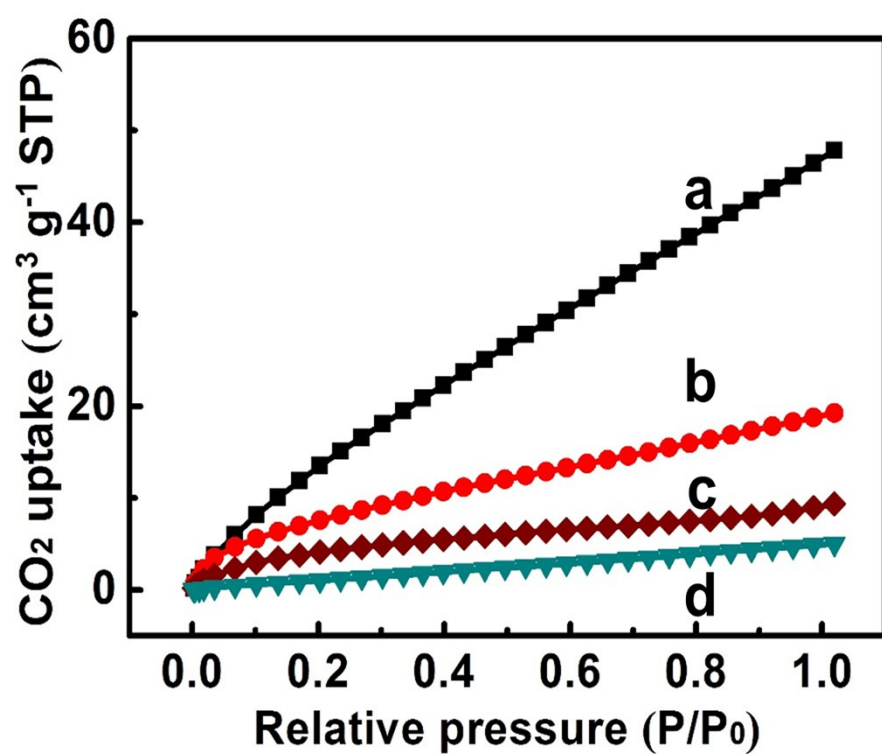
**Action spectrum for the photocatalytic reaction.** The system was similar with the above of photoreduction of CO<sub>2</sub>, excepting that the 420 nm cut-off filter was replaced by the 420 nm, 475nm, 550nm, 600nm and 675nm optical band-pass filter, respectively.



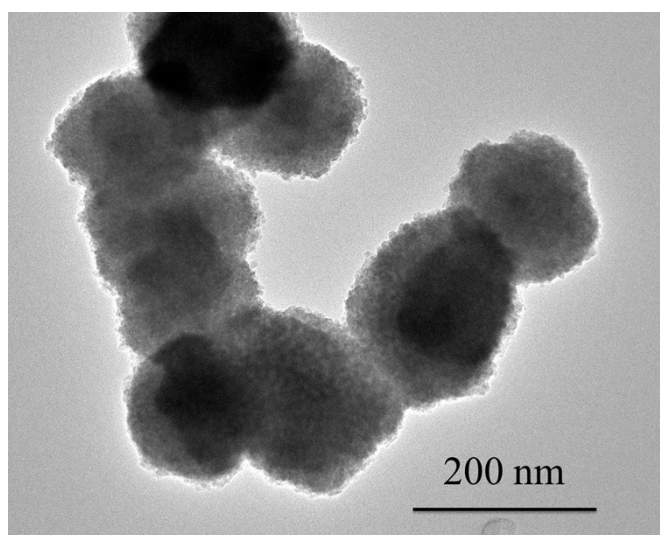
**Figure S1.** XRD patterns of UiO-bpy (a), CdS/UiO-bpy (b), CdS/UiO-bpy/Co(c) and CdS (d).



**Figure S2** The adsorption-desorption isotherms of UiO-bpy(a), CdS/UiO-bpy(b), CdS/UiO-bpy/Co(c), and CdS(d). The BET surface areas (S<sub>BET</sub>) are provided in the corresponding figures.

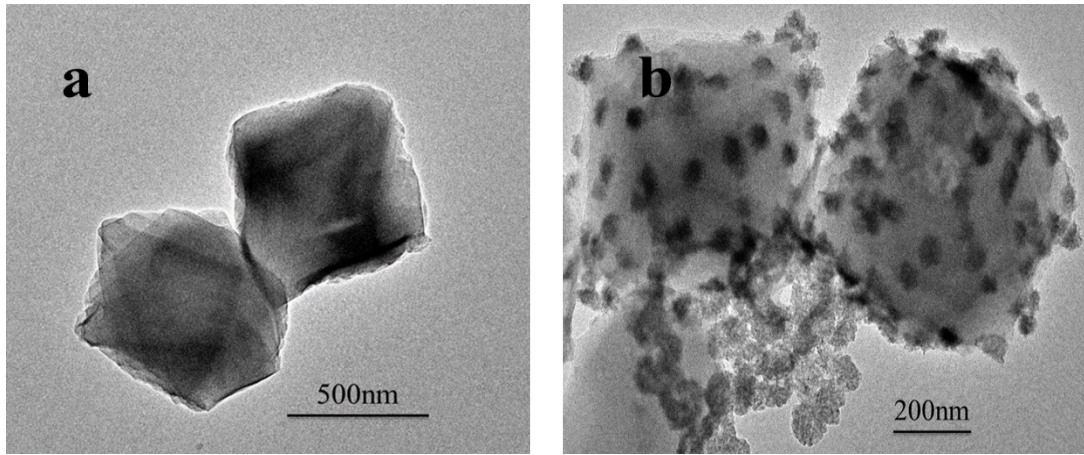


**Figure S3** The CO<sub>2</sub> adsorption behaviors of UiO-bpy (a), CdS/UiO-bpy (b), CdS/UiO-bpy/Co (c), and CdS (d).

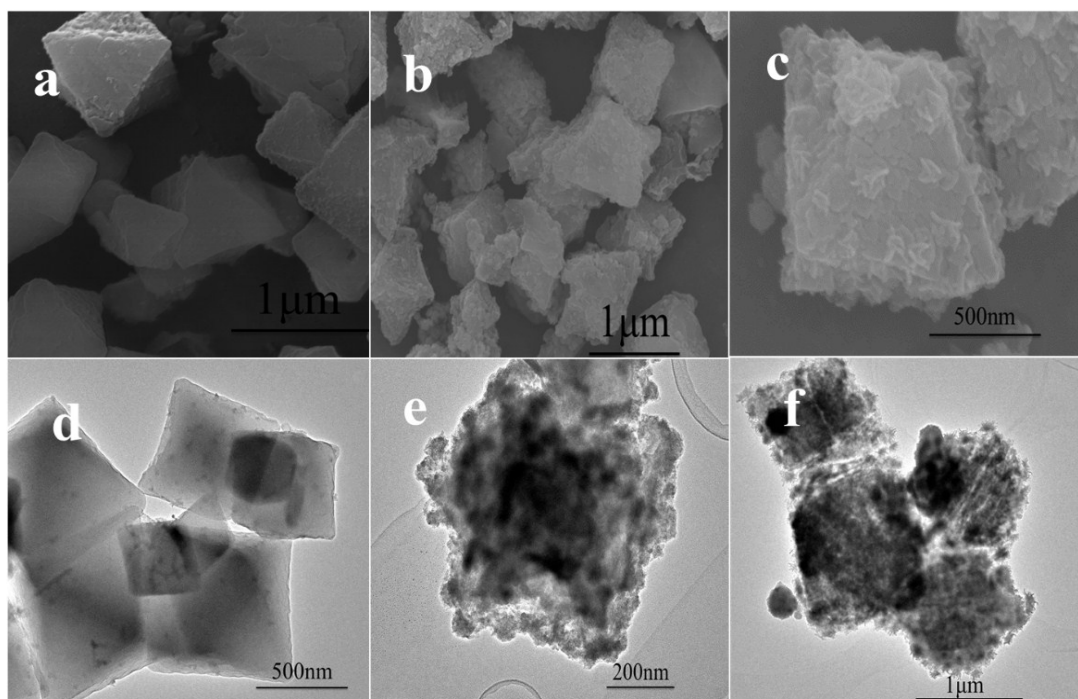


**Figure S4.** The TEM image of the pure CdS.



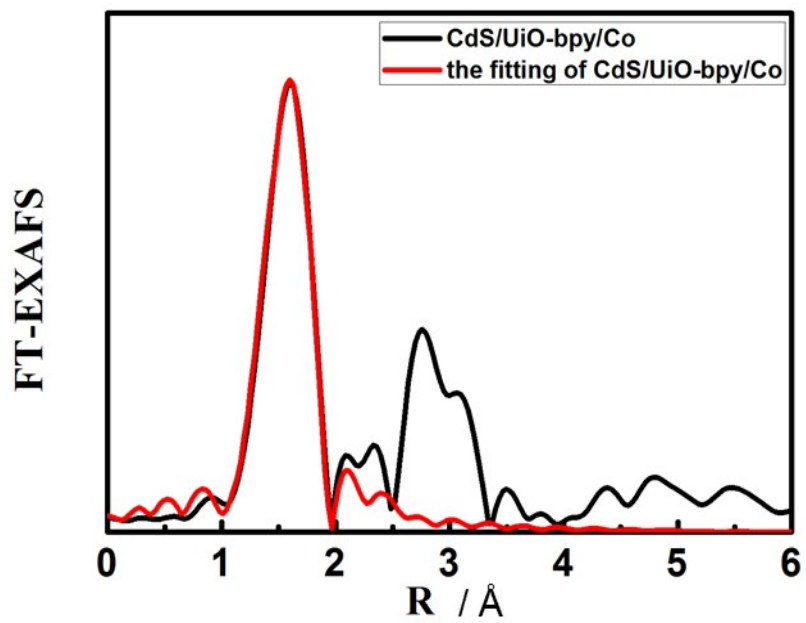


**Figure S5.** The TEM images of UiO-67 (a) and CdS/UiO-67 (b).

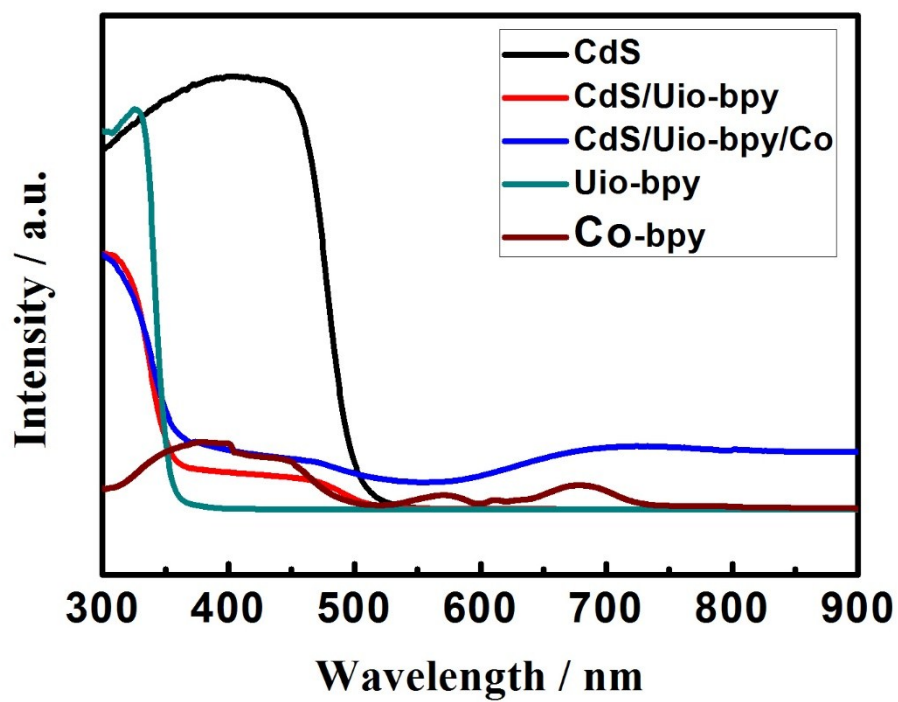


**Figure S6.** The SEM and TEM images of CdS/UiO-bpy with different contents of  $\text{Cd}(\text{CH}_3\text{COO})_2$ : the cadmium acetate was 10 mg (a, d); the cadmium acetate was 60 mg (b, e); the cadmium acetate was 90 mg (c, f). The amount of UiO-bpy were all 300 mg.

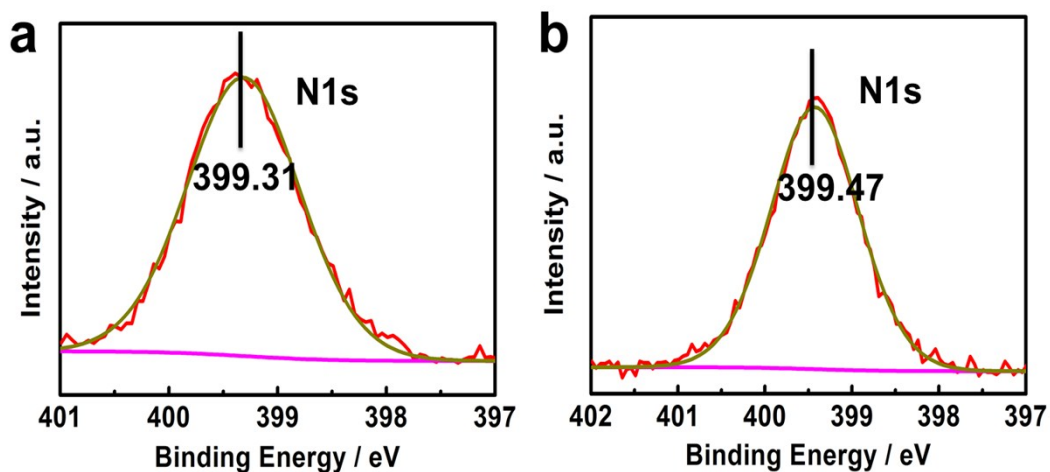
We found that the amount of cadmium acetate had an important effect on the size of CdS. The UiO-bpy(300 mg) and cadmium acetate(10 mg) were added firstly into DMSO for 1 h under stirring, and then transformed to teflon kettle under  $180^\circ\text{C}$  for 12 h to form CdS/UiO-bpy. Only small amount of CdS nanoparticles were formed with the size of about 10 nm on the surface of UiO-bpy, as shown in Figures S6a and S6d. When the amount of cadmium acetate increased to 30 mg, although the number of CdS nanoparticles increased, the size of CdS nanoparticles on the UiO-bpy framework was still about 10 nm, as show in Figures 2B, 2C. As the amount of cadmium acetate increased to 60 mg and 90 mg, the size of CdS become bigger and covered a thick layer on the UiO-bpy, as shown in Figures S6b, 6c, 6e, and 6f. This is probably due to the fact that the growth rate of CdS was faster than the release rate of  $\text{Cd}^{2+}$  from the bridging ligands when the amount of cadmium acetate exceeds the critical value.



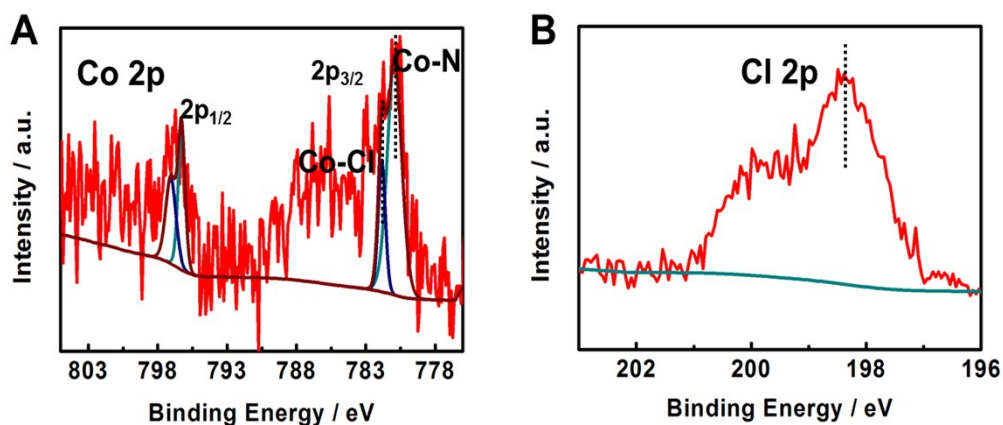
**Figure S7.** The EXAFS fitting curve of CdS/UiO-bpy/Co composites.



**Figure S8.** The diffuse reflectance UV/Vis spectra of CdS, UiO-bpy, CdS/UiO-bpy, CdS/UiO-bpy/Co composites and Co-bpy.

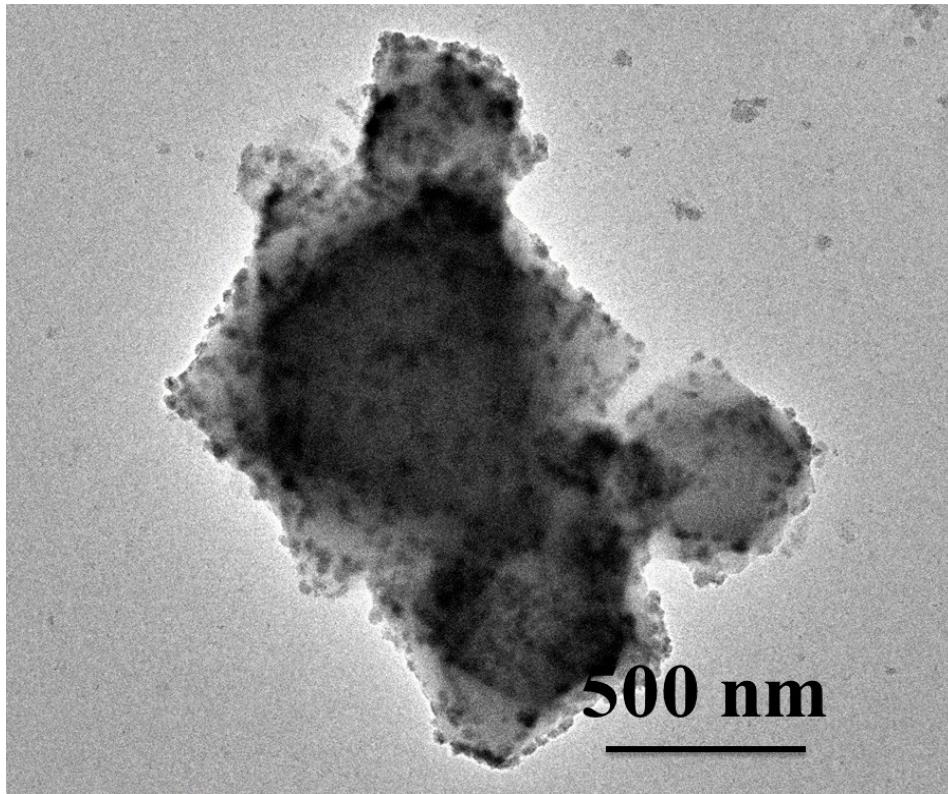


**Figure S9.** The XPS spectra of N 1s: the CdS/UiO-bpy (a) and the CdS/UiO-bpy/Co (b).

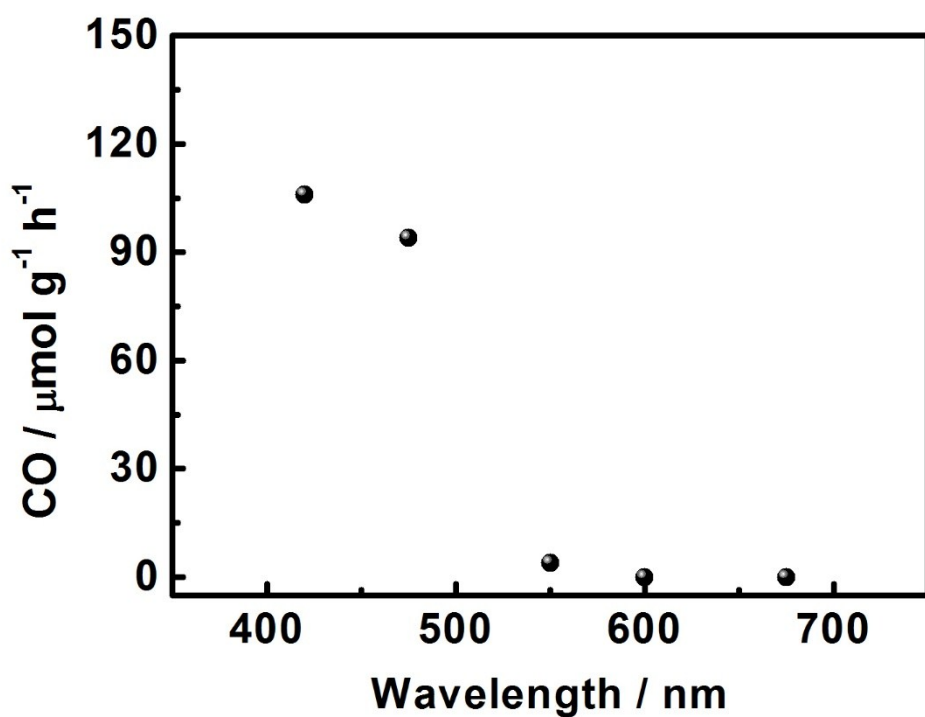


**Figure S10.** The XPS spectra of Co in CdS/UiO-bpy/Co (A); the XPS spectra of Cl in CdS/UiO-bpy/Co(B).

As shown in Figure S10A, we can find that the Co2p XPS spectrum of 780.8 eV and 781.8 eV can be assigned to the Co-N and Co-Cl, indicating that the Co was connected to the nitrogen and chlorine atoms simultaneously. These results were also certified by the XANES spectrum.

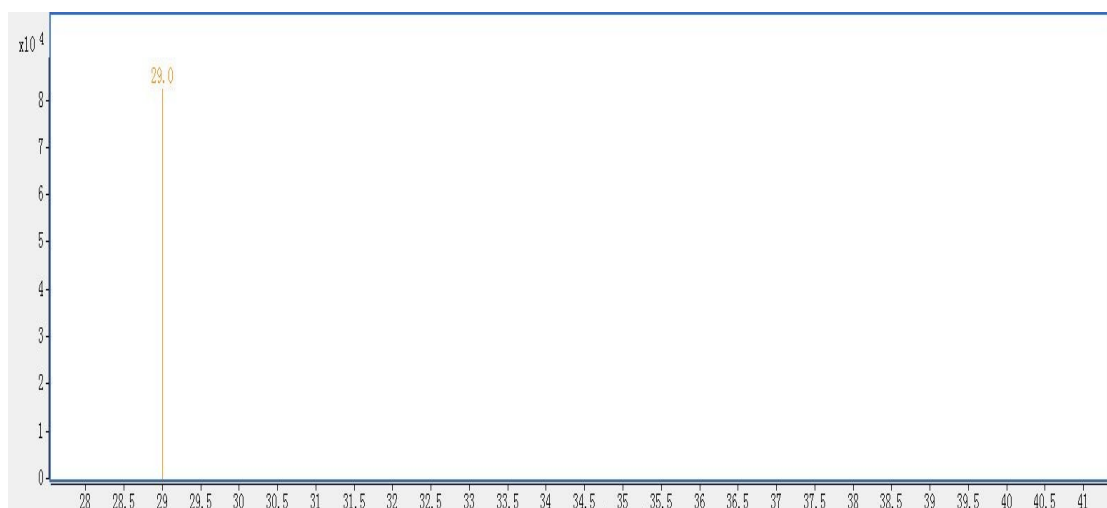


**Figure S11.** The TEM image of the CdS/UiO-bpy/Co after the five cycles.



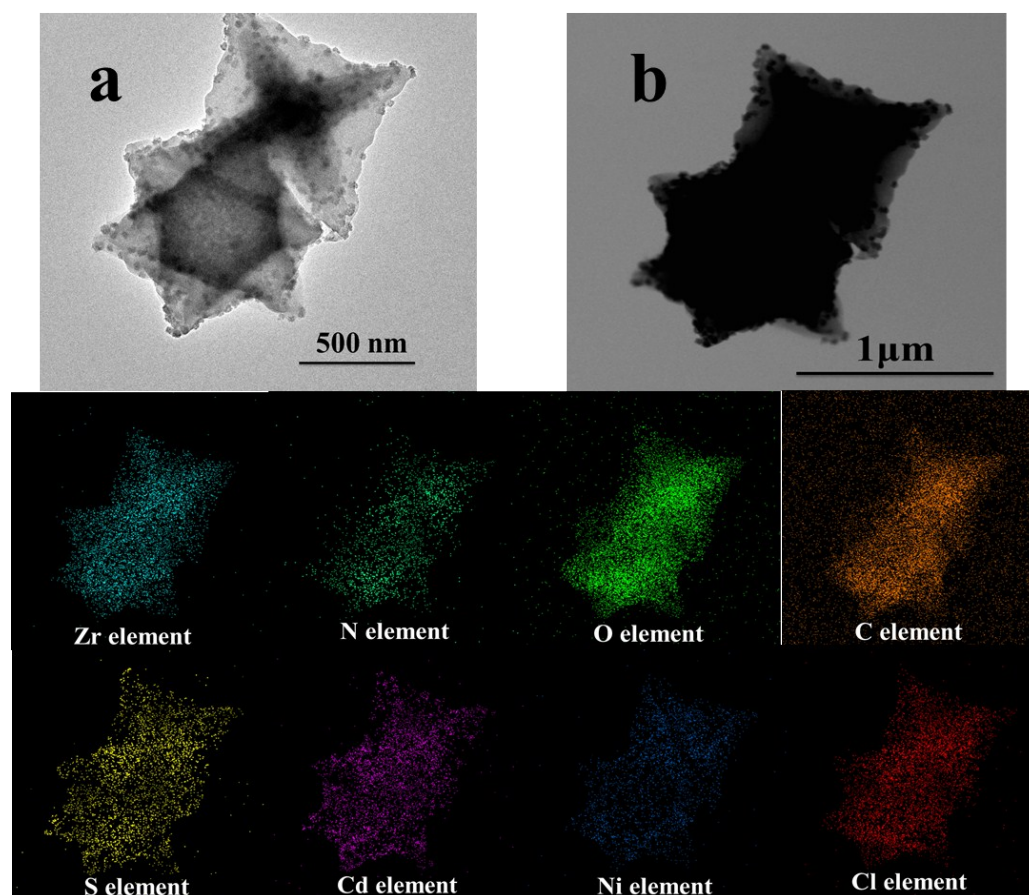
**Figure S12.** The action spectrum for the photocatalytic of CdS/UiO-bpy/Co composites.

As shown in Figure S12, the evolution rate of CO was 106, 94 and 4  $\mu\text{mol/g/h}$ , respectively when the incident wavelength was 420, 475 and 550 nm. When the incident wavelength was 600 and 675 nm, the CO could not be detected. The performance of CdS/UiO-bpy/Co composites was consistent with the absorption behavior of CdS(Figure 4b). We can confirm that the reaction is induced by the light absorption of CdS.



**Figure S13** Mass spectrum of photogenerated product  $^{13}\text{CO}$  ( $m/z=29$ ) from photoreduction of  $^{13}\text{CO}_2$  over the CdS/UiO-bpy/Co composites.





**Figure S14.** The TEM image of the CdS/UiO-bpy/Ni (a) and the EDX mapping of CdS/UiO-bpy/Ni(b).

**Table S1.** The contents of CdS and  $\text{Co}^{2+}$  ( $\text{Ni}^{2+}$ ) in the CdS/UiO-bpy/Co (Ni) determined by ICP-AES method. 30 mg of  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  was used when preparing CdS/UiO-bpy.

Samples	Cd (wt%)	S (wt%)	Cd / S(atomic ratio)	Co or Ni (wt%)
<b>CdS/UiO-bpy/Co</b>	7.6	2.31	17 : 18	6.18
<b>CdS/UiO-bpy/Ni</b>	7.16	2.2	37 :39	6.01

**Table S2.** Structural parameters of CdS/UiO-bpy/Co extracted from the EXAFS fitting. ( $S_0^2=0.80$ )

Sample	Scattering pair	CN	R(Å)	$\sigma^2(10^{-3}\text{Å}^2)$	$\Delta E_0(\text{eV})$	R factor
CdS/UiO-bpy/Co	Co-N	2±0.9	1.95±0.02	9.6±1.7	5.6±1.4	0.0063
	Co-Cl	2.1±0.8	2.10±0.02	9.9±1.7	5.7±1.4	0.0074

$S_0^2$  is the amplitude reduction factor; CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms);  $\sigma^2$  is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances);  $\Delta E_0$  is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.

**Table S3.** Summary of the various photocatalytic systems employed for CO<sub>2</sub> reduction.

Catalyst	Co-catalyst / Sacrificial agent	Light source	Major products Rate	Ref.
CdS/UiO-bpy/Co	- /(MeCN/TEOA =5:1)	Visible light: 300 W Xe lamp with a cut-off filter (420< $\lambda$ < 800 nm).	CO 235 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup> (0.8MPa CO <sub>2</sub> ) 195 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup> (0.1MPa CO <sub>2</sub> )	This study
MOF-525-Co <sup>a</sup>	- /(MeCN/TEOA =4:1)	Visible light: 300 W Xe lamp with a cut-off filter (400< $\lambda$ < 800 nm).	CO 201.6 $\mu$ molg <sup>-1</sup> h <sup>-1</sup> , CH <sub>4</sub> 36.67 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>	Zhang et.al. <i>Angew. Chem. Int. Ed.</i> 2016, 55, 14310.
PCN-222 <sup>b</sup>	- /(MeCN/TEOA =4:1)	Visible light: 300 W Xe lamp with a cut-off filter (400< $\lambda$ < 800 nm).	HCOOH 75 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>	Jiang et.al <i>J. Am.Chem. Soc.</i> 2015,137, 13440.
Bismuth tungstate layers	- /H <sub>2</sub> O	300 W Xe lamp with a standard AM1.5 filter.	CH <sub>3</sub> OH 75 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>	Xie et.al <i>Angew. Chem. Int. Ed.</i> 2015, 54, 13971.
RuRu' /C <sub>3</sub> N <sub>4</sub> <sup>c</sup>	Ag/ EDTA·2Na	Visible light: A 400 W high-pressure Hg lamp (SEN) ( $\lambda$ > 400 nm).	HCOOH 96 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>	Maeda et.al <i>J. Am. Chem. Soc.</i> 2016, 138, 5159.
UiO-66/C <sub>3</sub> N <sub>4</sub> <sup>d</sup>	- /(MeCN/TEOA =4:1)	Visible light: 300 W Xe lamp with a cut-off filter (400< $\lambda$ < 800 nm).	CO 9.79 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>	Ye et. al <i>Adv. Funct. Mater.</i> 2015, 25, 5360.
ZIF-9 <sup>e</sup>	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> /acetonitrile: H <sub>2</sub> O = 4: 1)	UV light: 300 W Xe lamp with a	CO 41.8 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>	Wang et al. <i>Angew. Chem. Int.</i>

		cut-off filter ( $\lambda < 400$ nm).		<i>Ed. 2014, 53,</i> 1034
ZnIn <sub>2</sub> S <sub>4</sub> Layers	- /H <sub>2</sub> O	300 W Xe lamp with a standard AM1.5 filter.	CO 33.2 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>	Xie et.al. <i>J. Am. Chem. Soc.</i> 2017, 139, 7586
In <sub>2</sub> S <sub>3</sub> -CdIn <sub>2</sub> S <sub>4</sub>	bipyridine (bpy), CoCl <sub>2</sub> / acetonitrile: H <sub>2</sub> O:TEOA = 3: 2:1)	Visible light: 300 W Xe lamp with a cut-off filter (400< $\lambda$ < 800 nm).	CO 825 $\mu$ mol g <sup>-1</sup> h <sup>-1</sup>	Wang et.al. <i>J. Am. Chem. Soc.</i> 2017, 139, 17305
a, b Porphyrin based MOF; c Ru(II) binuclear complex; d Zirconium containing MOF; e ZIF=zeolitic imidazolate framework.				

S1 B. An, J. Zhang, K. Cheng, P. Ji, C. Wang, W. Lin, *J. Am. Chem. Soc.* **2017**, 139, 3834-3840.