Electronic Supplementary Information

Fabrication of CdS hierarchical multi-cavity hollow particles for efficient visible light CO_2 reduction

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Experimental details

Synthesis of Co-G SSs: 0.375 mmol of $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 40 mL of isopropanol. Then, 12 mL of glycerol was added to form a transparent solution, which was transferred to a Teflon-lined stainless steel autoclave and kept at 130 °C for 6 h. The products were collected by centrifugation and washed with ethanol 3 times, which were then dried in an oven at 70 ^{o}C.

Synthesis of Co-G@ZIF-8 HSSs: 2 mg of as-prepared Co-G SSs was dissolved in 10 mL of 10 mM $Zn(NO_3)_2 \cdot 6H_2O$ methanol solution for 10 min. Then, 10 mL of 10 mM 2-methylimidazole methanol solution was added. After reaction for 15 min, the products were collected by centrifugation and washed with ethanol 3 times.

Synthesis of CoS_x@ZnS HMCHPs: The obtained Co-G@ZIF-8 HSSs were transferred into 5 mL of ethanol solution containing 20 mg of thioacetamide. Solvothermal sulfidation reaction was conducted at 120 ^{o}C for 1 h. The obtained CoS_x@ZnS HMCHPs were collected by centrifugation and washed with ethanol 3 times.

Synthesis of CdS HMCHPs: The obtained CoS_x@ZnS HMCHPs were transferred into 5 mL of aqueous solution containing 10 mg of $CdCl_2 \cdot xH_2O$. Hydrothermal cation-exchange reaction was conducted at 120 ^oC for 4 h. The obtained CdS HMCHPs were collected by centrifugation and washed with ethanol 3 times, which were then dried in an oven at 70 ^oC.

Synthesis of CdS SSs: 0.25 mmol of cadmium acetate and 1.25 mmol of thiourea were dissolved in 18 mL of H_2O. The solution was transferred to a Teflon-lined stainless steel autoclave and kept at 140 °C for 5 h. The obtained CdS SSs were collected by centrifugation and washed with ethanol 3 times, which were then dried in an oven at 70 ^oC.

Synthesis of CdS HSs: 2 mg of as-prepared Co-G SSs was transferred into 5 mL of ethanol solution containing 20 mg of thioacetamide. Solvothermal sulfidation reaction was conducted at 120 ^oC for 1 h. The obtained CoS_x HSs were collected by centrifugation and washed with ethanol 3 times. Then, the CoS_x HSs were transferred into 5 mL of aqueous solution containing 10 mg of $CdCl_2 \cdot xH_2O$. Hydrothermal cation-exchange reaction was conducted at 120 ^oC for 4 h. The obtained CdS HSs were collected by centrifugation and washed with ethanol 3 times, which were then dried in an oven at 70 ^oC.

Synthesis of Au@CdS HMCHPs: 8 mg of CdS HMCHPs was dissolved in 10 mL of H_2O. Then, certain volume (50 uL, 100 uL or 200 uL) of 1 mM aqueous solution of $HAuCl_4$ was added under vigorous stirring for 1 h. The obtained Au@CdS HMCHPs were collected by centrifugation and washed with ethanol 3 times, which were then dried in an oven at 70 ^oC.

Materials characterization. The crystal phase was examined by X-ray diffraction (XRD) on a Bruker D2 Phaser X-Ray Diffractometer. Field-emission scanning electron microscope (FESEM; JEOL-6700F) and transmission electron microscope (TEM; JEOL, JEM-2010) were used to characterize the morphology and structure. The composition was analyzed by energy-dispersive X-ray (EDX) spectroscope attached to the FESEM instrument. The light absorption ability was characterized by ultraviolet-visible (UV-Vis) spectroscopy (Shimadzu, UV-2450). The content of Au was measured by ICP-OES (Optima 5300 V, PerkinElmer). PL spectra are collected by a fluorescence spectrometer (PerkinElmer, LS 55) with an excitation wavelength of 350 nm. Transient photocurrent densities were characterized using a three-electrode cell with the electrophoretic-deposited working electrode, saturated Ag/AgCl as the reference electrode and platinum foil as the counter electrode. An aqueous solution containing 0.5 M Na_2SO_4 was used as the electrolyte. The working electrode was irradiated by a 300W Xe lamp with a 400 nm longpass cutoff filter. Nyquist plots were collected by measuring the electrochemical impedance spectra (EIS) in a frequency range of 10 kHz to 1 Hz at the open circuit potential. Both transient photocurrent densities and EIS were collected using an electrochemical workstation (CHI760e, CH Instruments).

Photocatalytic CO_2 reduction. Typically, 4 mg of photocatalyst, 15 mg of 2’2-bipyridine (bpy), 2 µmol of $CoCl_2$, 1 mL of triethanolamine (TEOA), 2 mL of H_2O and 3 mL of acetonitrile (MeCN) were added into a gas-closed glass reactor (80 mL in capacity). Then, high purity CO_2 was introduced into the reactor with a partial pressure of 1 atm. A 300W Xe lamp with a 400 nm longpass cutoff filter was used as the light source. During the photocatalytic process, the reaction system was vigorously stirred by a magnetic stirrer. After each reaction, the generated products from the CO_2 photoreduction system were quantified by an Agilent 7890B gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a packed column (TDX-01). Ar was used as the carrier gas. To evaluate the wavelength-dependent CO_2 photoreduction performance of the sample, the wavelength of incident light was controlled by applying appropriate long-pass cutoff filters (e.g., 400, 420, 455, and 495 nm). Other reaction conditions were the same as those of the normal reaction. To check the carbon source of CO, ^{13}C-leballed isotope experiments were conducted using $^{13}CO_2$ as the reactant and the produced gases were analysed by GC-mass spectrometry (GC-MS). Liquid products were analysed by GC-MS, nuclear magnetic resonance (NMR), and high-performance liquid chromatography (HPLC). Apparent quantum yield (AQY) of the photocatalytic CO_2 reduction system was determined under monochromatic light irradiation with a wavelength of 420 nm. The equation for the calculation is as follows.

$$\text{AQY (\%)} = \frac{(\text{number of produced molecules}) \times 2}{(\text{number of photons})} \times 100\%$$

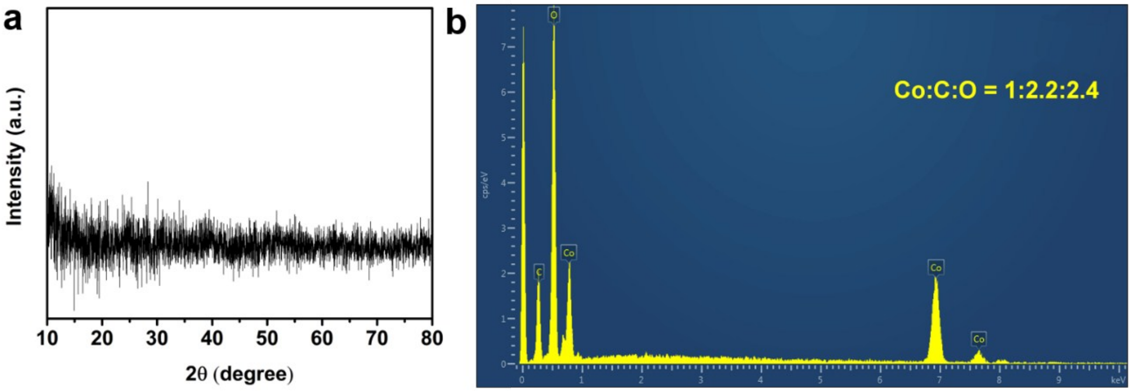

Fig. S1 (a) XRD pattern and (b) EDX spectrum of Co-G SSs.

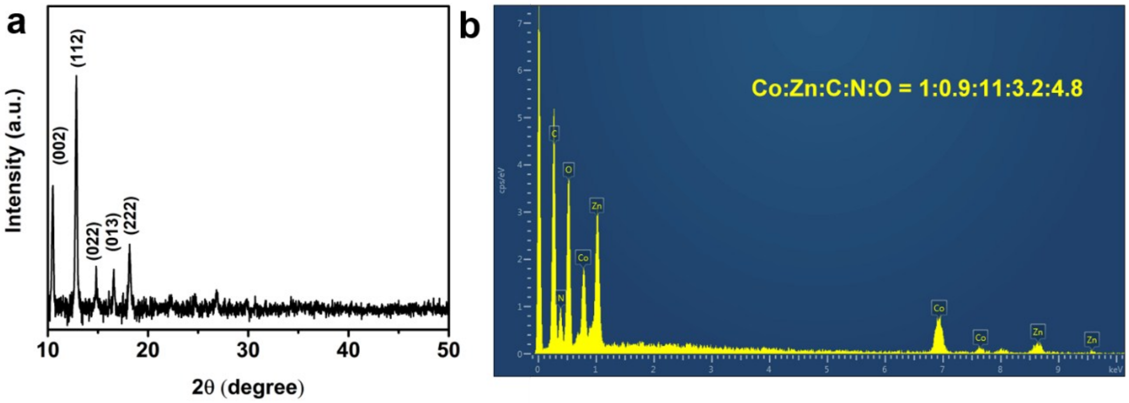

Fig. S2 (a) XRD pattern and (b) EDX spectrum of Co-G@ZIF-8 HSSs.

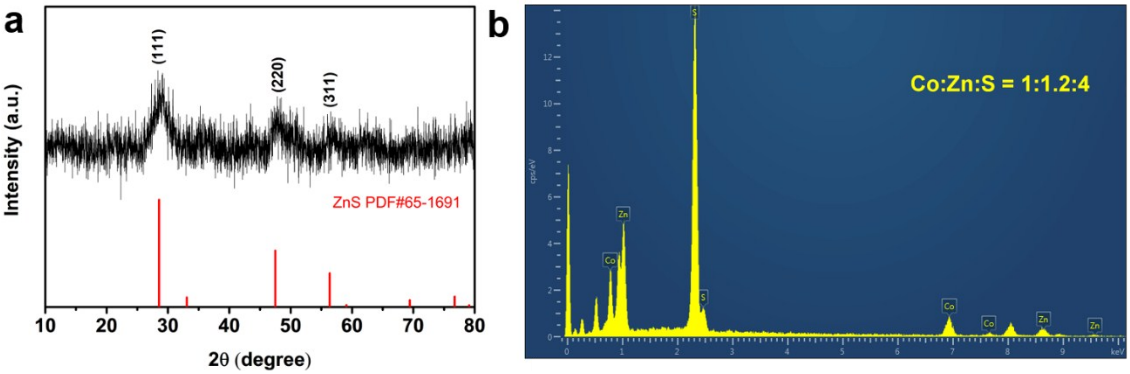

Fig. S3 (a) XRD pattern and (b) EDX spectrum of CoS_x@ZnS HMCHPs.

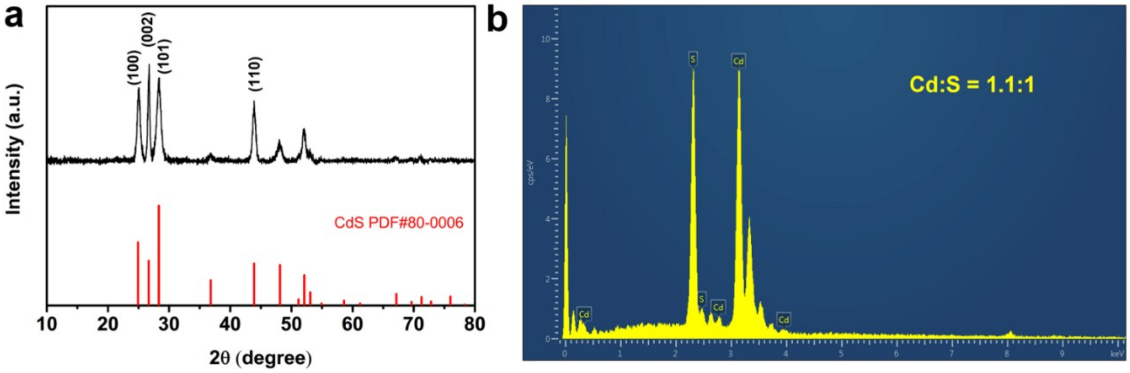

Fig. S4 (a) XRD pattern and (b) EDX spectrum of CdS HMCHPs.

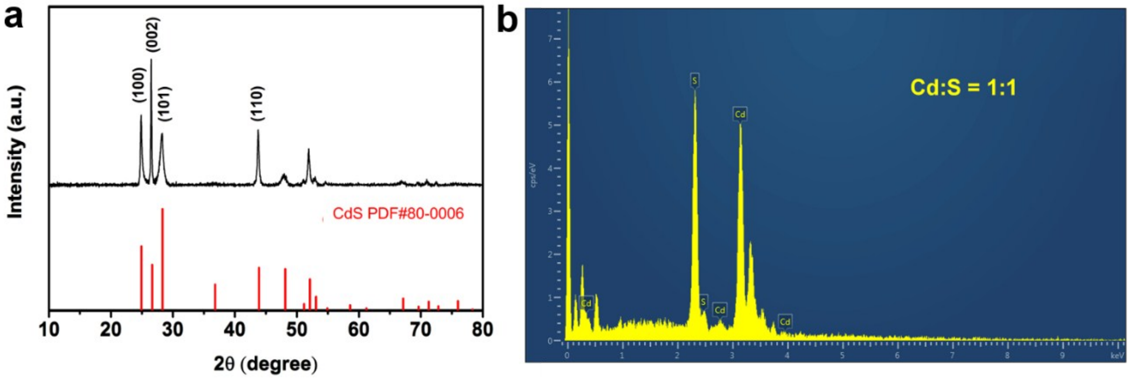

Fig. S5 (a) XRD pattern and (b) EDX spectrum of CdS SSs.

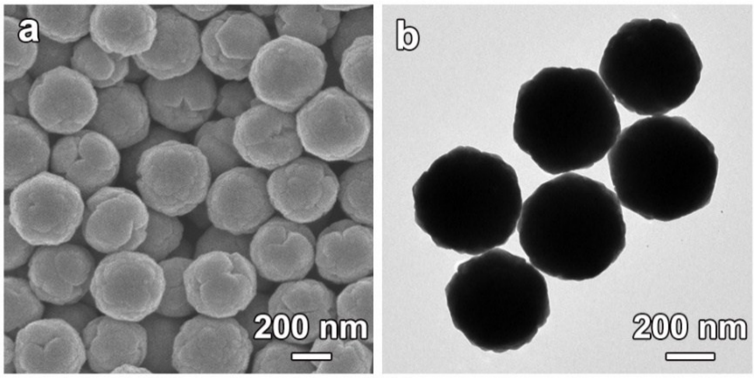

Fig. S6 (a) FESEM and (b) TEM images of CdS SSs.

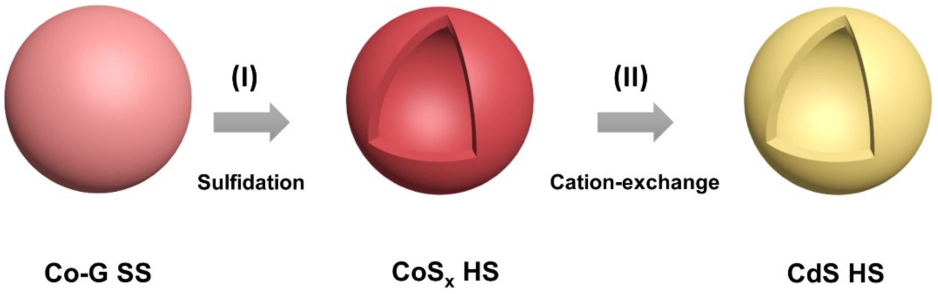

Fig. S7 Schematic illustration of the formation process of CdS HS. (I) Conversion of Co-G SS into CoS$_x$ HS via a sulfidation treatment. (II) Conversion of CoS$_x$ HS into CdS HS through a cation-exchange reaction.

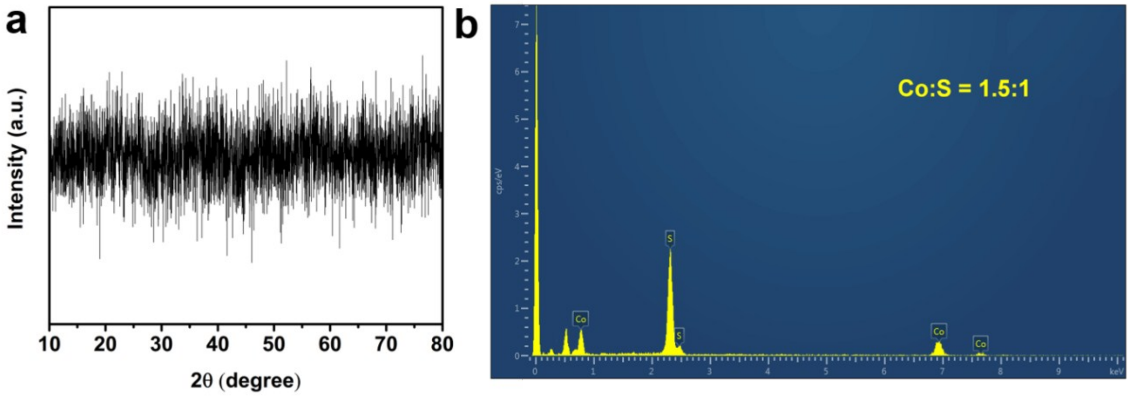

Fig. S8 (a) XRD pattern and (b) EDX spectrum of CoS$_x$ HSs.

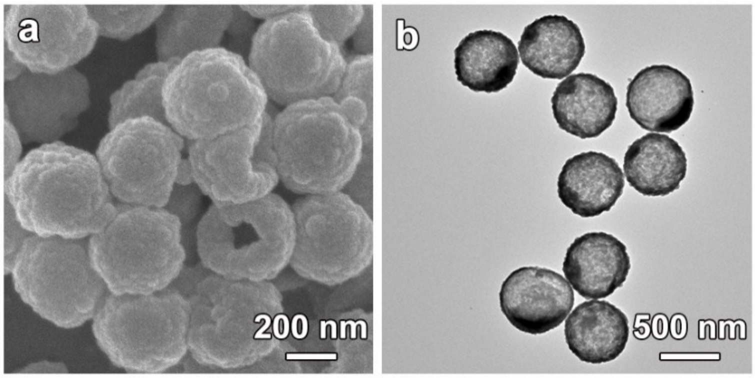

Fig. S9 (a) FESEM and (b) TEM images of CoS_x HSs.

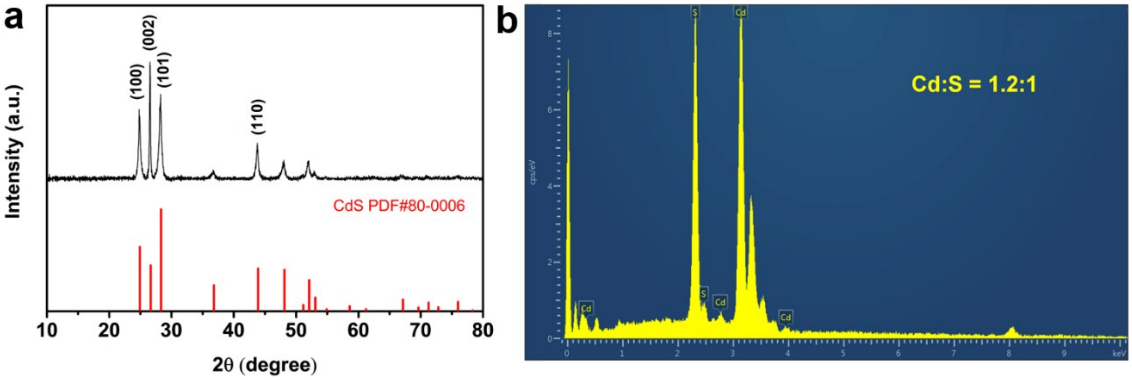

Fig. S10 (a) XRD pattern and (b) EDX spectrum of CdS HSs.

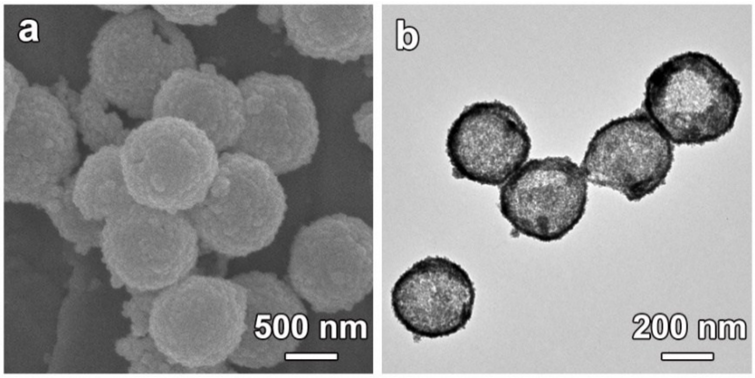

Fig. S11 (a) FESEM and (b) TEM images of CdS HSs.

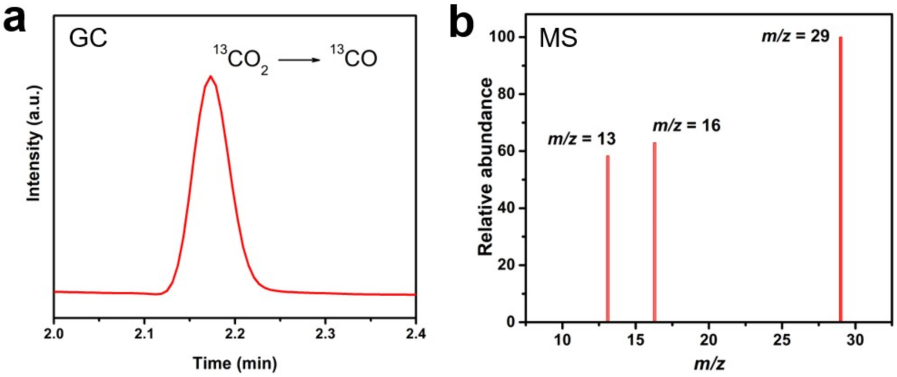

Fig. S12 (a) GC and (b) MS spectra of GC-MS analysis of produced CO from the CO_2 reduction system using $^{13}CO_2$ as the gas feedstock.

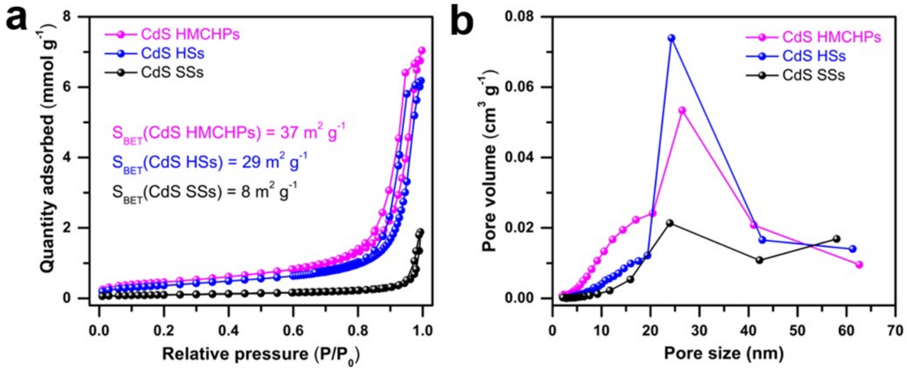

Fig. S13. (a) N_2 sorption isotherms and (b) the corresponding pore size distribution plots of CdS SSs, CdS HSs and CdS HMCHPs.

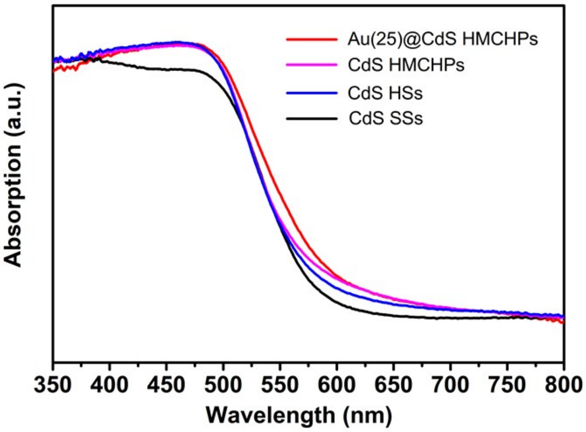

Fig. S14 UV-Vis absorption spectra of CdS SSs, CdS HSs, CdS HMCHPs and Au(25)@CdS HMCHPs.

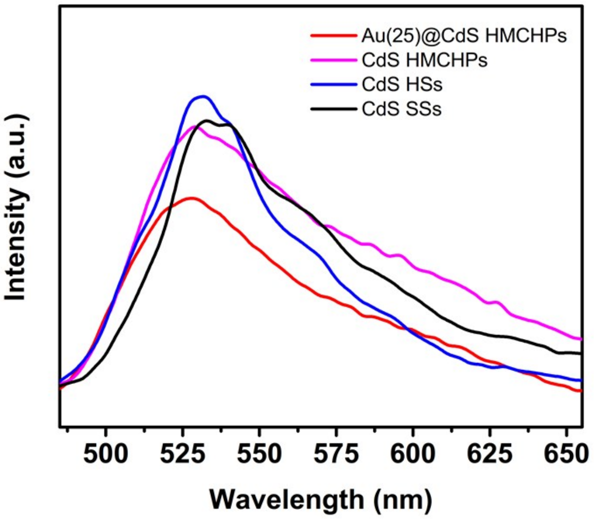

Fig. S15 PL spectra of CdS SSs, CdS HSs, CdS HMCHPs and Au(25)@CdS HMCHPs.

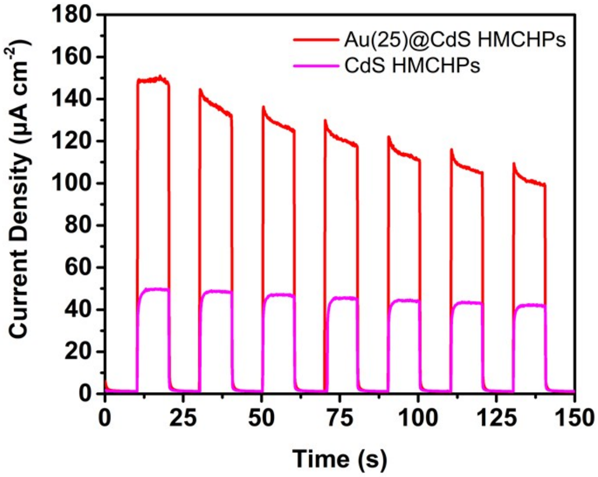

Fig. S16 Transient photocurrent densities of CdS HMCHPs and Au(25)@CdS HMCHPs.

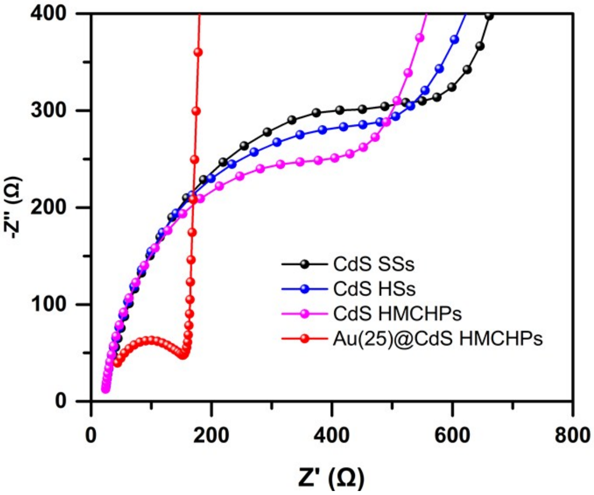

Fig. S17 Nyquist plots of EIS for CdS SSs, CdS HSs, CdS HMCHPs and Au(25)@CdS HMCHPs.

Table S1. Comparison of CO_2 photoreduction performance of different photocatalysts.

Catalyst	Cocatalyst	Sacrificial agent	Major product: evolution rate (μmol h^{-1} g^{-1})	Ref.
Au@CdS	$Co(bpy)_3^{2+}$	TEOA	CO: 3758	This work
CdS/BCN	$Co(bpy)_3^{2+}$	TEOA	CO: 250	1
HR-CN	$Co(bpy)_3^{2+}$	TEOA	CO: 297	2
BCN	$Co(bpy)_3^{2+}$	TEOA	CO: 94	3
$ZnIn_2S_4$-In_2O_3	$Co(bpy)_3^{2+}$	TEOA	CO: 3075	4
In_2S_3-$CdIn_2S_4$	$Co(bpy)_3^{2+}$	TEOA	CO: 825	5
$CuCo_2O_4$/CdS	$Co(bpy)_3^{2+}$	TEOA	CO: 2000	6
Co(II)/CdS	N.A.	Na_2SO_3	CO: 392	7
Ag/CdS	N.A	TEOA	CO: 260	8
Co-ZIF-9/CdS	bpy	TEOA	CO: 2520	9
CdS-WO_3	N.A.	N.A.	CH_4: 1.02	10
Bi_2WO_6/Au/CdS	N.A.	N.A.	CH_4: 1.52	11
$Fe_2V_4O_{13}$/RGO/CdS	N.A.	N.A.	CH_4: ~2.2	12
(Mo-Bi)S_x/CdS	N.A.	N.A.	HCOOH: 208	13

Supplementary References:

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