Supplementary Information

Highly-efficient cocatalyst-free H₂-evolution over silica-supported CdS nanoparticle photocatalysts under visible light

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Experimental Section

1. Photocatalysts synthesis

All chemicals used in the experiments were of analytical grade. Double-distilled water was used in all of the experiments. CdO@SiO₂ with different CdO contents was prepared with a sol-gel method in the presence of citric acid.¹ Typically, 20 mL tetraethyl orthosilicate (TEOS) was added into an aqueous solution containing citric acid and Cd(NO₃)₂. Then, an aqueous HNO₃ solution (2 mol·L⁻¹) was used to adjust the pH value of the solution to 2.0. After standing for 0.5 h, the mixture was heated at 80 °C in open air to remove water and all other volatiles to obtain the as-synthesized precursor. After that, the dried solid was calcined at 600 °C for 3 h to obtain the CdO@SiO₂ (heating rate 10 K·min⁻¹). For comparison, pure SiO₂ was prepared under the same procedure as described above for the CdO@SiO₂ without the addition of Cd(NO₃)₂.

CdS@SiO₂ was prepared through direct anion exchange reaction.² Typically, a certain amount of CdO@SiO₂ was sonicated in 20 mL distilled water to disperse it evently. Subsequently, Na₂S solution at a predetermined concentration was added dropwise to the above mixture of CdO@SiO₂ with magnetic stirring at room temperature. After stirring for another 12 h, CdS@SiO₂ formed in the suspension was filtered and washed with distilled water to remove non-reacted reactants (S²⁻). After that, the products were fully dried at 80 °C in an oven to obtain the final CdS@SiO₂. Different metal sulfides were prepared under the same procedure as described above for the $CdS@SiO_2$ except using different metal nitrates. The content of different metal oxides in the composites is 15%, and the metal sulfide materials were denoted as $MS@SiO_2$.

2. Characterizations

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer using CuK α radiation (λ =1.5418 Å). UV-vis diffused reflectance spectra of the samples were obtained from UV-vis-NIR spectrophotometer (Shimadzu-3600). N₂ adsorption-desorption isotherms were measured at 77 K, using a Micromeritics ASAP 2010N analyzer. Samples were degassed at 423 K for 20 h before measurements. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) model. Pore size distributions were evaluated from adsorption branches of nitrogen isotherms using the Barret-Joyner-Halenda (BJH) model. XPS was performed on a Thermo ESCA LAB 250 system with MgK α source (1254.6 eV). Transmission electron microscopy (TEM) images were taken with a FEI Tecnai F20 EM with an accelerating voltage of 200 kV equipped with an energy-dispersive spectroscopy analyzer. The photoluminescence (PL) measurement was carried out on the FLS920 (Edinburgh Instrument) at room temperature using the excitation wavelength of 390 nm.

3. Photocatalytic Reaction

The photocatalytic H_2 evolution reactions were carried out in a flowing gas diffluent system. The catalyst powder (0.1 g) was dispersed by a magnetic stirrer in 100 mL of 0.35 M Na₂S and 0.25 M Na₂SO₃ aqueous solution in a reaction cell made of Pyrex glass. The reaction temperature was maintained at 15 °C. The reaction solution was evacuated 30 min to ensure complete air removal prior to light irradiation. Magnetic stirring was used to keep the photocatalyst particles in a suspension state. A 300 W Xe-lamp with a cutoff filter was employed for visible-light ($\lambda \ge 420$ nm) irradiation. The amounts of evolved H₂ was determined by an online gas chromatograph (GC122, TCD) equipped with a 4 m 5 A molecular sieve columns and Ar as gas.

The apparent quantum yield was measured under the same photocatalytic reaction except for the wavelength of irradiation light. The apparent quantum yields of 0.3 g photocatalysts in one continuous reaction under visible light with different wavelengths of 420, 450, 500, 550, 600 nm were measured. Apparent quantum yields at different wavelengths were calculated by the following function. The band-pass and cutoff filters and a photodiode were used in measurement.

$$AQY(\%) = \frac{\text{Number of reacted electrons}}{\text{Total number of incident photons}} \times 100$$
$$= \frac{2 \times \text{The number of evoluted H}_2 \text{ molecules}}{\text{Total number of incident photons}} \times 100$$

Reference

- 1 G. Liu, X. L. Wang, X. Wang, H. X. Han, C. Li. J. Catal. 2012, 293, 61.
- 2 N. Z. Bao, L. M. Shen, T. Takata, K. Domen. Chem. Mater. 2008, 20, 110.

Sample	$S_{BET} \left(m^2 g^{-1}\right)$	Pore vol (cm ³ g ⁻¹)	Pore size ^a (nm)
SiO ₂	782	0.70	4.2
CdS(1)@SiO ₂	487	0.62	5.6
$CdS(2)@SiO_2$	387	0.61	6.7
$CdS(5)@SiO_2$	404	0.56	7.9
CdS(10)@SiO ₂	330	0.55	8.7
CdS(15)@SiO ₂	296	0.50	9.4
CdS(20)@SiO ₂	255	0.40	9.5
CdS(30)@SiO ₂	210	0.37	9.6
CdS(40)@SiO ₂	159	0.30	10.2
CdS(50)@SiO ₂	105	0.20	10.7
CdO(15)@SiO ₂	560	0.45	5.2
CdS	43	0.15	13.5

 Table S1. Texture properties of various samples.

^a Average pore diameters were calculated from adsorption branches using BJH model.



Fig. S1 TEM images and corresponding particle size distribution of CdO(15)@SiO₂ (a and

b) and CdS(15)@SiO₂ (c and d).



Fig. S2 Typical time course for H₂ production over of CdS(15)@SiO₂ under visible light irradiation. Condition: 100 mg photocatalysts in 100 mL Na₂S (0.35 M)-Na₂SO₃ (0.25 M) solution, 300 W Xe-lamp equipped with cut-off filter ($\lambda \ge 420$ nm).



Fig. S3 XRD patterns (A) and Cd 3d XPS spectra (B) of CdS(15)@SiO₂ before and after photoreaction.



Fig. S4 The apparent quantum yield for hydrogen evolution over different amount of $CdS(15)@SiO_2$. It was proceed in Na₂S (0.35 M) and Na₂SO₃ (0.25 M) aqueous solution under various wavelengths of 420, 450, 500, 550, and 600 nm.



Fig. S5 Photocatalytic H₂ evolution activity of CdS@SiO₂ with different CdS contents under visible light irradiation. Reaction condition: 0.1 g photocatalysts in 100 mL Na₂S (0.35 M)-Na₂SO₃ (0.25 M) solution, 300 W Xe-lamp equipped with cut-off filter ($\lambda \ge 420$ nm).



Fig. S6 XRD patterns of CdS@SiO₂ with different CdS contents.



Fig. S7 UV-vis diffuse reflection spectra of CdS@SiO₂ with different CdS contents.



Fig. S8 Apparent quantum yield for hydrogen evolution over various metal-sulfides supported on silica. Reaction condition: 0.3 g photocatalysts in Na₂S (0.35 M) and Na₂SO₃ (0.25 M) aqueous solution under 420 nm wavelength irradiation



Fig. S9 XRD patterns of different metal-sulfides supported on silica.



Fig. S10 UV-vis diffuse reflection spectra of different metal-sulfides supported on silica.