Supporting information

Partially Cu Ion Exchange Induced Triangle Hexagonal Mn_{0.45}Cu_{0.05}Cd_{0.5}S Nanocrystal for Enhanced Photocatalytic Hydrogen Evolution

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Experimental Section

Materials and reagents

Oleylamine (OAm,80–90%), cadmium acetate dihydrate (99.99%), copper acetate (97%), manganese(II) chloride tetrahydrate (MnCl₂·4H₂O, 99%) and elemental sulfur (S, 99.99%) were purchased from Aladdin. Na₂S·9H₂O (98%, AR) and Na₂SO₃ (97%, AR) were purchased from Shanghai Macklin Biochemical Co. Ltd. Hexane and acetone were purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents were used without further purification.

Instrumentation

XRD patterns were measured on Ultima IV diffractometer (Rigaku, Japan) with a Cu K_a irradiation source (λ = 1.54056 Å). TEM images and HRTEM images were obtained on JEM-2100 with an accelerating voltage of 200 kV. UV-Vis absorption spectra of the photocatalysts were recorded on a Shimadzu UV-2600 spectrometer using BaSO₄ as reference. XPS spectra was recorded on a Perkin-Elmer PHI 5000C ESCA system equipped with Al K_a radiation. PL spectra and TRPL spectra of the samples were conducted with a Fluoromax-4 fluorescence spectrometer (Horiba).

Synthesis of $Mn_{0.5-m}Cu_mCd_{0.5}S$ (m=0-0.10) nanocrystals

Colloidal $Mn_{0.5-m}Cu_mCd_{0.5}S$ nanocrystals were prepared by a standard Schlenk techniques under purified N₂ atmosphere. In a typical synthesis of $Mn_{0.45}Cu_{0.05}Cd_{0.5}S$, 1 mmol $Cd(OAc)_2 \cdot 2H_2O$, 0.90 mmol $MnCl_2 \cdot 4H_2O$, and 0.1 mmol $Cu(OAc)_2$, were dissolved with 10 mL OAm in three-neck flask. The mixture was degassed at 120 °C under vacuum for 30 min. Next, the mixture containing 2 mmol elemental sulfur and 5 mL OAm was rapidly injected into the metal sources solution. The reaction was proceeded at 260 °C for 3 h. After cooling down to room temperature naturally, the final product was allowed to precipitate and washed with excess ethanol and hexane for three times and then dried at 60 °C over 6 h in a vacuum oven. The variable compositions of $Mn_{0.5-m}Cu_mCd_{0.5}S$ solid solution were successfully prepared with the

increase of m value from 0 to 0.1. $Mn_{0.5}Cd_{0.5}S$ nanorods were generally synthesized according to the above procedure without adding metal copper salts.

Photocatalytic performance test

Photocatalytic H₂ evolution experiments were performed in a closed gas circulation system using a 300 W Xe lamp (Perfectlight, PLS-SXE300) equipped with a cut-off filter (λ > 400 nm) and system temperature was maintained at 25 ± 0.2 °C. Before the test, the as-prepared Mn_{0.5-m}Cu_mCd_{0.5}S solid solutions were transferred into water using 3-mercaptopropionic acid assisted phase transfer method. Normally, 10 mg of prepared photocatalyst was dispersed in 80 mL of aqueous solution containing Na₂S·9H₂O (0.57 M) and Na₂SO₃ (1.25 M) as sacrificial reagents. The system was vacuumed and purged with nitrogen to remove air and water in the reactor. The generated H₂ content was measured by an online gas chromatography (GB-9890, TCD, Ar carrier gas) at an half-hourly auto sampling interval.

According to Eq.(1), the apparent quantum efficiency (AQE) was calculated with a 400 nm band pass filter under the same photocatalytic reaction condition. The average intensity of irradiation was 100 mW/cm² and the irradiation area was determined to be 23.74 cm².

$$AQE[\%] = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100$$

$$= \frac{\text{number of evolved H2 molecules } \times 2}{\text{number of incident photons}} \times 100$$

(1)



Fig. S1 The XRD patterns of the powdered $Mn_{0.5-m}Cu_mCd_{0.5}S$ (m=0-0.10) solid solutions (a) full range, and (b) enlarged view of 20 between 24-30 degree



Fig. S2 Digital photographs of synthesized Mn_{0.5-m}Cu_mCd_{0.5}S (m=0-0.10) samples.



Fig. S3 HRTEM images of synthesized $Mn_{0.5}Cd_{0.5}S$ samples (a) top view, and (b) the sectional view.



Fig. S4 Nitrogen adsorption and desorption isotherms of $Mn_{0.5}Cd_{0.5}S$ and

Mn_{0.45}Cu_{0.05}Cd_{0.5}S nanocrystal.



Fig. S5 (a) UV-Vis diffuse reflection spectra, and (b) the $(\alpha hv)^2$ - hv plots of the powered Mn_{0.5-m}Cu_mCd_{0.5}S (m=0-0.10) solid solutions with different molar ratios of Cu.



Fig. S6 Mott–Schottky plots of $Mn_{0.45}Cu_{0.05}Cd_{0.5}S$ and $Mn_{0.5}Cd_{0.5}S$ samples in aqueous 0.2 M K₂SO₄ solution. Frequencies was set at 10 kHz.



Fig. S7 The XPS spectra of $Mn_{0.45}Cu_{0.05}Cd_{0.5}S$ solid solutions: (a) survey spectrum, and high resolution XPS spectra of (b) Mn 2*p* (c) Cd 3*d* (d) S 2*p* (e) Cu 2*p*.

XPS peak	Atomic %	Theoretical Mn :Cu	Experimental Mn:Cu	
Cu 2p	2.44		0.441:0.059	
Mn 2p	18.34			
Cd 3d	20.88	0.450:0.050		
S 2p	31.26			
C 1s	27.08			

Table S1 XPS analysis of Mn_{0.45}Cu_{0.05}Cd_{0.5}S

Table S2 The photocatalytic hydrogen evolution performance of $Mn_{0.45}Cu_{0.05}Cd_{0.5}S$ photocatalysts with sacrificial agents of different concentrations. (A higher concentration of sacrificial agent could cause a decrease in catalytic activity, possibly because the oxidation products (Na₂S₂O₃and Na₂SO₄) would adhere to the catalyst surface, blocking the active sites, thereby reducing the photocatalytic reaction.)

The sacrificial agent		Mn _{0.45} Cu _{0.05} Cd _{0.5} S	
Na ₂ S(M)	Na ₂ SO ₃ (M)	Rate of H ₂ evolution(µmol·g ⁻¹ ·h ⁻¹)	
0.57	1.25	147921	
0.4275	0.9375	197273	
0.285	0.525	151946	
0.114	0.250	78711	



Fig. S8 Photocatalytic H_2 production activities of $Mn_{0.5-m}Cu_mCd_{0.5}S$ (m=0-0.10) solid solutions under visible-light irradiation

No.	Photocatalyst	Rate of H ₂	Preparation Method	Ref.
		Evolution		
1	Cu doped Mn-Cd-S	750 μmol·g ⁻¹ ·h ⁻¹		[1]
2	Ag-doped Mn-Cd sulfide	4400 μmol·g ⁻¹ ·h ⁻¹	hydrothermal method	[2]
3	Cu ²⁺ doped In _{2x} Zn _{3(1-x)} S ₃	790 μmol·g ⁻¹ ·h ⁻¹		[3]
4	Cu _{2-x} S/Mn _{0.5} Cd _{0.5} S/MoS ₂	13752 μmol g ⁻¹ ·h ⁻¹		[4]
5	P-doped $Zn_xCd_{1-x}S$	419 μmol g ⁻¹ ·h ⁻¹	hydrothermal method and thermal phosphorization	[5]
6	Cu-doped ZnS	105 μmol g ⁻¹ ·h ⁻¹	coprecipitation method	[6]
7	Cu-modified Zn _x Cd _{1-x} S	4638.5 μmol·g ⁻¹ ·h ⁻¹	cation-exchange and coprecipitation methods	[7]
8	Cu-doping Zn _{1-x} Cd _x S	21400 μmol·g ⁻¹ ·h ⁻¹		[8]
9	MoS ₂ modified Mn _{0.25} Cd _{0.75} S	12470 μmol·g ⁻¹ ·h ⁻¹	solvothermal method	[9]
10	Mn _{0.2} Cd _{0.8} S/CoP ₃ composite	29530 µmol·g ⁻¹ ·h ⁻¹		[10]
11	NiS/Mn _x Cd _{1-x} S	419.3 μmol/h	hydrothermal method and suit precipitation process	[11]
12	Cu _{1.94} S–Zn _x Cd _{1-x} S	7735 μmol·g ⁻¹ ·h ⁻¹		[12]
13	Mn _{0.45} Cu _{0.05} Cd _{0.5} S nanotriangle	147921 μmol·g ⁻¹ ·h ⁻¹	colloidal method	This work

Table S3 Comparison of H_2 evolution rate with other Mn-Cd-S solid solutions.



Fig. S9 Recycle H₂ production of $Mn_{0.45}Cu_{0.05}Cd_{0.5}S$ under visible-light irradiation ($\lambda > 400$ nm).



Fig. S10 XRD patterns of the $Mn_{0.45}Cu_{0.05}Cd_{0.5}S$ solid solution photocatalyst before and after the photocatalytic reactions.



Fig. S11 The PL spectra of $Mn_{0.5}$ mCu_mCd_{0.5}S (m=0-0.10) samples.

Table. S4 PL lifetime fitting results for $Mn_{0.45}Cu_{0.05}Cd_{0.5}S$ and $Mn_{0.5}Cd_{0.5}S$

Sample	τ1	τ ₂	τ ₃
Mn _{0.45} Cu _{0.05} Cd _{0.5} S	1.06	5.64	104.36
Mn _{0.5} Cd _{0.5} S	1.04	5.42	81.79



Fig.S12 I-t curves of $Mn_{0.5}Cd_{0.5}S$ and $Mn_{0.45}Cu_{0.05}Cd_{0.5}S$ samples



Fig.S13 EIS curves of as-prepared $Mn_{0.45}Cu_{0.05}Cd_{0.5}S$ and $Mn_{0.5}Cd_{0.5}S$ samples.



Fig. S14 Schematic illustration of the possible mechanism for the photocatalytic H_2 production of under visible light irradiation.

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