

Preparation of ZnS-CdSe@Co/N-C core/shell composite for visible light  
photoconversion of CO<sub>2</sub>

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Supporting Information

**1. Experimental Section**

1. Synthesis of N-doping carbon (N-C) sphere

In a typical synthesise procedure, 1.00 g freshly distilled pyrrole (14.80 mmol) and 2.00 g terephthaldehyde (14.80 mmol) were dissolved into 180.0 mL propionic acid to obtain a clear solution in a dried round bottom flask under Ar atmosphere. After polymerized in a 500.0 mL Teflon lined autoclave for 72 h at 180 °C, the obtained suspension was filtered and then washed with 200.0 mL ethanol to obtain 2.1 g dark brownish porphyrin polymer material. The N-doping carbon material (N-C) was synthesized after the carbonization at 700 °C for 2 h in a tube furnace under Ar protection.

2. Preparation of CdSe/ZnS nanoparticle material

The CdSe/ZnS nanoparticle material was prepared via the thermal injection method under Ar protection. 1.84 g zinc acetate (10.00 mmol) and 0.30 g cadmium oxide (1.00 mmol) was initially dispersed into 80.0 mL liquid paraffin in a four-neck round-bottom flask under Ar protection. And then 36.00 g oleic acid was charged into the obtained dispersion and heated to 150 °C subsequently under Ar protection. After heating and stirring at 150 °C for 0.5 h, a solution of 0.32 g of sulfur powder (10.00 mmol), 0.08 g of selenium powder (1.00 mmol) and 11.0 mL of trioctylphosphine were injected into the above solution and continued to react until the reaction was complete. The CdSe/ZnS nanoparticle material was purified and centrifuged at a rate of 10000 rpm/min for 3 min using the mixed solvent of hexane and ethanol. CdSe/ZnS nanoparticle material can dispersed stably in chloroform for a period of time. Therefore, CdSe/ZnS is eventually dispersed into chloroform for storage and use.

3. Preparation of ZnS-CdSe@Co/N-C material

Chloroform dispersion of 30.0 mL CdSe/ZnS nanomaterial was added into a 500.0 mL beaker, then 1 g of N-doping carbon sphere (N-C) and 150.0 mL of ethanol and water mixture were added respectively. The resulting mixed solution was stirred at room temperature for 12 h after 1 h ultrasound, and then 0.39 g CoCl<sub>2</sub> (3.00 mmol) was added. The obtained mixed solution system was ultrasonic for 1 h, stirred at room temperature for 12 h, and finally filtered, washed, vacuum dried at 80 °C for 12 hours to obtain the ZnS-CdSe@Co/N-C.

4. Photocatalytic test for CO<sub>2</sub> reduction.

Photocatalytic performance for CO<sub>2</sub> reduction of the obtained photocatalyst was comprehensive evaluated in a closed home-made glass reactor (350.0 mL in capacity). A 300 W Xe lamp ( $\lambda \geq 420$  nm) was used as the light source. Before the photocatalytic reaction, 10.0 mg catalyst was dispersed in the mixture solvent of 5.0 mL of triethanolamine (TEOA), 10.0 mL of H<sub>2</sub>O and 15.0 mL of acetonitrile (MeCN). Then, the reactor was sealed and purged for 30.0 min with a partial pressure of 1 atm at room temperature using high purity CO<sub>2</sub> (99.99%) to remove the impurity gas. The gas products were analyzed qualitatively and quantitatively by gas chromatography (GC9790II). For photocatalyst stability test, photocatalyst was centrifugal recovered, washed with water and ethanol, and dried a vacuum drying oven. Another cycle of photoassisted CO<sub>2</sub> reduction was performed using the recycled ZnS-CdSe@CoCl<sub>2</sub>/N-C and fresh reaction solution.

## 2. Characterization

To study the crystalline state of samples, the powder X-ray diffraction (XRD) patterns were recorded on a XRD diffractometer (SHIMADZU XRD-6100). To investigate the morphology and microstructure of the samples, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) investigations were determined on Carl Zeiss Sigma 300 and FEI Tecnai G20, respectively. To measure the elemental composition and valence states of the samples, X-ray photoelectron spectroscopy (XPS) was performed on a VG Multilab 2000. To analysis the pore structure including BET surface areas, pore volumes and pore size distribution of the samples, the samples were evaluated on an automatic Micromeritics ASAP2020 analyzer at -196 °C. To confirm the success of synthesis, Fourier transform infrared spectroscopy (FTIR) was recorded with a Thermo Scientific Nicolet IN10 MX microscope (USA). To study the thermal stability of the samples, thermogravimetric curves were obtained on a thermal analyser (NETZSCH STA 449C).

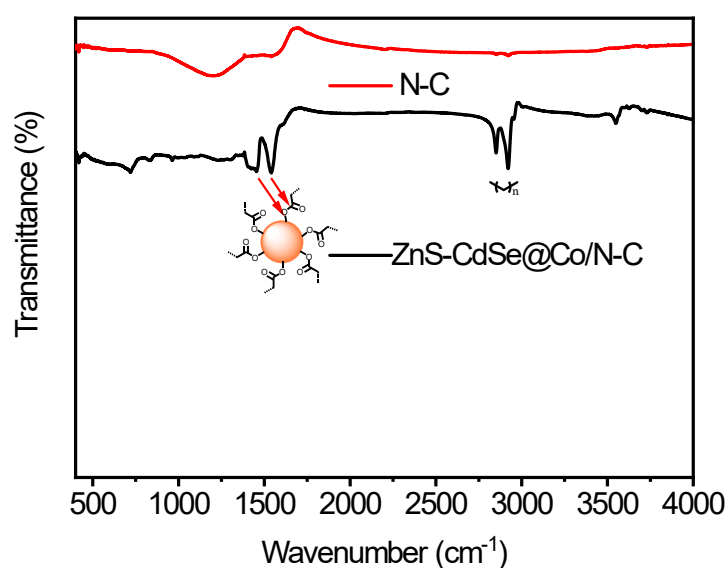


Fig.S1. FT-IR spectra of samples.

The peaks at  $1449\text{ cm}^{-1}$  and  $1544\text{ cm}^{-1}$  represented the typical absorption peaks of the surface protective carboxylate of nanoparticles. The broad peaks at  $2853\text{ cm}^{-1}$  and  $2930\text{ cm}^{-1}$  were assigned to the symmetric and asymmetric absorption peaks of methylene in the protective group.

Fig.S2. TEM images of ZnS-CdSe.

Fig.S3. TEM images of N-C.

Fig.S4. Element distribution in the ZnS-CdSe@Co/N-C sample.

Fig.S5. SEM images of (a)N-C and (b) ZnS-CdSe@Co/N-C.

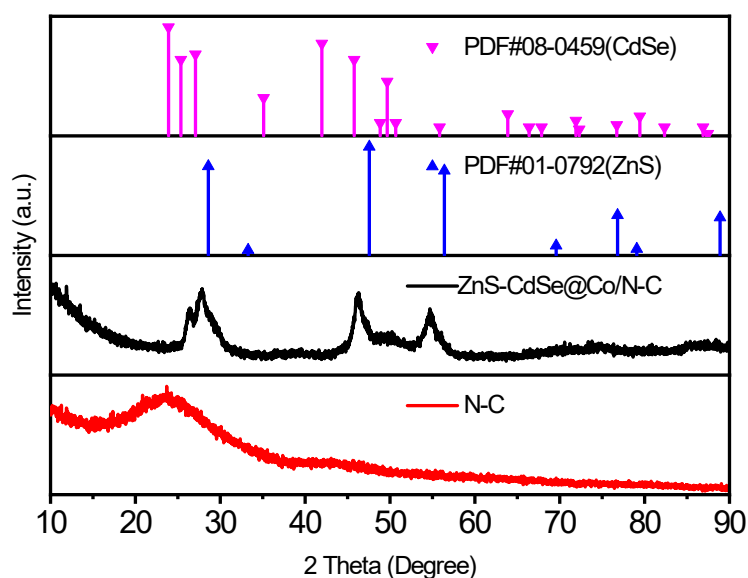


Fig.S6. XRD pattens of the samples.

The only broad diffraction peak for N-C at about  $23^\circ$  can be assigned to (002) characteristic diffraction peak of amorphous carbon<sup>20</sup>. ZnS-CdSe@Co/N-C composites exhibited broad peaks at  $2\theta$  values of  $26.3^\circ$ ,  $27.8^\circ$ ,  $46.3^\circ$  and  $54.7^\circ$ , which indicated diffraction patterns similar to the standard diffraction data of ZnS (JCPDS no. 01-0792)

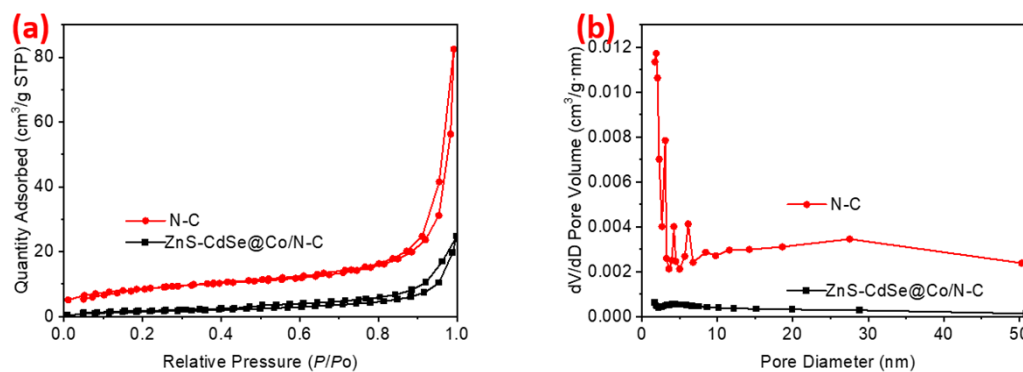


Fig.S7.Nitrogen adsorption isotherms and pore size distribution curves of samples.

**Table S1.** Textural parameters of ZnS-CdSe@Co/N-C and N-C.

Samples	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{micro}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{total}}$ ( $\text{cm}^3/\text{g}$ )	$S_{\text{exter}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{exter}}/S_{\text{micro}}$ (%)
N-C	29.6	4.6	0.0468	25.0	5.34
ZnS-CdSe@Co/N-C	5.8	0.5	0.0153	5.3	10.6

$S_{\text{exter}}$  means the surface area outside the microporosity.

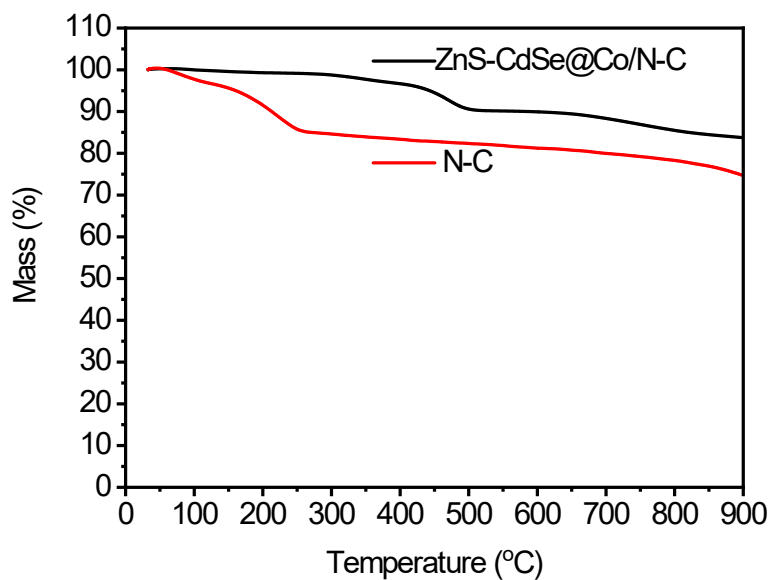


Fig.S8.TG curves of ZnS-CdSe@Co/N-C and N-C.

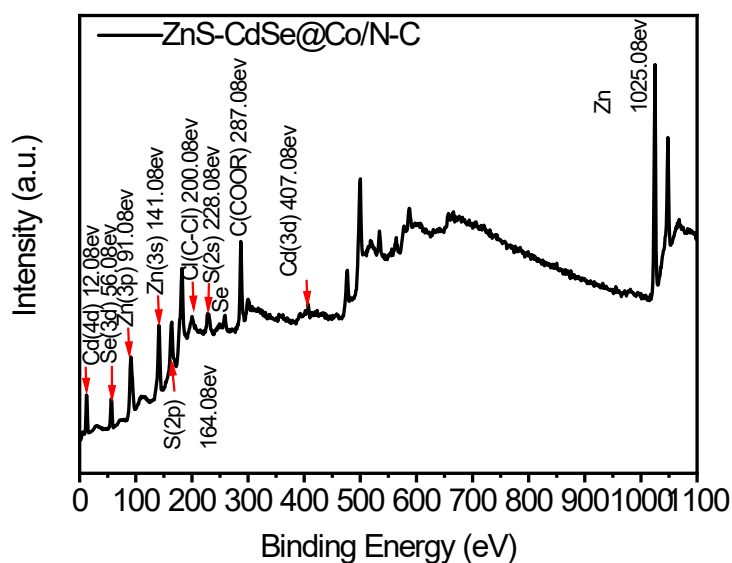


Fig.S9. XPS survey scan of ZnS-CdSe@Co/N-C.

Table S2. Chemical components of ZnS-CdSe@Co/N-C measured by XPS.

	Atomic %	Ato mic %	Atomic %	Atomi c %	Atomic %
1	S	18.29	S(ZnS) 15.6 8	S(-SO <sub>x</sub> -) 2.61	
2	O	5.35			
3	Se	4.88			
4	C	41.19			
5	Zn	16.87	Zn(ZnO) 4.59	Zn(ZnS) 12.28	
6	Cd	0.32	0	0	
7	Cl	7.84	0		
8	N	4.67	pyridinic-N-6 0.29	pyrrolic-N-5 0.23	quaternary-N-Q 3.96 pyridine-N-oxide 0.19
9	Co	0.59			

The formula was  $I = n \cdot S$ , and S was called the sensitivity factor (Empirical standard constants were available)

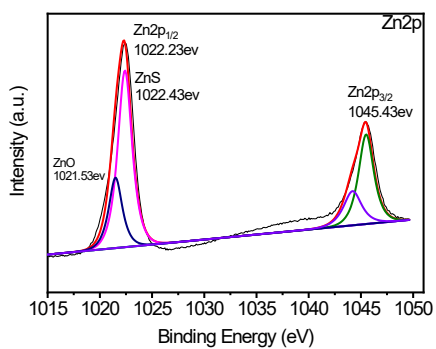


Fig. S10. XPS plots of Zn2p.

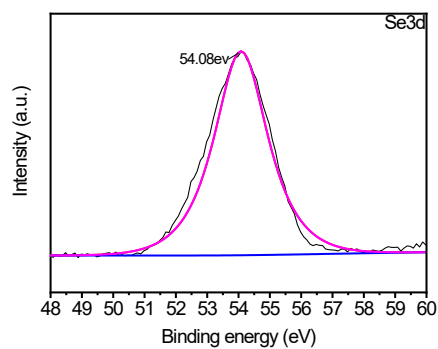


Fig. S11. XPS plots of Se3d.

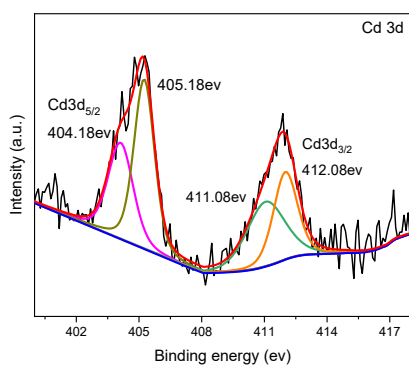


Fig. S12. XPS plots of Cd3d.

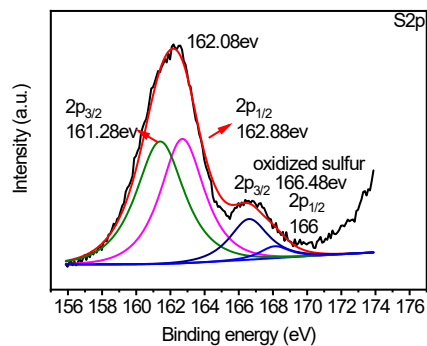


Fig. S13. XPS plots of S2p.

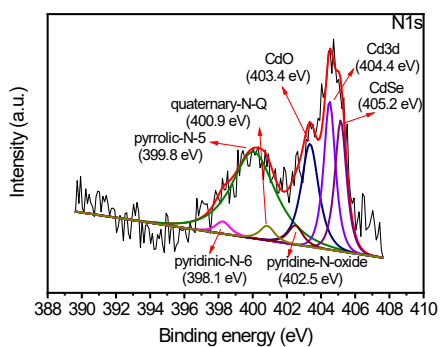


Fig. S14. XPS plots of N1s.

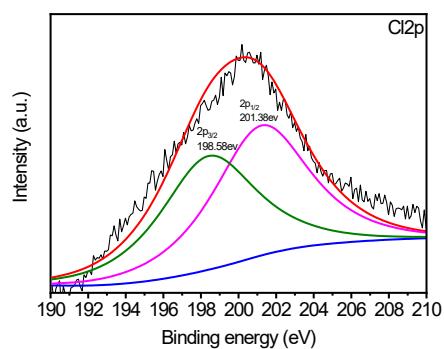


Fig. S15. XPS plots of Cl2p.



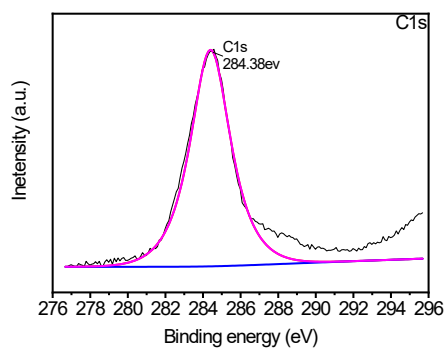


Fig. S16. XPS plots of C1s.

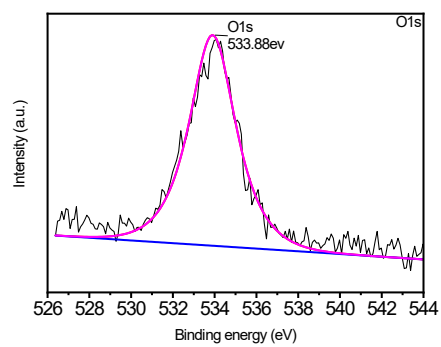


Fig. S17. XPS plots of O1s.

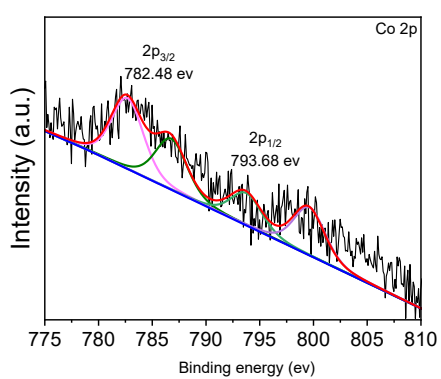


Fig. S18. XPS plots of Co2p.