Supplementary Information

Plasmonic Au nanoparticles embedding enhances the activity and stability of CdS for photocatalytic hydrogen evolution

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Experimental Section

Au Colloids Preparation. All chemicals were analytic grade reagents and used without further purification. Distilled water was used in all of the experiments. Au colloids were prepared by a sodium citrate reduction method.[1-3] Typically, an aqueous solution of $HAuCl_4$ (0.25 mM, 100 mL) was heated to boiling, followed by the rapid addition of sodium citrate solution (0.5 M, 200 μL). The solution was kept boiling for another 15 min, producing a stable and deep-red dispersion of Au nanoparticles with an average diameter of about 15 nm (see in Fig. 1a and 1b). The citrate-protected Au-colloids (denoted as Au-Cit) suspension was then cooled to room temperature for next use.

Au@CdS Preparation: Au@CdS photocatalysts with different amount of Au were prepared using a cysteine-assisted hydrothermal approach. Briefly, 100 mL *L*-cysteine solution (Cys, 50 mM) was mixed with $Cd(NO_3)_2$ in a 1:0.5 molar ratio of Cys to Cd^{2+}. The mixture was stirred for 30 min to form the stable complexes of cysteine-Cd^{2+}. Then Au-Cit colloids (0.25 mM, 1 mL) was added to the freshly prepared cysteine-Cd^{2+} solution under vigorous stirring for 30 min, leading to a complete coupling between amine group of Cys and Au surfaces. Subsequently, the cysteine-Cd^{2+}-coupled Au colloids were diluted to a total volume of 50 mL with deionized water, and transferred into 40 mL Teflon-lined stainless-steel autoclaves. The autoclaves were maintained at 130 °C for 6 h and then cooled to room temperature naturally. The products were filtered and washed with distilled water to remove remaining ions and impurities. After that, the products were fully dried at 80 °C in an oven to obtain the final product (i.e. Au@CdS). The amount of Au in the Au@CdS

composites was controlled by the amount of cysteine-Cd^{2+} in the synthesis process. The resultant photocatalysts were denoted as x %Au@CdS (x = 0.2, 0.5, 0.7, 1.0). As a reference, pure CdS was prepared with the same procedure as described above without adding Au-Cit colloids.

Characterization Methods: Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). UV-vis diffused reflectance spectra of the samples were obtained from UV-vis-NIR spectrophotometer (Shimadzu-3600). Transmission electron microscopy (TEM) images were taken on JEM-2100F with an accelerating voltage of 200 kV equipped with an energy-dispersive spectroscopy analyzer. XPS was performed on a Thermo ESCA LAB 250 system with MgKα source (1254.6 eV). The binding energies were calibrated using C 1s peak at 284.6 eV as standard. The photoluminescence (PL) measurement was carried out on the FLS920 (Edinburgh Instrument) at room temperature using the excitation wavelength of 390 nm.

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 Na_2S and 0.25 M Na_2SO_3 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 (λ ≥ 420nm) irradiation. The

amounts of evolved H_2 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 efficiency was measured under the same photocatalytic reaction except for the wavelength of irradiation light. The apparent quantum efficiency of 0.1 g photocatalysts in one continuous reaction under visible light with different wavelengths of 420, 450, 500, 550, 600 nm were measured. Apparent quantum efficiency at different wavelengths was calculated by the following function. The band-pass and cutoff filters and a photodiode were used in measurement.

$$\mathrm{QE}\ (\%) = \frac{\text{Number of reacted electrons}}{\text{Total number of incident photons}} \times 100$$

$$= \frac{2 \times \text{The number of evoluted } H_2 \text{ molecules}}{\text{Total number of incident photons}} \times 100$$

Reference

1. W. T. Chen, Y. K. Lin, T. T. Yang, Y. C. Pu and Y. J. Hsu, *Chem. Comm.*, 2013, **49**, 8486-8488.

2. X. Ji, X. Song, J. Li, Y. Bai, W. Yang and X. Peng, *J. Am. Chem. Soc.*, 2007, **129**, 13939-13948.

3. W.-T. Chen, T.-T. Yang and Y.-J. Hsu, *Chem. Mater.*, 2008, **20**, 7204-7206.

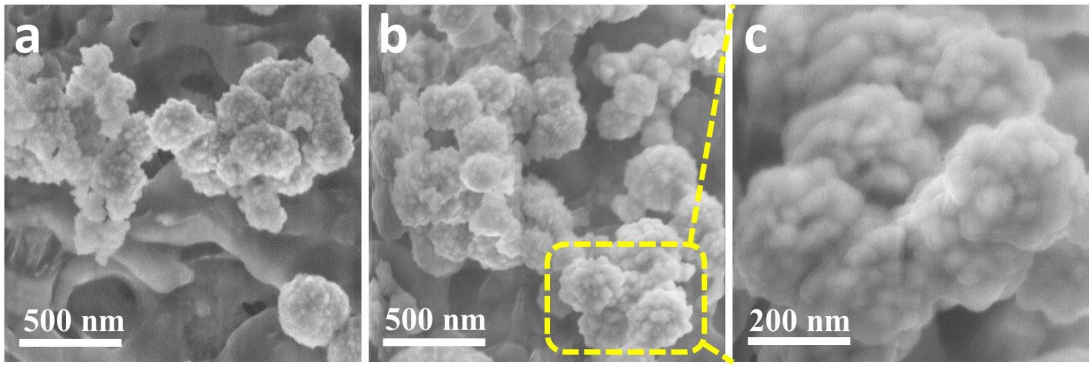


Fig. S1 SEM images of 0.5%Au@CdS (a) and 1.0%Au@CdS (b and c).

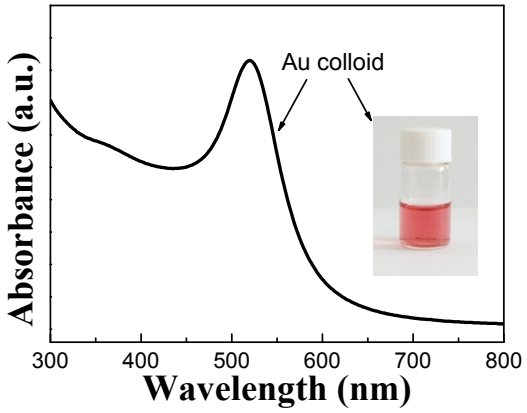


Fig. S2 UV-vis absorption spectra of Au colloid.

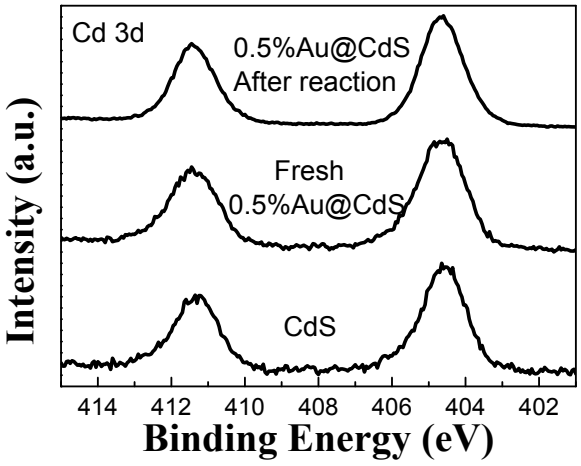


Fig. S3 Cd 3d XPS spectra of CdS, fresh 0.5%Au@CdS and 0.5%Au@CdS after reaction.

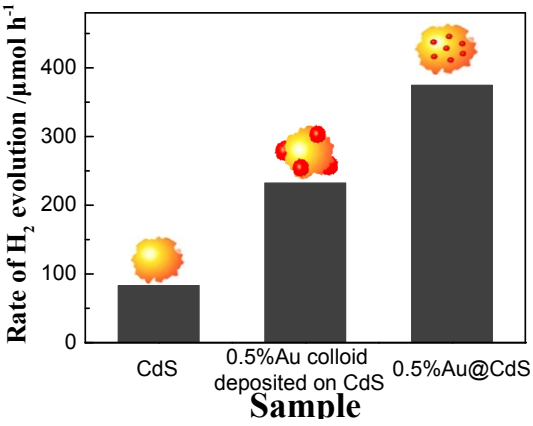
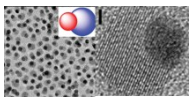
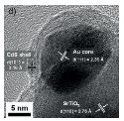
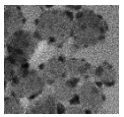
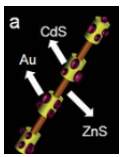
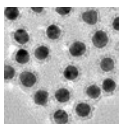
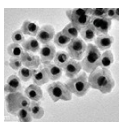


Fig. S4 Photocatalytic H_2 evolution activity of CdS, Au colloid (the content is 0.5%) deposited on the surface of CdS, and 0.5%Au@CdS under visible light irradiation. Reaction condition: 0.1 g photocatalysts in 100 mL Na_2S (0.35 M)-Na_2SO_3 (0.25 M) solution, 300 W Xe-lamp equipped with cut-off filter ($\lambda \geq 420$ nm).

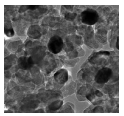
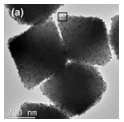
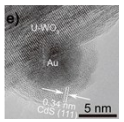
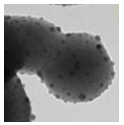
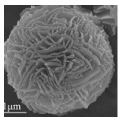
Table S1. Typical plasmonic Au-sulfide photocatalysts for hydrogen evolution

Photocatalyst	Morphology	Cocatalyst	Sacrifice reagent	Light source	H_2 evolution rate ($\mu mol.h^{-1}.g^{-1}$)[a]	QY (%)[b]	Reference
Au-CdS		—	Na_2S Na_2SO_3	λ≥400nm (300W Xe lamp)	7300	—	*Adv. Mater.*, 2014, **26**, 1387.
Au@CdS/$SrTiO_3$		1% Pt	Na_2S Na_2SO_3	λ≥400nm (300W Xe lamp)	1091	12.41 (420nm)	*Angew. Chem. Int . Ed.*, 2014, **53**, 11203.
Au-Cu_2ZnSnS_4		—	Na_2S Na_2SO_3	Full wavelength (300W Xe lamp)	800	—	*J. Am. Chem. Soc.*, 2014, **136**, 9236.
ZnS-(CdS/Au)		—	Na_2S Na_2SO_3	Full wavelength (300W Xe lamp)	1825	—	*Angew. Chem. Int . Ed.*, 2015, **54**, 11495.
Au@CdS core shell		—	Na_2S Na_2SO_3	λ≥420nm (300W Xe lamp)	80	—	*Small*, 2014, **10**, 4664.
Au-Cu_2ZnSnS_4		—	Na_2S Na_2SO_3	Full wavelength (150W Xe lamp)	102	—	*Adv. Mater.*, 2014, **26**, 3496.

[a] converted value according the optimized activity in the corresponding literature.

[b] Quantum yield

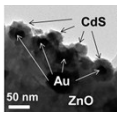
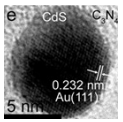
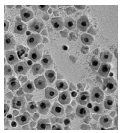
Table S1 Continued

Photocatalyst	Morphology	Cocatalyst	Sacrifice reagent	Light source	H_2 evolution rate ($\mu mol.h^{-1}.g^{-1}$)[a]	QY (%)[b]	Reference
Au@TiO_2 –CdS		—	Na_2S Na_2SO_3	λ≥420nm (300W Xe lamp)	2000	—	*ACS Appl. Mater. Interfaces*, 2013, **5**, 8088.
Au/Cu_2O–TiO_2		—	Ethanol	λ≥430nm (300W Xe lamp)	11400	—	*J. Catal.*, 2015, **322**, 109.
Au@CdS/U-WO_3		—	Na_2S Na_2SO_3	λ≥420nm (300W Xe lamp)	1600	—	*Chem. Commun.*, 2015, **51**, 13842.
Au/CdS		—	Na_2S Na_2SO_3	Full wavelength (500 W Warrior WEHL halogen bulb lamp)	10800	—	*Appl. Catal., B*, 2016, **182**, 266.
Au/ZnS		—	Na_2S Na_2SO_3	Full wavelength (350W Xe lamp)	3306	7.5	*ACS Appl. Mater. Interfaces*, 2013, **5**, 1031.

[a] converted value according the optimized activity in the corresponding literature.

[b] Quantum yield

Table S1 Continued

Photocatalyst	Morphology	Cocatalyst	Sacrifice reagent	Light source	H_2 evolution rate ($\mu mol.h^{-1}.g^{-1}$)[a]	QY (%)[b]	Reference
CdS/Au/ZnO		—	Na_2S Na_2SO_3	Full wavelength (300W Xe lamp)	600	—	*J. Mater. Chem. A*, 2013, **1**, 2773.
CdS/Au/g-C_3N_4		0.5%Pt	Na_2SO_4	λ≥420nm (300W Xe lamp)	16.81	—	*APL Mater.*, 2015, **3**, 104410.
Au/Cu_2FeSnS_4		—	Na_2S Na_2SO_3	λ≥420nm (150W Xe lamp)	90	—	*Appl. Mater. Interfaces*, 2015, **7**, 9072-9077.
Au@CdS		0.1% Pt	Na_2S Na_2SO_3	λ≥420nm (300W Xe lamp)	11500	45.6 (420nm)	Current work

[a] converted value according the optimized activity in the corresponding literature.

[b] Quantum yield