Supporting Information

Photocatalytic Reduction of CO_2 to CO Utilizing a Stable and Efficient Hetero-Homogeneous Hybrid System

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Outline

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Supporting Information

Chemicals. Acetonitrile (water less than 0.01%) was purchased from J&K SCIENTIFIC LTD.. Triethanolamine (TEOA) was purchased from Sinopharm Chemical Reagent Co., Ltd.. $3CdSO_4 \cdot 8H_2O$, $Na_2S \cdot 9H_2O$, and $CoCl_2 \cdot 6H_2O$ were purchased from Xilong Chemical Co., Ltd.. 2,2'-bipyridine was purchased from Beijing Yili Fine Chemicals Co., Ltd.. *N,N*-bis(2-hydroxyethyl)glycine (99%) was purchased from Alfa Aesar. These reagents were used without further purification.

Preparation of CdS. CdS was prepared according to the previously reported method.[1] 13.0 g $3CdSO_4 \cdot 8H_2O$ was dissolved in aqueous NH_3 solution (150 mL,10%) to obtain solution A. 50 mL of a solution of 13.2 g $Na_2S \cdot 9H_2O$ was added into solution A dropwisely over a period of 2 h under vigorous stirring at room temperature and then the resulting yellow suspension was stirred for 20 h. After separation by suction filtration, the precipitate was washed to neutral by water and then washed by absolute ethanol for 3 times. Afterwards, the residue was dried in vacuum at 338 K for 12 h. Yellow-orange powder-like CdS was finally obtained after grinding in an agate mortar.

Characterization. The UV-vis absorption spectra were obtained under the transmission mode using Hitachi U-4100 UV/Vis spectrophotometer. X-ray diffraction (XRD) characterization was performed on a Rigaku D/max-2500 diffractometer with Cu Kα radiation (λ = 0.1542 nm) using a current of 100 mA and a voltage of 40 kV. High resolution transmission electron microscopy (HRTEM) were performed on a FEI Tecnai F20 with an accelarating voltage of 200 kV.

Photocatalytic experiments. Photocatalytic experiments were performed in a stainless steel reactor with a quartz window (diameter is 4.5 cm). All the experiments were conducted under the temperature of 301 K. Typically, 9 mg CdS powder was added into reactor, then 15 mL MeCN/TEOA solution (v/v=4:1), $CoCl_2 \cdot 6H_2O$ (15 μmol) and 2,2'-bipyridine (15 μmol) were added. The mixture was degassed by CO_2 (99.995%) for three times and then purged for another 1 h. After the solution was saturated under certain pressure of CO_2, the solution was irradiated by a visible light ranging from 420 nm to 760 nm, which was obtained through a 300 W Xe lamp combined with UV and IR cut-off filters. The light intensity of the spot center was about 150 mW cm^{-2}. After a certain irradiation time, the gaseous products were sampled using a six-way valve and analyzed by gas chromatography equipped with carbon molecular sieve column (TDX-01) and 5A molecular sieve column. H_2 was detected by TCD. CO was converted to methane and then detected by FID to ensure high sensitivities. CO_2 was vented out by switch of a valve before it entered the 5A molecular sieve column. Ar was used as the carrier gas. The oxidation product of TEOA after irradiation was analyzed by GCMS (Agilent 7890A/5975B) with a DB-WAXETR column.

The apparent quantum yeild was measured using a 3W LED (470 nm) in a tube (diameter is 22 mm) at 1 atm. The shape of incident light was a circular spot (diameter is 1.0 cm). The incident light intensity was 3.85 mW determined by an optical power meter (Newport 840-C). The apparent quantum yield was calculated through dividing reaction rate by incident light intensity. As CO was reduced by two electrons, the apparent quantum yield for CO generation should be calculated as follows:

$$\text{A.Q.Y. } (\%) = \frac{N_e}{N_i} \times 100\% = \frac{2 \times r_{CO}}{I_i} \times 100\%$$

where N_e is the number of electrons that convert into product (CO), N_i is the number of incident photons, r_{CO} is the rate of CO generation (μmol/h), I_i is the incident light intensity determined by optical power meter (μmol photons/h).

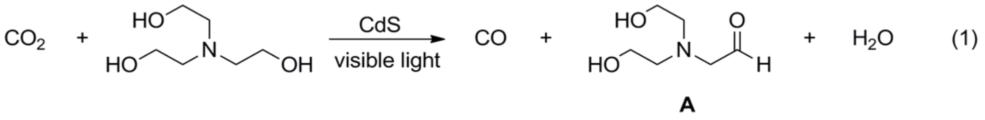
The ^{13}C labeled experiment was performed in a Schlenk flask using $^{13}CO_2$ (98 % abundance) instead of CO_2. The solution was degassed by freeze-pump-thaw cycle for three times and then backfilled with $^{13}CO_2$. Products were analyzed by a GC-MS (Agilent 7890A/5975B) with a GS-CARBONPLOT column.

The heat of formation was calculated by molecular mechanics method using PCMODEL for windows Version 9.10.0. MMX was chose as force field.

Table S1. Heat of formation list

	CO_2	TEOA	CO	H_2O	**A**
ΔH_f (kJ/mol)	-393.51[a]	-582.36[b]	-111.53[a]	-285.83[a]	-535.79[b]

[a] From David R. Lide, ed., *CRC Handbook of Chemistry and Physics, Internet Version 2005*, <http://www.hbcpnetbase.com>, CRC Press, Boca Raton, FL, 2005. [b] Calculated by molecular mechanics (MMX).



The heat of reaction of (1) was calculated as follows:

$$\begin{aligned}\Delta H_r &= [\Delta H_f(\mathrm{H_2O}) + \Delta H_f(\mathrm{CO}) + \Delta H_f(\mathbf{A})] - [\Delta H_f(\mathrm{CO_2}) + \Delta H_f(\mathrm{TEOA})] \\ &= [\Delta H_f(\mathrm{H_2O}) + \Delta H_f(\mathrm{CO}) - \Delta H_f(\mathrm{CO_2})] + [\Delta H_f(\mathbf{A}) - \Delta H_f(\mathrm{TEOA})] \\ &= [-285.83 + (-111.53) - (-393.51)] + [(-535.79) - (-582.36)]\ \mathrm{kJ/mol} \\ &= 42.72\ \mathrm{kJ/mol}\end{aligned}$$

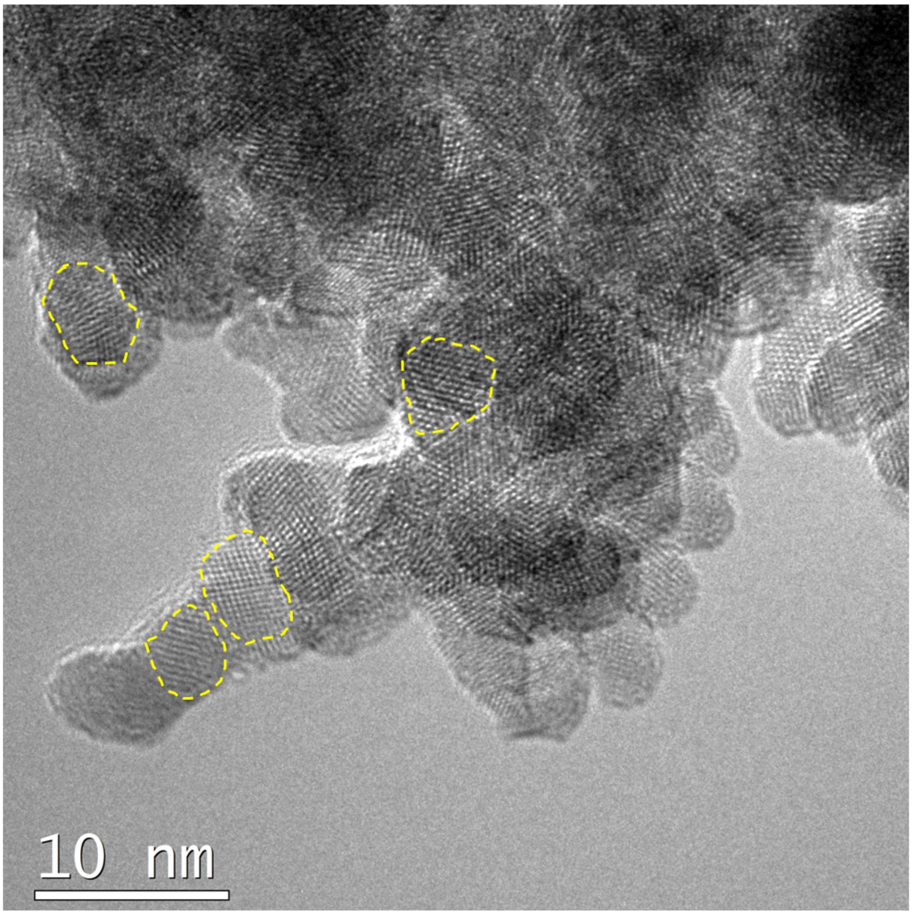


Figure S1**.** HRTEM images of as-prepared CdS nanocrystals.

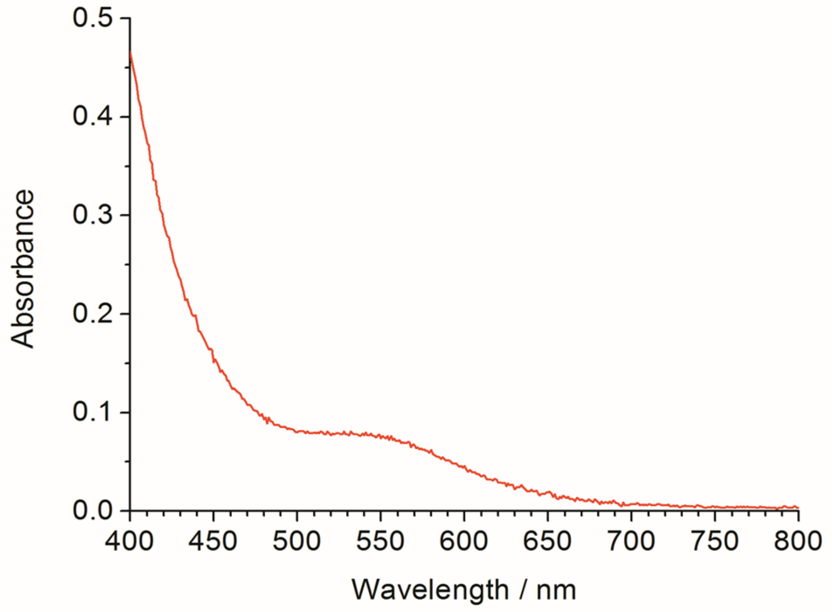


Figure S2. Absorption spectrum of 0.83 mM Co-bipy in MeCN/TEOA mixture (4/1, v/v).

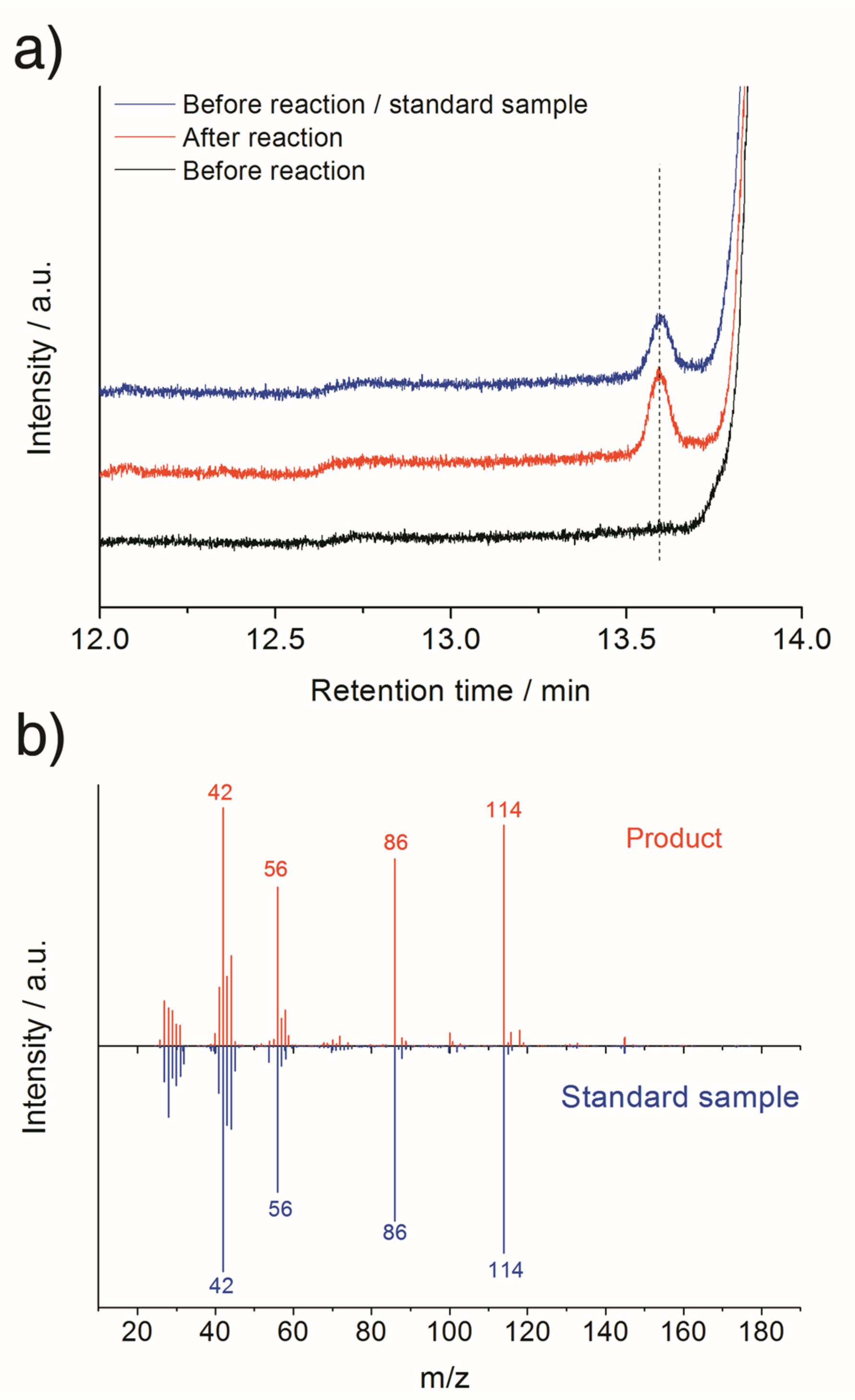


Figure S3. a). Total ion chromatograph of different samples obtained from GC-MS.

b). Mass spectrum of the product and standard sample(*N,N*-bis(2-hydroxyethyl)glycine), respectively.

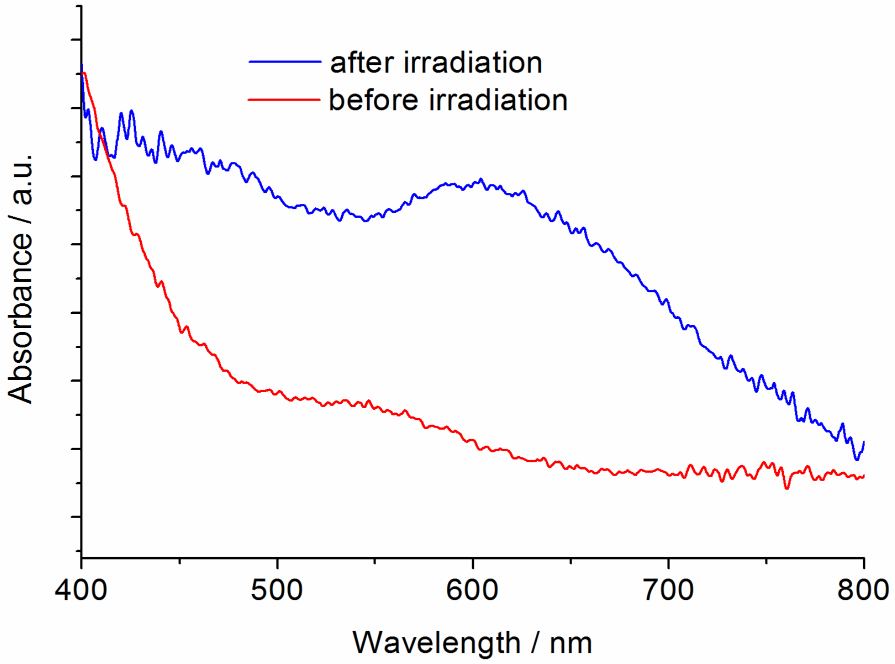


Figure S4. UV-vis spectra of the solution before and after irradiation.

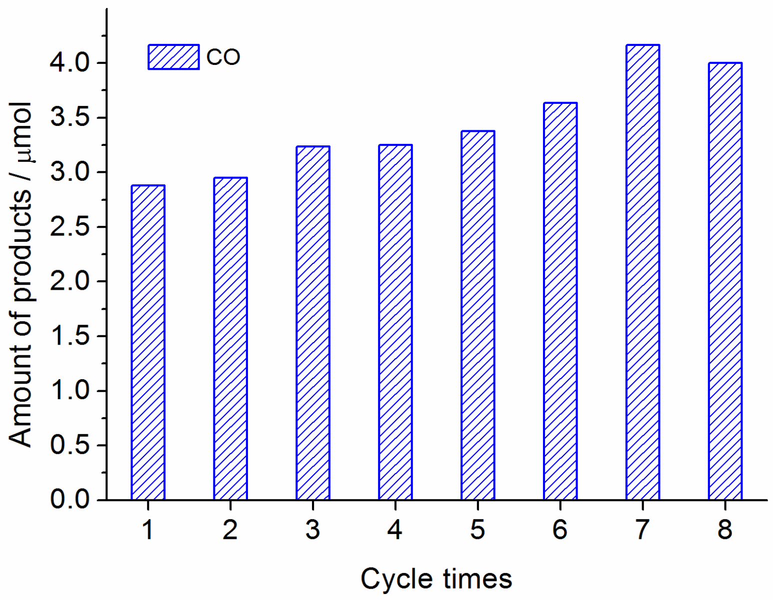
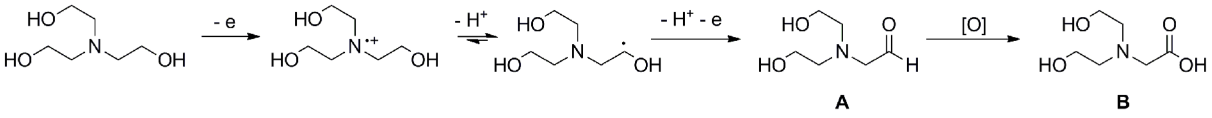


Figure S5. Cycle experiments performed at 1 atm (CdS 20 μmol, Co-bipy 20 μmol).



Scheme S1. Possible mechanism of the oxidation of TEOA.[2]

References

1. A. Reinheimer, R. van Eldik and H. Kisch, *J. Phys. Chem. B*, 2000, **104**, 1014-1024.
2. K. Kalyanasundaram, J. Kiwi and M. Grätzel, *Helv. Chim. Acta*, 1978, **61**, 2720-2730.