Fabrication of CdS hierarchical multi-cavity hollow particles for efficient visible light CO\textsubscript{2} reduction

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Experimental details

Synthesis of Co-G SSs: 0.375 mmol of Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O 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 °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\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O 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\textsubscript{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 °C for 1 h. The obtained CoS\textsubscript{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$xH$_2$O. Hydrothermal cation-exchange reaction was conducted at 120 °C 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 °C.

Synthesis of CdS SSs: 0.25 mmol of cadmium acetate and 1.25 mmol of thiourea were dissolved in 18 mL of H$_2$O. 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 °C.

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 °C 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$xH$_2$O. Hydrothermal cation-exchange reaction was conducted at 120 °C 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 °C.

Synthesis of Au@CdS HMCHPs: 8 mg of CdS HMCHPs was dissolved in 10 mL of H$_2$O. 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 °C.

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$_2$SO$_4$ 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$_2$O 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 CoS₈@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 CO₂ photoreduction performance of different photocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cocatalyst</th>
<th>Sacrificial agent</th>
<th>Major product: evolution rate (µmol h⁻¹ g⁻¹)</th>
<th>Ref.</th>
</tr>
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<tr>
<td>Au@CdS</td>
<td>Co(bpy)₃²⁺</td>
<td>TEOA</td>
<td>CO: 3758</td>
<td>This work</td>
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<tr>
<td>CdS/BCN</td>
<td>Co(bpy)₃²⁺</td>
<td>TEOA</td>
<td>CO: 250</td>
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<td>HR-CN</td>
<td>Co(bpy)₃²⁺</td>
<td>TEOA</td>
<td>CO: 297</td>
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<tr>
<td>BCN</td>
<td>Co(bpy)₃²⁺</td>
<td>TEOA</td>
<td>CO: 94</td>
<td>3</td>
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<tr>
<td>ZnIn₂S₄-In₂O₃</td>
<td>Co(bpy)₃²⁺</td>
<td>TEOA</td>
<td>CO: 3075</td>
<td>4</td>
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<tr>
<td>In₂S₃-CdIn₂S₄</td>
<td>Co(bpy)₃²⁺</td>
<td>TEOA</td>
<td>CO: 825</td>
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<tr>
<td>CuCo₂O₄/CdS</td>
<td>Co(bpy)₃²⁺</td>
<td>TEOA</td>
<td>CO: 2000</td>
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<tr>
<td>Co(II)/CdS</td>
<td>N.A.</td>
<td>Na₂SO₃</td>
<td>CO: 392</td>
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<tr>
<td>Ag/CdS</td>
<td>N.A.</td>
<td>TEOA</td>
<td>CO: 260</td>
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<td>Co-ZIF-9/CdS</td>
<td>bpy</td>
<td>TEOA</td>
<td>CO: 2520</td>
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<td>CdS-WO₃</td>
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<td>N.A.</td>
<td>CH₄: 1.02</td>
<td>10</td>
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<td>Bi₂WO₆/Au/CdS</td>
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<td>N.A.</td>
<td>CH₄: 1.52</td>
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<tr>
<td>Fe₂V₄O₁₃/RGO/CdS</td>
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<td>N.A.</td>
<td>CH₄: ~2.2</td>
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<tr>
<td>(Mo-Bi)Sₓ/CdS</td>
<td>N.A.</td>
<td>N.A.</td>
<td>HCOOH: 208</td>
<td>13</td>
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</table>

**Supplementary References:**