Supporting Information

One-step facile synthesis and high H_2 -evolution activity of suspensible $Cd_xZn_{1-x}S$ nanocrystal photocatalysts in a S^{2-}/SO_3^{2-} system

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Initial x	Final x (EDS)	Final <i>x</i> (ICP-OES)	Crystallite size ^{<i>a</i>} (nm)	Band gap ^b (eV)	H ₂ - production rate (µmol·h ⁻¹)	Quantum efficiency (%) ^c
1.0	1.0	1.0	6.9	2.25	320.99	12.84
0.8	0.72	0.79	6.0	2.44	518.61	20.74
0.6	0.58	0.60	5.5	2.53	717.19	28.69
0.4	0.32	0.41	5.2	2.64	570.25	22.81
0.2	0.17	0.20	5.0	2.86	353.53	14.14
0	0	0	4.7	3.52	5.89	0.24

Table S1 Summary of physical and chemical properties for the prepared suspensible $Cd_xZn_{1-x}S$ nanocrystals.

^{*a*} crystallite size is determined by the (111) diffraction peak of suspensible $Cd_xZn_{1-x}S$ nanocrystals using Scherrer equation.

 b the band gaps of the suspensible Cd_xZn_{1-x}S nanocrystals were calculated according to the UV-vis spectra.

^c the quantum efficiency (QE) was calculated by using the following Eq:

QE[%]=(number of evolved H₂ molecules*2)/(number of incident photons) *100%



Fig. S1. Photographs of $Cd_{0.6}Zn_{0.4}S$ nanocrystals synthesized in (A) a sulfur-rich S²⁻/SO₃²⁻ solution with an atom ratio of M²⁺(Cd²⁺/Zn²⁺):S²⁻ = 1:81 and (B) a conventional solution with an atom ratio of M²⁺(Cd²⁺/Zn²⁺):S²⁻ = 1:1.



Fig. S2. FESEM images and their EDS spectra (inset) of suspensible $Cd_xZn_{1-x}S$ nanocrystals: (A) CdS, (B) $Cd_{0.8}Zn_{0.2}S$, (C) $Cd_{0.6}Zn_{0.4}S$, and (D) ZnS.



Fig. S3. Photographs of suspensible $Cd_{0.6}Zn_{0.4}S$ nanocrystals (left) and its corresponding aggregates (right) in the sulfur-rich S²⁻/SO₃²⁻ solution.

To demonstrate the importance of pre-adsorption of S²⁻/SO₃²⁻ ions on the Cd_xZn_{1-x}S nanocrystal surface, the above suspensible Cd_{0.6}Zn_{0.4}S nanocrystal suspension (left) was filtered and washed with deionized water several times to remove the adsorbed S²⁻/SO₃²⁻ ions. After drying at 60 °C for 12 h, the obtained Cd_{0.6}Zn_{0.4}S powder was redispersed into the sulfur-rich S²⁻/SO₃²⁻ solution, which shows a typical precipitation at the bottom of cuvette (right).



Fig. S4. Photographs of traditional hexagonal CdS (calcined at 550°C under N_2) before (a) and after (b) photocatalytic H₂-evolution reaction.



Fig. S5. Photocatalytic H₂-evolution activity of suspensible $Cd_xZn_{1-x}S$ nanocrystals before and after loading Pt cocatalyst (1 wt%): (a) CdS, (b) $Cd_{0.8}Zn_{0.2}S$, (c) $Cd_{0.6}Zn_{0.4}S$, (d) $Cd_{0.4}Zn_{0.6}S$, (e) $Cd_{0.2}Zn_{0.8}S$ and (f) ZnS.

The Pt-modified $Cd_xZn_{1-x}S$ photocatalyst was obtained via a typical photodeposition method. Briefly, 134 µL of H₂PtCl₆ solution (10 g L⁻¹) was injected into the prepared suspensible $Cd_xZn_{1-x}S$ nanocrystals suspension (the synthesis details are shown in **Section 2.1**), where the amount of metallic Pt to $Cd_xZn_{1-x}S$ is controlled to be 1 wt%. After bubbled with N₂ for 15 min to remove the dissolved oxygen, the above suspension was irradiated by UV-light irradiation (a 3 W and 365 nm LED, Shenzhen Lamplic Science Co. Ltd.) for 30 min under vigorous stirring to induce the deposition of metallic Pt nanoparticles on $Cd_xZn_{1-x}S$ surface. Finally, the suspension solution was bubbled with N₂ for 15 min to remove the generated hydrogen, and the system was directly used for the following H₂-evolution experiment.



Fig. S6. (A) The *i-t* and (B) EIS curves of various samples: (a) CdS, (b) Cd_{0.6}Zn_{0.4}S and (c) ZnS.

Photoelectrochemical measurements were performed CHI 660E on а electrochemical work station (Chenhua Instrument, Shanghai, China) use a standard three-electrode system configuration in Na₂S(0.35 M)/Na₂SO₃(0.25 M) electrolyte solution, where the photocatalyst-coated FTO as the working electrode, Ag/AgCl as a reference electrode and platinum wire as the counter electrode. A 3 W and 365 nm LED (Shenzhen Lamplic Science Co. Ltd.) served as the irradiation light source. The photocatalyst-coated FTO working electrodes were prepared as follows. Briefly, the Cd_xZn_{1-x}S power (10 mg) was dispersed into the ethanol-Nafion solution (1 mL of anhydrous ethanol and 1 mL of D-520 Nafion (5%, w/w, in water and 1-propanol, Alfa Aesar)), and then ultrasonicated for 30 min to obtain the suspension solution. The resulting Cd_xZn_{1-x}S suspension was coated on the FTO (the FTO washed with deionized water, ethanol and acetone for three times, respectively, and then was dried at 60 °C) surface with the side protected by Scotch tape and then dried at 40 °C for 24 h. The transient photocurrent responses (*i*-t curve) were measured at the open circuit

voltage during repeated ON/OFF illumination cycles and EIS was measured in the frequency range of $0.001-10^6$ Hz with an ac amplitude of 10 mV at the open circuit voltage.