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Electronic Supplementary Information

Enhanced visible-light photocatalytic hydrogen production activity of three-dimensional mesoporous p-CuS/n-CdS nanocrystal assemblies

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Table S1. Comparison of H_2-production activity of different metal sulfide photocatalysts studied under similar experimental conditions.

Photocatalyst	**Reaction conditions**	**Light source**	**H_2-production activity (QE at λ=420 nm)**	**Ref.**
MoS_2/CdS composites	0.1 g catalyst, 10 vol% lactic acid solution	300-W Xe lamp (λ>420 nm)	~0.53 mmol h^{-1}	[5]
WS_2/CdS particles	0.1 g catalyst, 10 vol% lactic acid solution	300-W Xe lamp (λ>420 nm)	~0.42 mmol h^{-1} (QE~5%)	[6]
NiS/CdS composites	0.3 g catalyst, 30 vol% lactic acid solution	300-W Xe lamp (λ>420 nm)	~2.18 mmol h^{-1} (QE~51.3%)	[7]
Pt/CdS nanostructures	0.15 g catalyst, 0.25 M Na_2SO_3/0.35 M Na_2S solution	300-W Xe lamp (λ>420 nm)	~4.1 mmol h^{-1} (QE~60.3%)	[8a]
Pt/CdS NCAs	20 mg catalyst, 10 vol% ethanolic alkaline (5M NaOH) solution	300-W Xe lamp (λ>420 nm)	~1.2 mmol h^{-1} (QE~70%)	[8b]
CuS/ZnS nanosheets	0.2 g catalyst, 0.25 M Na_2SO_3/0.35 M Na_2S solution	350-W Xe lamp (λ>420 nm)	~0.21 mmol h^{-1} (QE~20%)	[14]
Co_3O_4/CdS nanocomposites	50 mg catalyst, 10 vol% lactic acid solution	350-W Xe lamp (λ>420 nm)	~0.15 mmol h^{-1} (QE~9.7%)	[25a]
Cu_2S/CdS nanoparticles	0.2 g catalyst, 0.25 M Na_2SO_3/0.35 M Na_2S solution	300-W Xe lamp (λ>420 nm)	~0.4 mmol h^{-1} (QE~9.5%)	[25b]
$Cd_{0.8}Zn_{0.2}S$ particles	0.2 g catalyst, 0.25 M Na_2SO_3/0.35 M Na_2S solution	350-W Xe lamp (λ>430 nm)	~0.18 mmol h^{-1} (QE~10.2%)	[25c]
CdS/$Zn_{0.2}Cd_{0.8}S$ composites	0.2 g catalyst, 0.04 M Na_2SO_3/0.1 M Na_2S solution	350-W Xe lamp (λ>400 nm)	~0.11 mmol h^{-1} (QE~6.3%)	[25d]
$Cd_{0.1}Cu_{0.01}Zn_{0.89}S$ particles	0.3 g catalyst, 0.3 M Na_2SO_3/0.2 M Na_2S solution	350-W Xe lamp (λ>430 nm)	~0.35 mmol h^{-1} (QE~9.6%)	[25e]
$(Zn_{0.95}Cu_{0.05})_{0.67}Cd_{0.33}S$ NCs	0.3 g catalyst, 0.35 M Na_2SO_3/0.25 M Na_2S solution	300-W Xe lamp (λ>420 nm)	~0.51 mmol h^{-1} (QE~15.7%)	[25f]
CdS/CNTs nanocomposites	35 mg catalyst, 0.25 M Na_2SO_3/0.35 M Na_2S solution	300-W Xe lamp (λ>420 nm)	~0.17 mmol h^{-1} (QE~2.1%)	[25g]
ZnS-In_2S_3-CuS nanospheres	0.3 g catalyst, 1.2 M Na_2SO_3/0.1 M Na_2S solution	300-W Xe lamp (λ>400 nm)	~3.6 mmol h^{-1} (QE~22.6%)	[25h]
CdS-ZnS-In_2S_3 microspheres	15 mg catalyst, 1.4 M Na_2SO_3/0.1 M Na_2S solution	300-W Xe lamp (λ>400 nm)	~0.12 mmol h^{-1} (QE~40.9%)	[25i]
ZnS-In_2S_3-Ag_2S nanostructures	15 mg catalyst, 0.35 M Na_2SO_3/0.25 M Na_2S solution	300-W Xe lamp (λ>400 nm)	~3.3 mmol h^{-1} (QE~19.8%)	[25j]

$Pt/Ag_2S/CdS$ composites	0.1 g catalyst, 0.25 M Na_2SO_3/0.35 M Na_2S solution	150-W solar simulator (AM1.5)	~0.09 mmol h^{-1}	[25k]
MoS_2/mpg-C_3N_4 composites	20 mg catalyst, 10 vol% lactic acid solution	300-W Xe lamp (λ>420 nm)	~0.02 mmol h^{-1} (QE~2.1%)	[25l]
CuS/CdS NCAs	**20 mg catalyst, 0.25 M Na_2SO_3/0.35 M Na_2S solution**	**300-W Xe lamp (λ>420 nm)**	**~0.28 mmol h^{-1} (QE~12.6%)**	**In this work**

Table S2. Analytical data obtained from Mott-Schottky plots for pristine CdS and different Cu-loaded CdS NCAs.

Sample	E_{FB} (V vs. NHE)	Slope[a] ($F^{-2}cm^4V^{-1}$)	Donor concentration[b] (cm^{-3})
CdS NCAs	-0.41	4.034×10^{10}	3.93×10^{16}
3% CuS/CdS	-0.44	4.825×10^{10}	3.28×10^{16}
5% CuS/CdS	-0.43	4.267×10^{10}	3.71×10^{16}
8% CuS/CdS	-0.51	3.466×10^{10}	4.55×10^{16}

[a]Slope (k) = $1/(E–E_{FB})C^2$, where C is the space charge capacitance, E is the applied potential and E_{FB} is the flat-band potential. [b]Donor concentration (N_D) given by $N_D = 2(E–E_{FB})\cdot C^2/\varepsilon\varepsilon_o e$, where ε is the relative dielectric constant of CdS (8.9), ε_o is the dielectric permittivity (8.8542×10^{-10} F cm^{-1}) and e is the elementary charge (1.602×10^{-19} C).

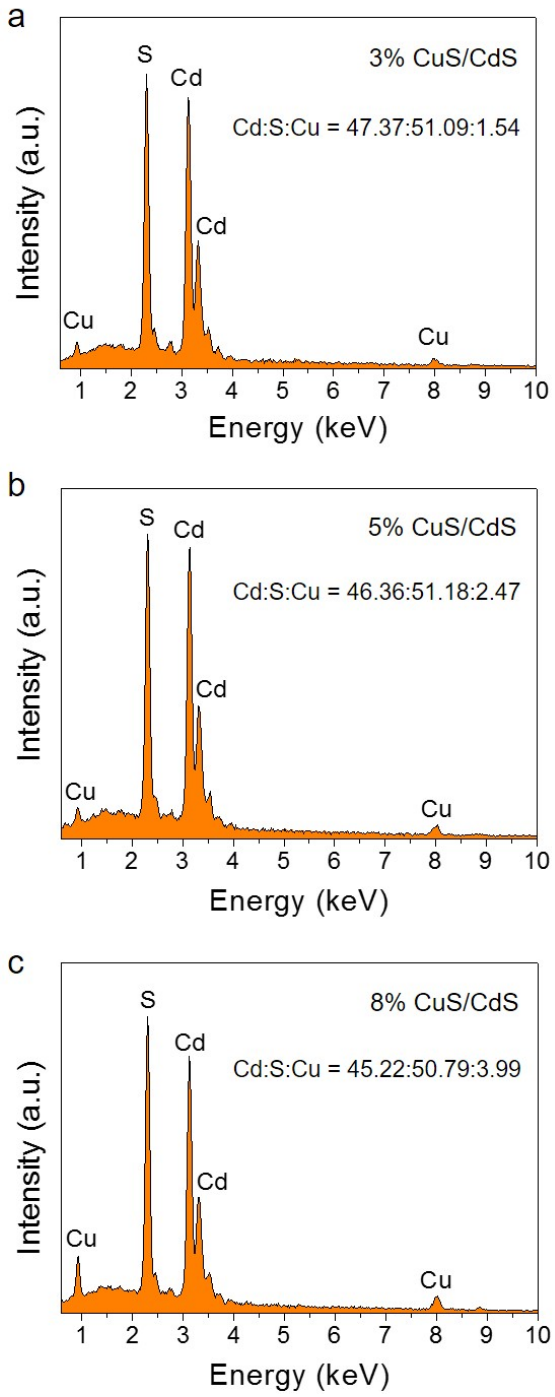

Fig. S1 Typical EDS spectra of the mesoporous Cu-loaded CdS NCAs.

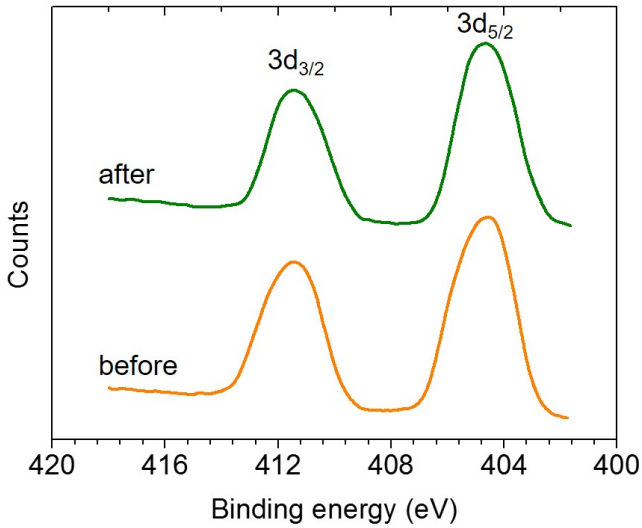

Fig. S2 High-resolution Cd $3d_{5/2}$ and $3d_{3/2}$ core-level photoelectron spectra of the mesoporous 5% CuS/CdS NCAs before and after photocatalytic reaction.

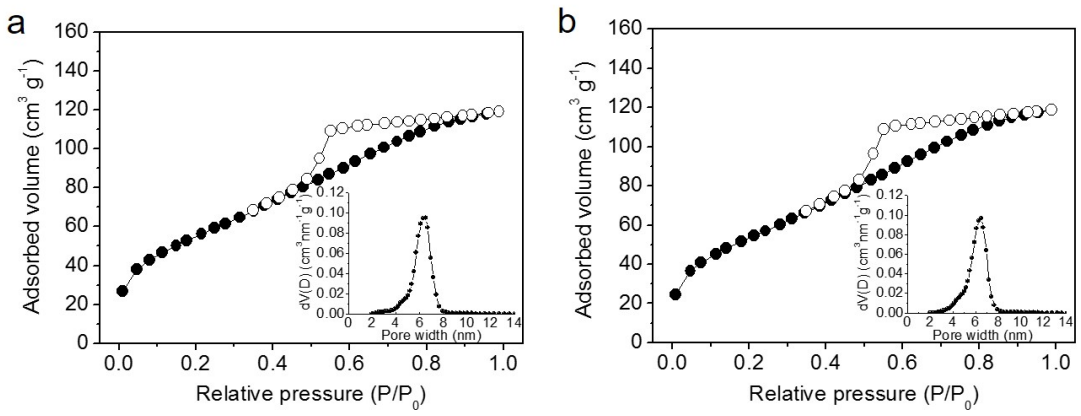

Fig. S3 Nitrogen adsorption-desorption isotherms at -196 ^{o}C for the mesoporous (a) 3% CuS/CdS and (b) 8% CuS/CdS NCAs catalysts. Insets: The corresponding NLDFT pore size distributions calculated from the adsorption branch of isotherms.

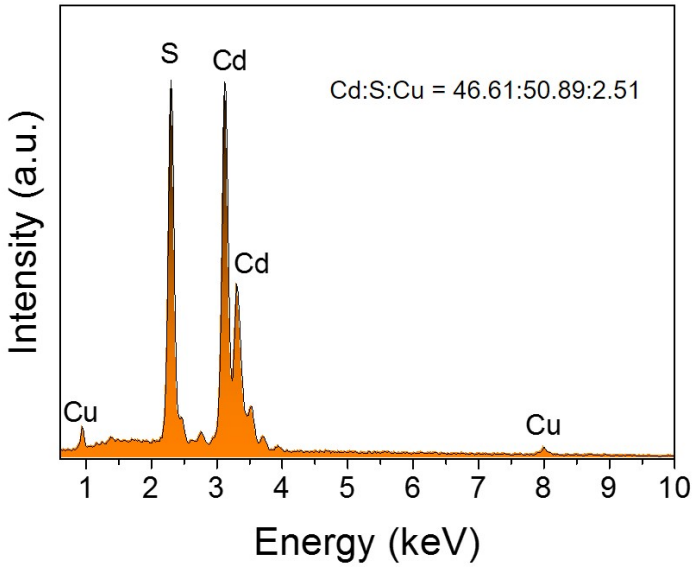

Fig. S4 Typical EDS spectrum of the bulk Cu-loaded CdS solid.

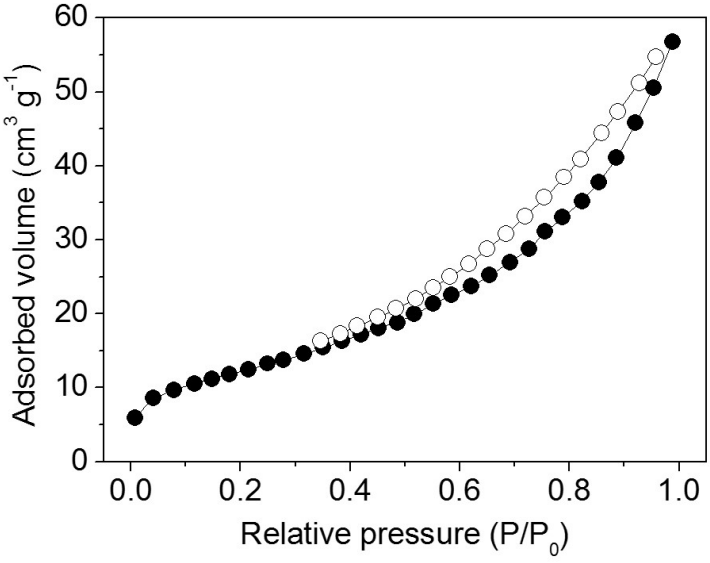

Fig. S5 Nitrogen adsorption-desorption isotherms at -196 ^{o}C for the bulk Cu-loaded CdS solid (5% CuS/CdS bulk). Analysis of the adsorption data indicates a BET surface area of 45 m^2 g^{-1} and a total pore volume of 0.08 cm^3 g^{-1}.

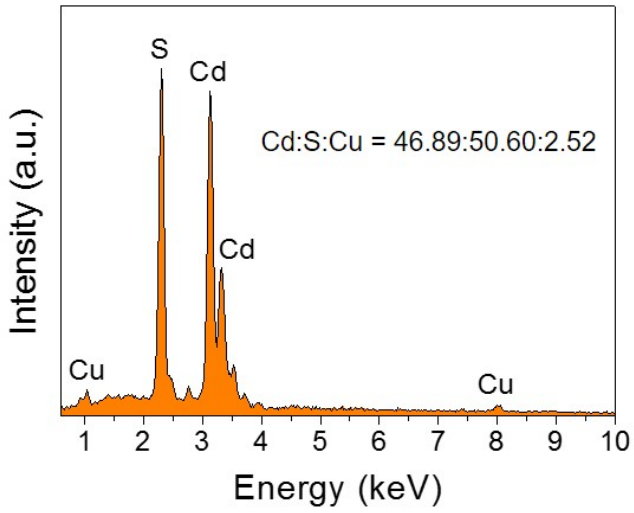

Fig. S6 Typical EDS spectrum of the regenerated mesoporous 5% CuS/CdS NCAs catalyst, showing a Cu content of ~5.09 mol%.

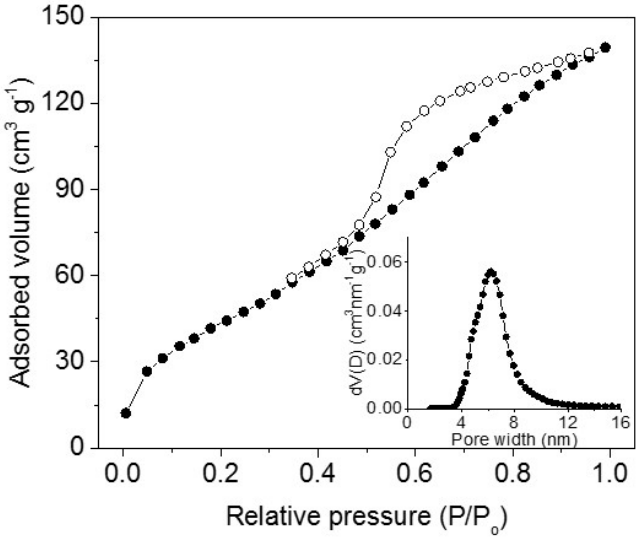

Fig. S7 Nitrogen adsorption-desorption isotherms at -196 ^{o}C and the corresponding NLDFT pore size distribution (inset) for the 5% CuS/CdS NCAs catalyst retrieved after 20 hours of photocatalytic reaction.