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Electronic Supplementary Information

The Function-Led Design of Z-Scheme Photocatalytic Systems Based on Hollow Carbon Nitride Semicondutors

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Experimental Section

Synthesis of HCNS: HCNS was prepared by thermal polymerization according to the literature. First, the monodisperse SiO_2 template were synthesized according to the Stöber method. Briefly, 3.10 g of aqueous ammonia (32 wt.%, Sigma-Aldrich) and 10 g of deionised water were added in 58.5 g of ethanol to from a mixture solution after stirring for 30 min at 30 °C. 5.6 ml of tetraethoxysilane (TEOS, Sigma-Aldrich) was added to the above solution with vigorous stirring and was left stationary for 1 h to yield uniform nonporous silica spheres. A mixture of adequate TEOS and n-octadecyltrimethoxysilane (C_{18}TMOS, Sigma-Aldrich) was then added dropwise to the above solution with magnetic stirring, sat quietly maturing for another 3 h at ambient temperature. The nanostructured silica was centrifuged, dried at 70 °C and calcined at 550 °C for 6 h in air. The as-prepared monodisperse SiO_2 templates were neutralized with a 1-M HCl solution and then dried at 80 °C overnight. Then, these monodisperse silica nanoparticles were used as a template to prepare HCNS. 2 g of the SiO_2 template was added to 10 g of cyanamide (Alfa Aesar), and kept under sonication and vacuum at 60 °C for 2 h. After that, the mixture was stirred at 60 °C overnight, which was then centrifuged, dried, and calcined at 550 °C for 4 h. The obtained powder was treated with 4 M NH_4HF_2 for 12 h to remove the silica template, then centrifuged and washed three times with distilled water and once with ethanol. The final yellow HCNS powders were obtained by drying at 80 °C in a vacuum oven overnight.

Synthesis of Au-HCNS: A certain amount of 1M $HAuCl_4$ trihydrate and poly(vinyl pyrrolidone) (PVP K30) were added to 5 mL of deionized water and stirred. Then, a certain amount of freshly-prepared 0.1 M $NaBH_4$ was added and stirred 2h. Next, 50 mg of prepared HCNS was added and magnetically stirred at room temperature for 3 h, meanwhile kept under vacuum. The particles were centrifugally separated and washed several times with distilled water, then heated at 80 °C overnight.

Synthesis of xCdS-Au-HCNS: A suitable amount of S8 and $Cd(ClO_4)_2 \cdot 6H_2O$ was dissolved in 50 mL ethanol suspension to form a clear solution after stirring for 30 min at room temperature. Subsequently, 50 mg prepared Au-HCNS was added in the above solution and bubbled with argon for 30 min in the dark, irradiation was carried out for a given period with a 300W Xe lamp and a water-cooling filter. Then, the precipitate was harvested by centrifugation and washed several times with deionized water before being dried in oven at 60 ^{o}C.

Synthesis of (CdS+Au)-HCNS: A suitable amount of prepared Au and CdS were added to 50 mL of deionized water and stirred. Then, 50 mg prepared HCNS was added and stirred 3h. The particles were centrifugally separated and washed several times with distilled water, then drying at 60 °C overnight.

Synthesis of CdS: the same method as synthesis of CdS-Au-HCNS samples, but instead of Au-HCNS by SiO_2, which has same diameter of HCNS.

Synthesis of CdS-M (M=Pd, Ag, Pt)-HCNS: the same method and experimental conditions with synthesis of CdS-Au-HCNS, except use different noble metals precursors.

Characterization: The morphology of the sample was investigated by field emission scanning electron microscopy (SEM) (JSM-6700F). Transmission electron microscopy (TEM) was obtained by Zeis 912 microscope. The nitrogen adsorption–desorption isotherms were collected at 77 K using Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Powder X-ray diffraction (XRD) measurements were performed on Bruker D8 Advance diffractometer with Cu Ka1 radiation (k = 1.5406 Å). Fourier transformed infrared (FTIR) spectra were recorded on BioRad FTS 6000 spectrometer. X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo ESCALAB250 instrument with a monochromatized Al Kα line source (200 W). The solid-state ^{13}C-NMR spectra were collected using a Bruker Advance III 500 Spectrometer. UV–Vis diffuse reflectance spectra (UV–Vis DRS) were performed on Varian Cary 500 Scan UV–visible system. Photoluminescence spectra were recorded on an Edinburgh FI/FSTCSPC 920 spectrophotometer. Electron paramagnetic resonance (EPR) measurements were performed using a Bruker model A300 spectrometer. Electrochemical measurements were conducted with a BAS Epsilon Electrochemical System in a conventional three electrode cell, using a Pt plate as the counter electrode and an Ag/AgCl electrode (3 M KCl) as the reference electrode. The working electrode was prepared on indium-tin oxide (ITO) glass that was cleaned by sonication in ethanol for 30 min and dried at 353 K. The boundary of ITO glass was protected using Scotch tape. The 5 mg sample was dispersed in 1 mL of DMF by sonication to get a slurry. The slurry was spread onto pretreated ITO glass. After air-drying, the working electrode was further dried at

393 K for 2 h to improve adhesion. Then, the Scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin.

Photocatalytic hydrogen evolution: Photocatalytic H_2 production was carried out in a Pyrex top-irradiation reaction vessel connected to a glass-closed gas circulation system. For each reaction, 20 mg well-ground catalyst powder was dispersed in an aqueous solution (100 mL) containing triethanolamine (10 vol%) as sacrificial electron donor. 3 wt% Pt was photodeposited onto the catalysts using H_2PtCl_6 dissolved in the reactant solution. The reactant solution was evacuated several times to remove air completely prior to irradiation under a 300W Xe lamp and a water-cooling filter. The wavelength of the incident light was controlled by using an appropriate long pass cut-off filter. The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were analyzed by gas chromatography equipped with a thermal conductive detector (TCD) with argon as the carrier gas.

Photocatalytic CO_2 reduction: A 300 W Xe lamp with a 420 nm cut-off filter was utilized as the light source for the typical photocatalytic reactions. In brief, 30 mg catalyst, 1 μmol $CoCl_2$, 15 mg 2, 2-bipyridine, 1 mL triethanolamine (TEOA) and 5 mL solvent were added to the Schlenk flask reactor (80 mL in capacity). After 3 times vacuum degassing and backfilling the reactor with pure CO_2, the reaction system was finally filled with CO_2 (1 atm). In the whole reaction process, the reaction system was energetically stirred and the reaction temperature was maintained at 30 °C with cooling water system. After the photocatalytic reactions, the produced gases were analyzed by a gas chromatography.

Table S1. Physicochemical properties of the *x*CdS-Au-HCNS and HCNS samples.

Sample	C/N atomic	CdS [a] [wt.%]	SA [b] [m^2 g^{-1}]	PV [c] [cm^3 g^{-1}]
HCNS	0.72	0	80	0.31
1CdS-Au-HCNS	0.72	4.1	85	0.36
2CdS-Au-HCNS	0.72	12.7	87	0.32
3CdS-Au-HCNS	0.73	21.6	86	0.34

[a] Calculated from elemental analysis result about S amount; [b] BET surface area calculated from the linear part of the BET plot (P/P_o = 0.1-0.2); [c] Total pore volume, taken from the volume of N_2 adsorbed at P/P_o = 0.99.

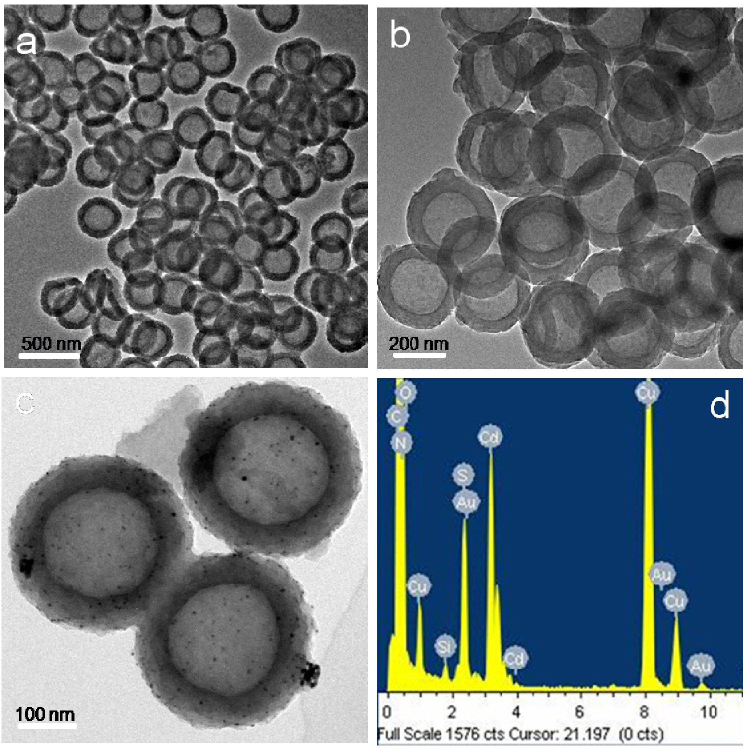

Figure S1. TEM image of (a) HCNS, (b) Au-HCNS, and (c) 2CdS-Au-HCNS samples; (d) TEM-EDX spectrum of 2CdS-Au-HCNS.

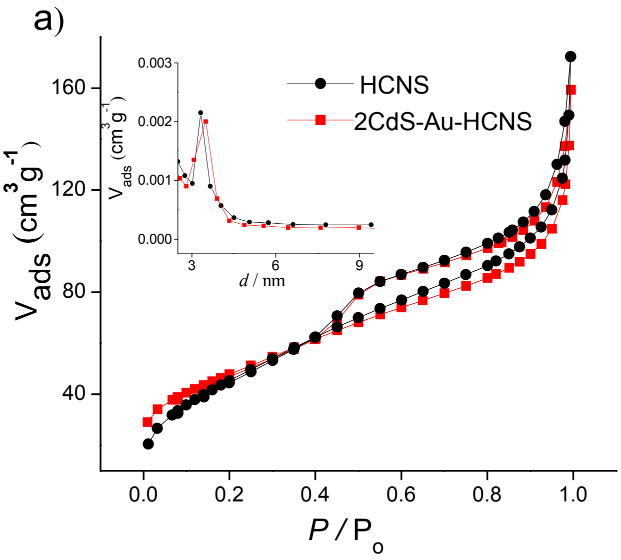

Figure S2. N_2 adsorption-desorption isotherms and the corresponding Barrett-Joyner-Halenda pore-size distribution (inset) of 2CdS-Au-HCNS.

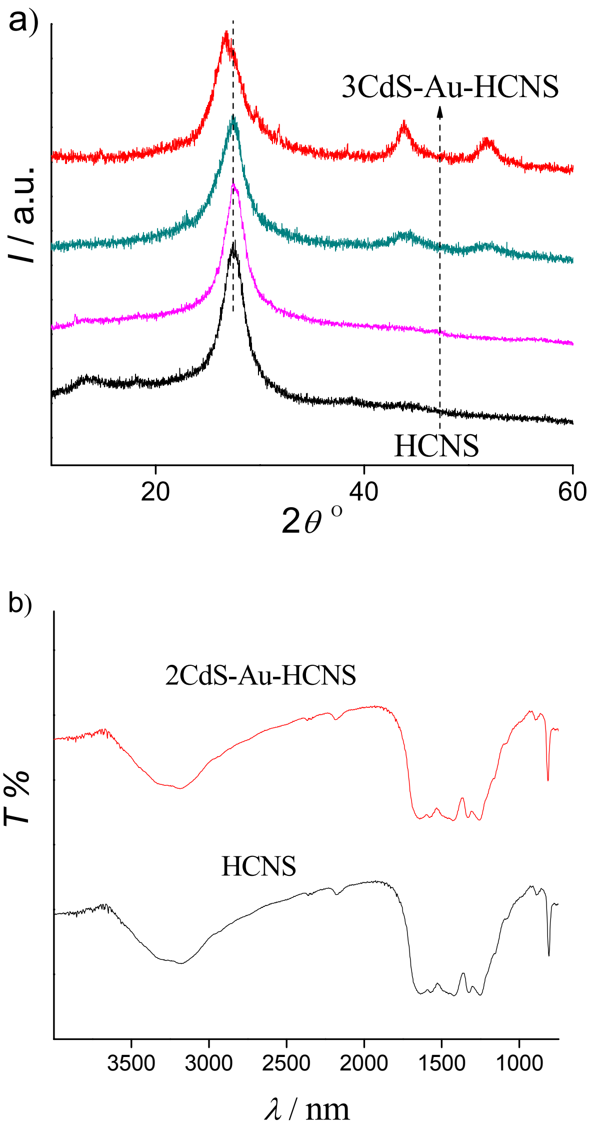

Figure S3. (a) XRD patterns (b) FT-IR spectra of 2CdS-Au-HCNS and HCNS samples.

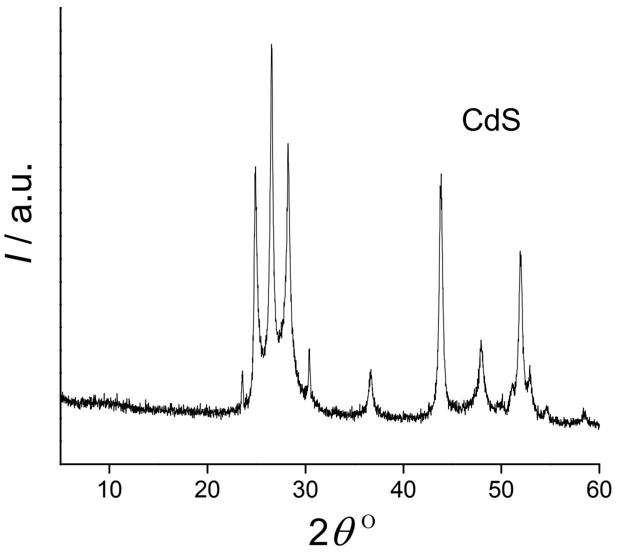

Figure S4. XRD patterns of CdS.

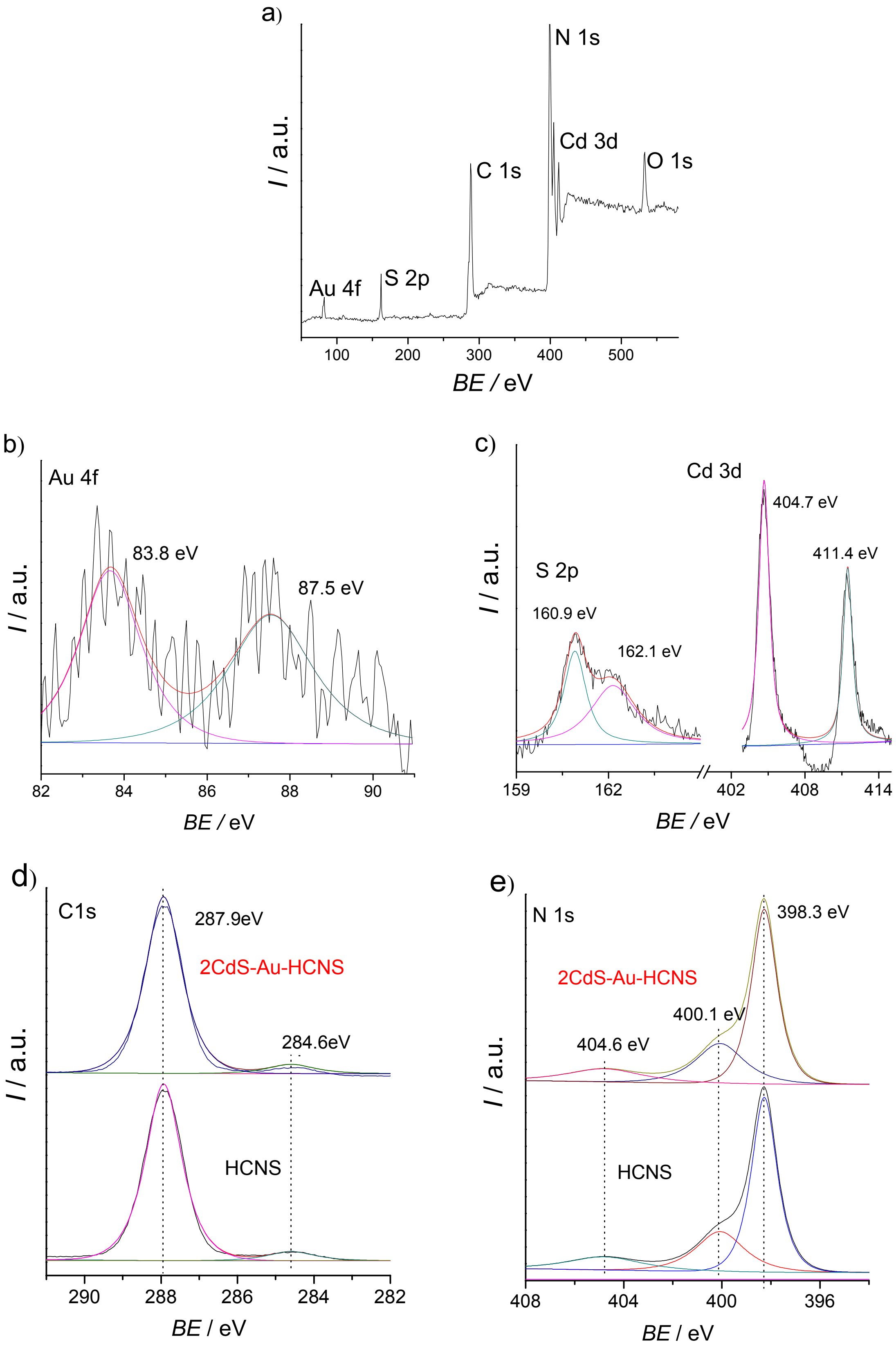

Figure S5. XPS analysis of 2CdS-Au-HCNS samples, with reference of HCNS.

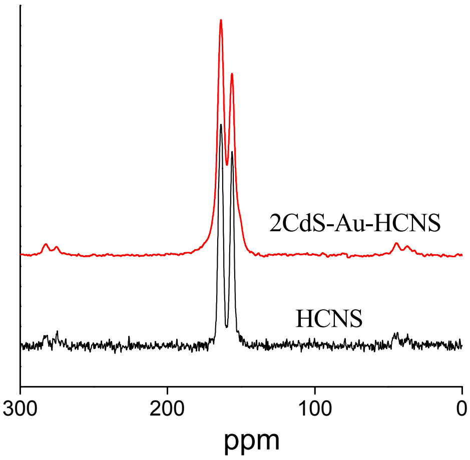

Figure S6. Solid-state ^{13}C NMR spectra of 2CdS-Au-HCNS photocatalysts.

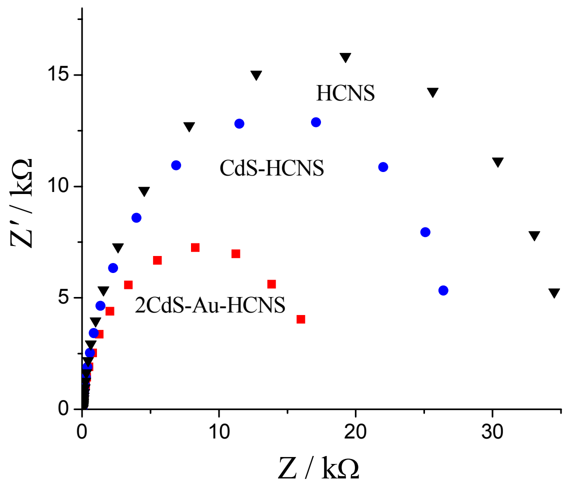

Figure S7. EIS Nyquist plots of 2CdS-Au-HCNS, CdS-HCNS and HCNS samples**.**

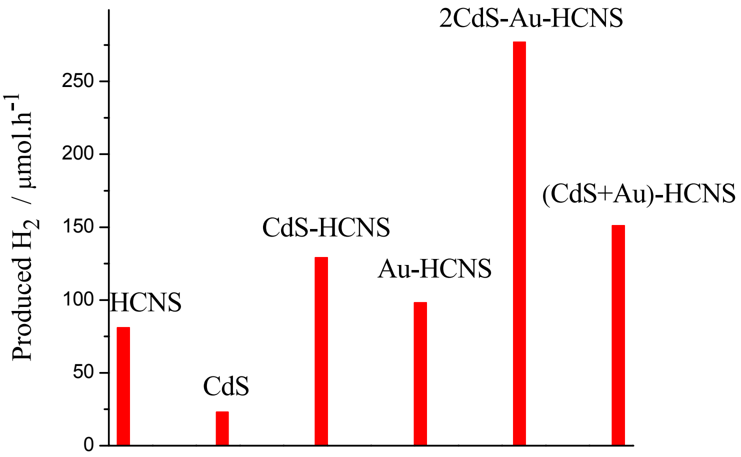

Figure S8. Photocatalytic hydrogen evolution by 2CdS-Au-HCNS under visible-light irradiation (λ>455 nm), together with HCNS, CdS, CdS-HCNS, Au-HCNS and (CdS+Au)-HCNS samples as the comparison**.**

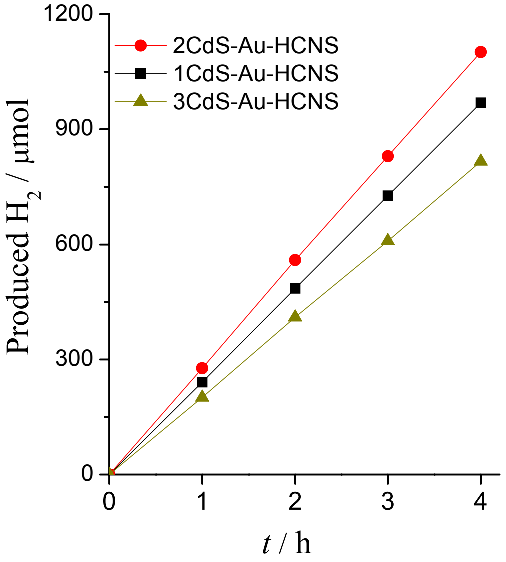

Figure S9. Photocatalytic hydrogen evolution by CdS-Au-HCNS samples under visible-light irradiation (λ>455 nm).

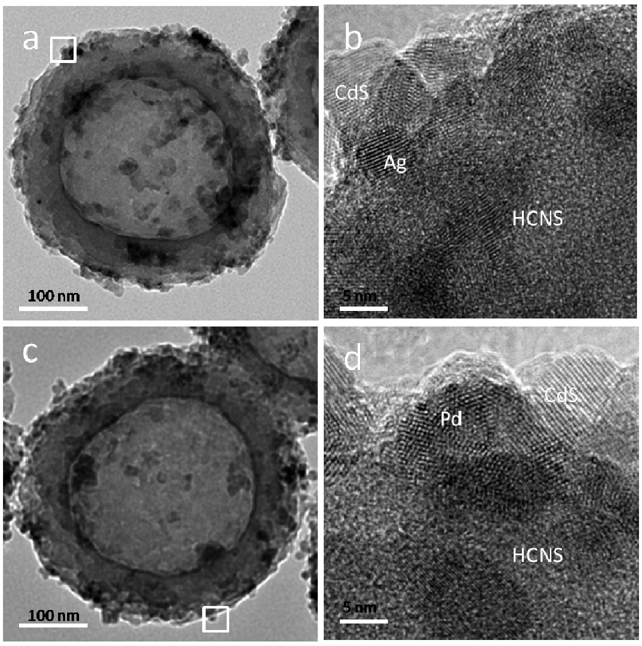

Figure S10. TEM and HRTEM images of a), b) CdS-Ag-HCNS samples, and c), d) CdS-Pd-HCNS photocatalysts, repectively.

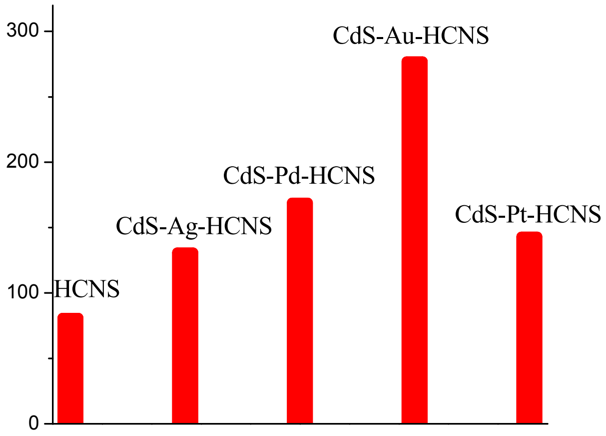

Figure S11. Photocatalytic hydrogen evolution by Z-sheme photocatalysts with differents electron mediator under visible-light irradiation (λ>455 nm).

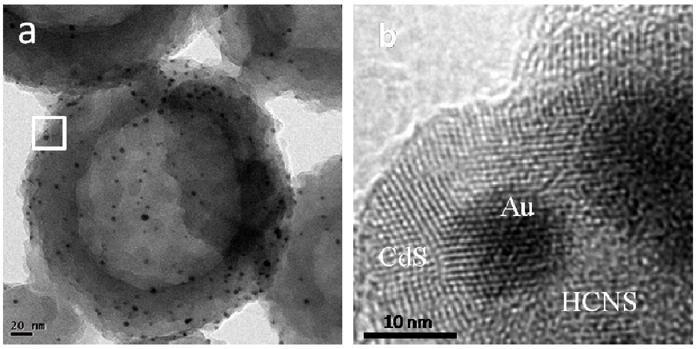

Figure S12. TEM images of the 2CdS-Au-HCNS sample recovered after the photocatalytic reaction.

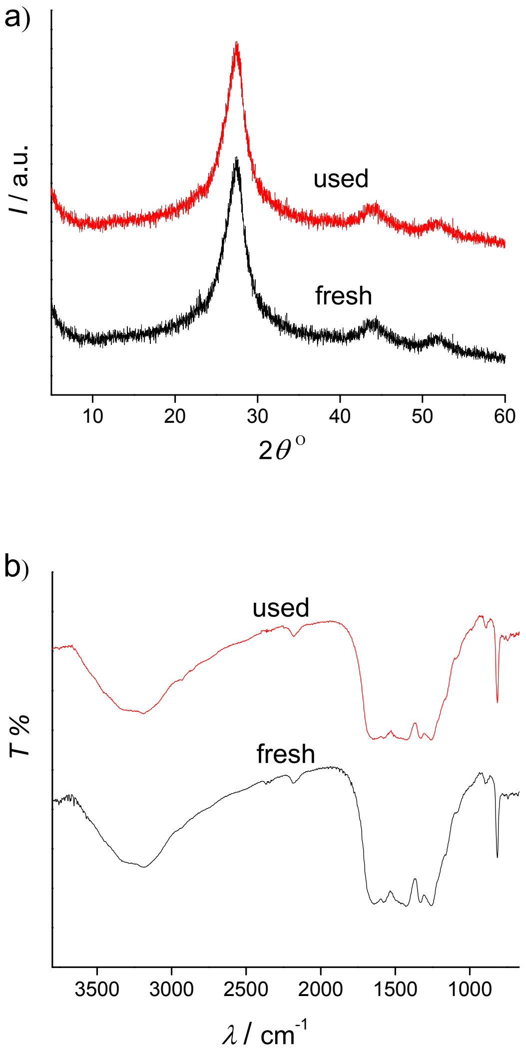

Figure S13. Structure of 2CdS-Au-HCNS samples before and after the photochemical reaction. a) XRD pattern; b) FTIR spectra.

Table S2. The reactivity of photocatalysts for CO_2 reduction.

Catalyst	CO / µmol	H_2 / µmol	CO+H_2 / µmol	TON[a]	Selectivity[b] / %
2CdS-Au-HCNS	6.8	1.2	8.0	8.0	85.0
HCNS	2.6	0.5	3.1	3.1	83.9
2CdS-HCNS	3.2	0.7	3.9	3.9	82.1
(2CdS+Au)/HCNS	3.4	4.1	7.5	7.5	45.3
2CdS-Au-HCNS[c]	n.d.[d]	n.d.	-	-	-
- [e]	n.d.	n.d.	-	-	-
2CdS-Au-HCNS[f]	n.d.	0.5	0.5	0.5	-

Reaction conditions: acetonitrile (3 mL), triethanolamine (1mL), CO_2 (1bar), bipyridine (15 mg), H_2O (1mL), $CoCl_2·6H_2O$ (1µmol), 30 mg catalyst, 30 °C, 1 h, and $\lambda > 420$ nm. [a]Turn over number = (mol amount of CO and H_2)/(mol amount of cobalt ion). [b]Selectivity = $n_{CO}/n_{(CO+H2)} \times 100$. [c] In dark. [d] Not detectable. [e] Without catalyst. [f] Using Ar instead of CO_2.