Electronic Supplementary Information (ESI) for

Metal-semiconductor yolk-shell heteronanostructures for plasmon-enhanced photocatalytic hydrogen evolution

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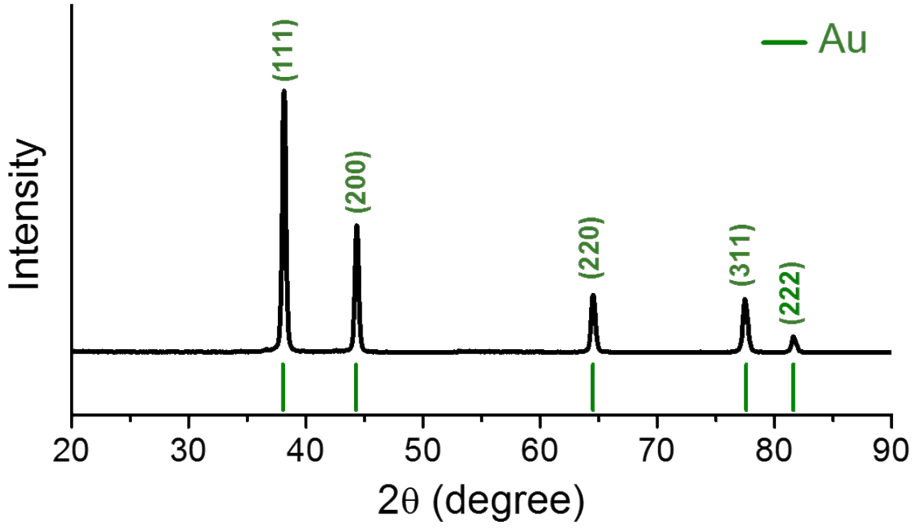

Fig. S1 XRD pattern of AuNRs. The positions of Au reference were taken from the JCPDS database (Au: 65-2870).

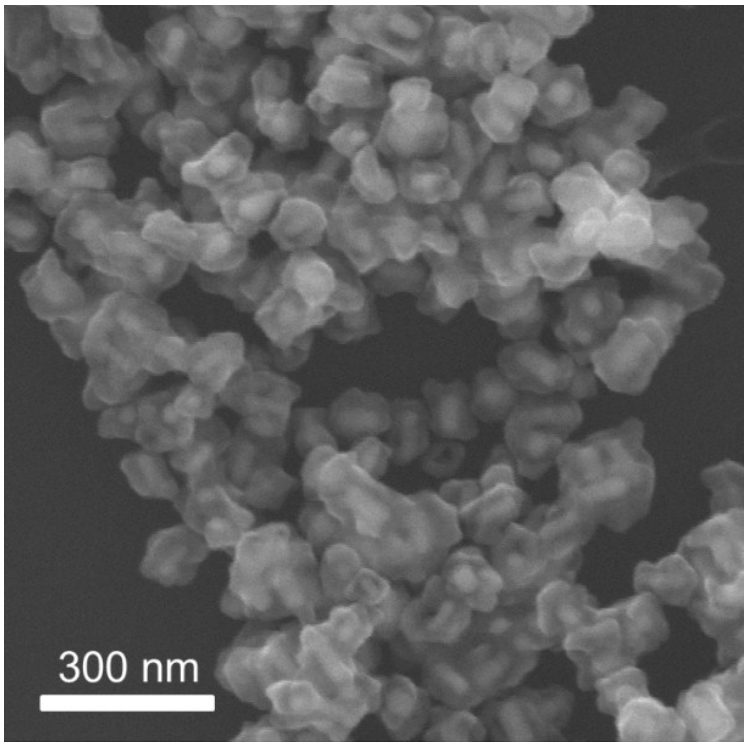

Fig. S2 Scanning electron microscopy image of AuNR-CdS YSNs, which was taken with a field-emission scanning electron microscope (FEI-INSPECT F50).

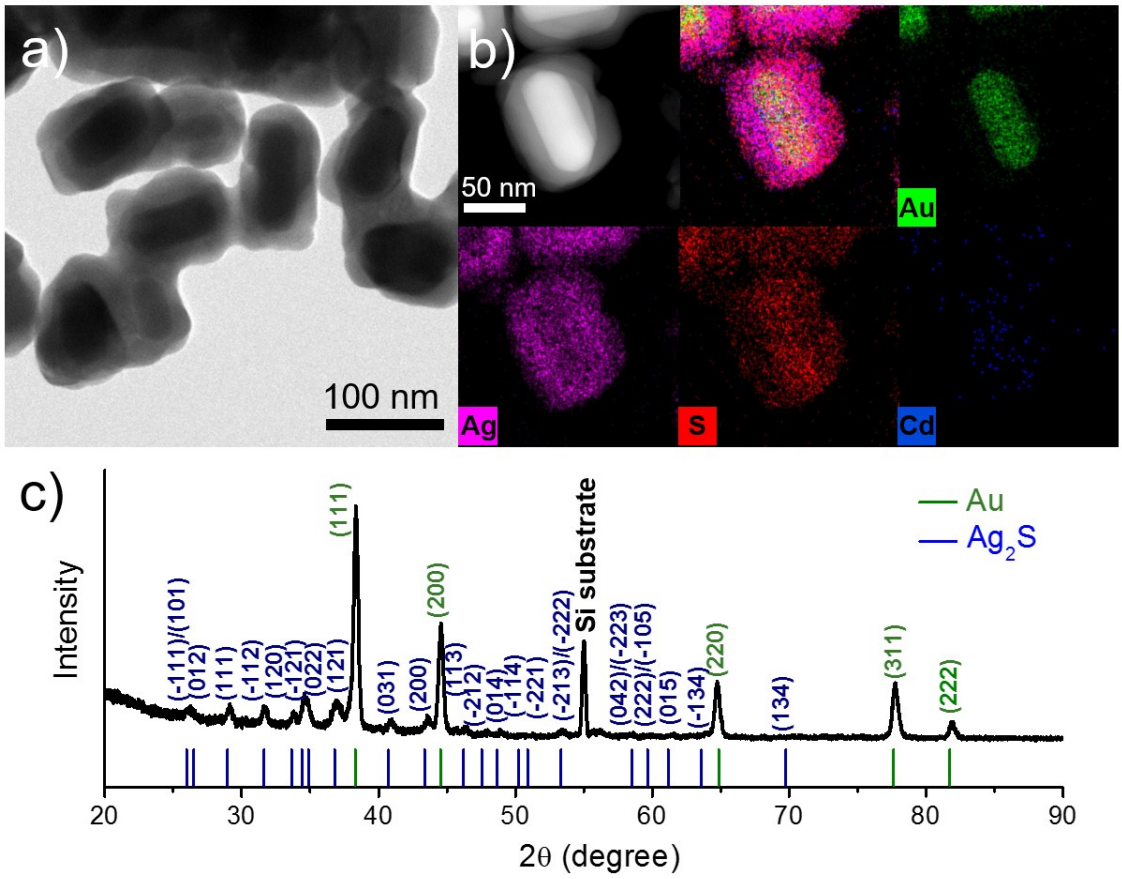

Fig. S3 (a) TEM, (b) HAADF-STEM and corresponding EDS elemental mapping images, and (c) XRD pattern of AuNR@Ag@Ag_2S CSSNs obtained after a cation exchange reaction in the absence of TBP, while keeping other reaction conditions the same as the typical synthesis of the AuNR-CdS YSNs. The positions of Au and Ag_2S references in the XRD pattern were taken from the JCPDS database (Au: 65-2870, Ag_2S: 14-0072).

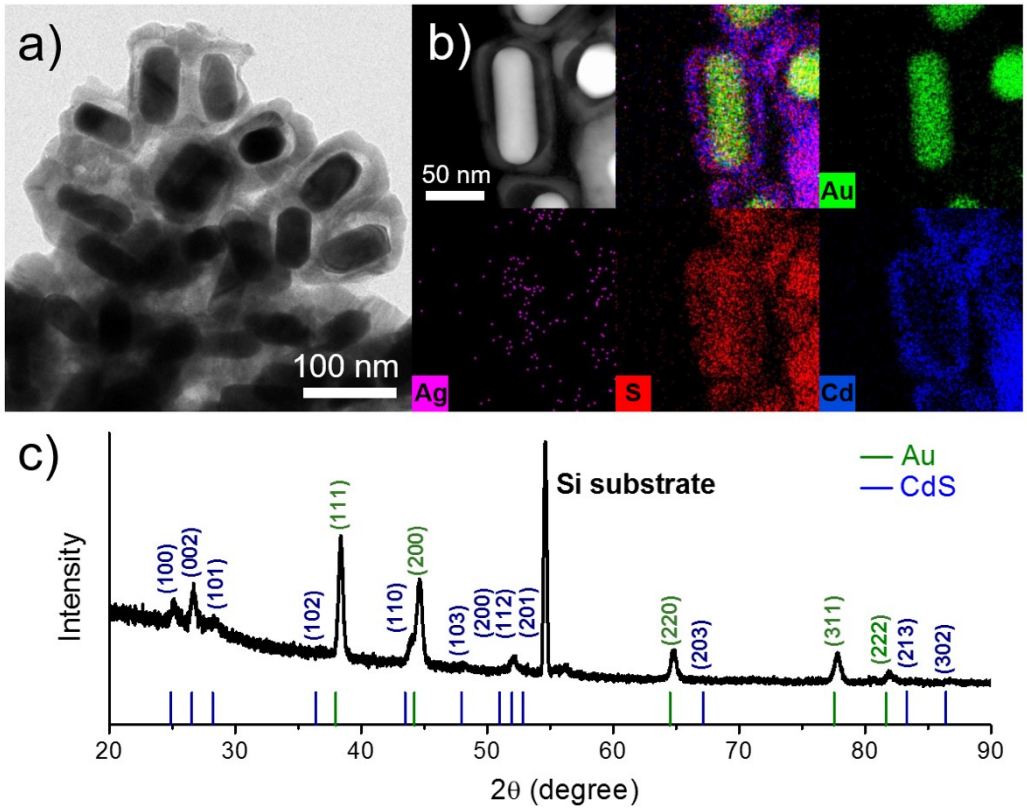

Fig. S4 (a) TEM, (b) HAADF-STEM and corresponding EDS elemental mapping images, and (c) XRD pattern of AuNR@CdS YSNs obtained after a cation exchange reaction in water, while keeping other reaction conditions the same as the typical synthesis of the AuNR-CdS YSNs. The positions of Au and CdS references in the XRD pattern were taken from the JCPDS database (Au: 65-2870, CdS: 41-1049).

Fig. S5 Photograph of a reaction mixture after the cation exchange reaction of AuNR@Ag@Ag_2S CSSNs in water.

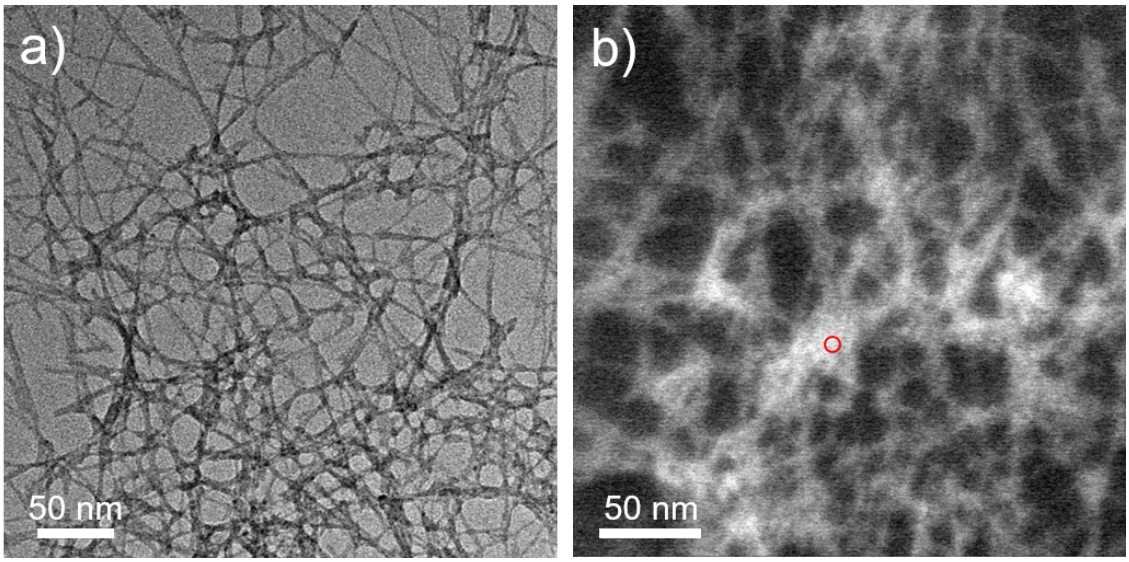

Fig. S6 (a) Bright- and (b) dark-field TEM images of tangled nanowires consisting Ag and Cd formed by the addition of $NaBH_4$ to the reaction mixture after the cation exchange reaction. The EDS-determined Ag:Cd atomic ratio of nanowires was 1:6.9. The position of EDS analysis is denoted by a red circle in b.

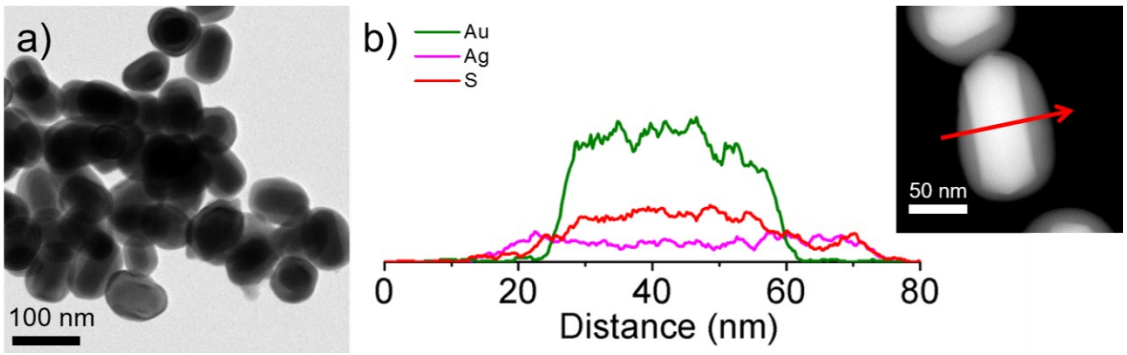

Fig. S7 (a) TEM image and (b) HAADF-STEM image and corresponding EDS cross-sectional compositional line profiles of AuNR@Ag@Ag_2S CSSNs stored in methanol containing TBP for 24 h.

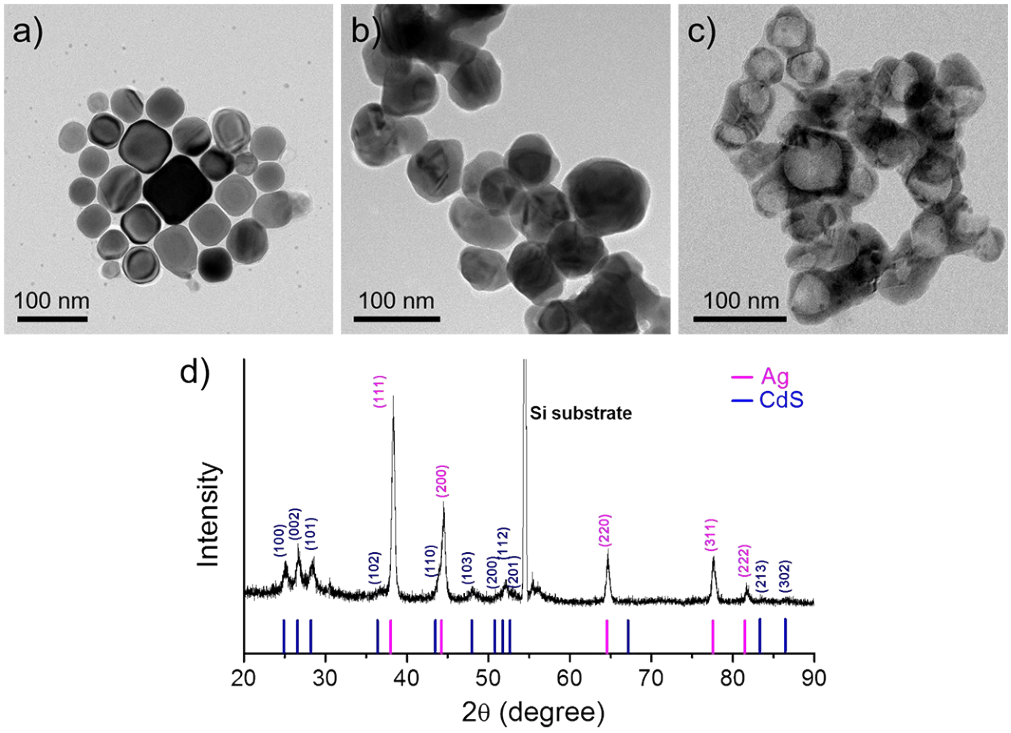

Fig. S8 TEM images of (a) Ag NPs, (b) Ag@Ag_2S core-shell NPs, and (c) CdS HNPs. CdS HNPs with distinct hollow interior were prepared by the cation exchange reaction of Ag@Ag_2S core-shell NPs, which were produced by the sulfidation reaction of Ag NPs. (d) XRD pattern of CdS HNPs. The positions of Ag and CdS references in the XRD pattern were taken from the JCPDS database (Ag: 04-0783, CdS: 41-1049).

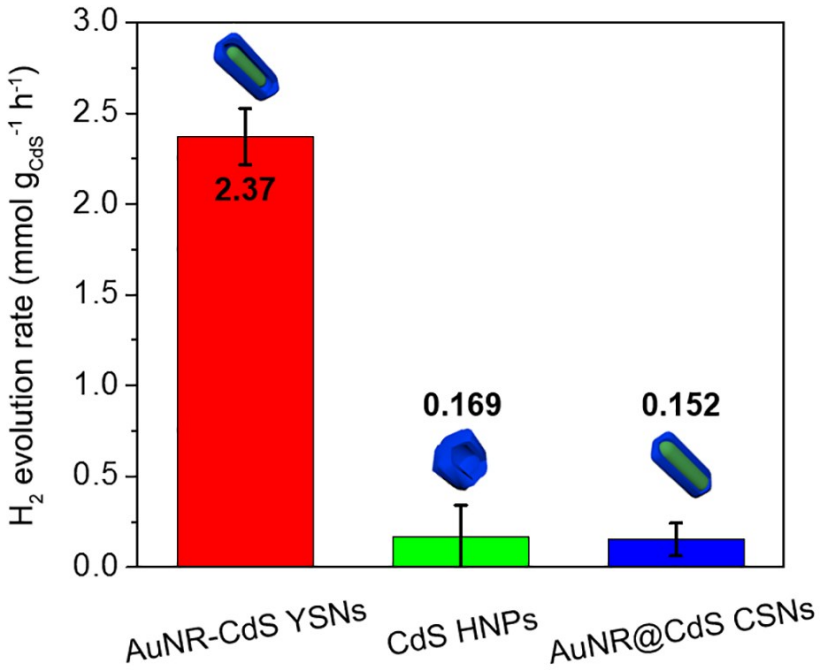

Fig. S9 Hydrogen evolution rates of different catalysts with respect to the mass of CdS in catalysts.

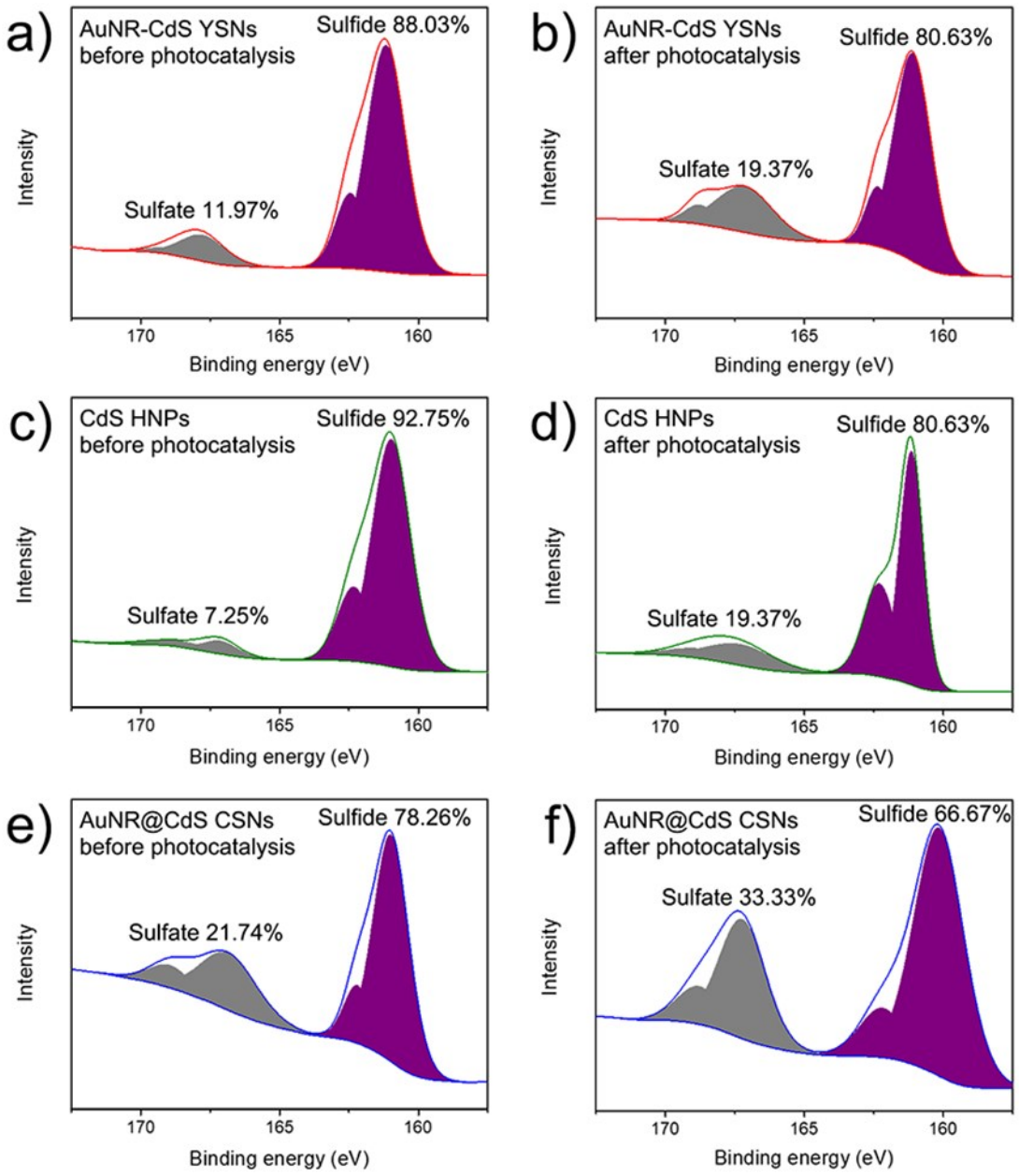

Fig. S10 XPS spectra of S 2p regions for (a,b) AuNR-CdS YSNs, (c,d) CdS HNPs, and (e,f) AuNR@CdS CSNs.

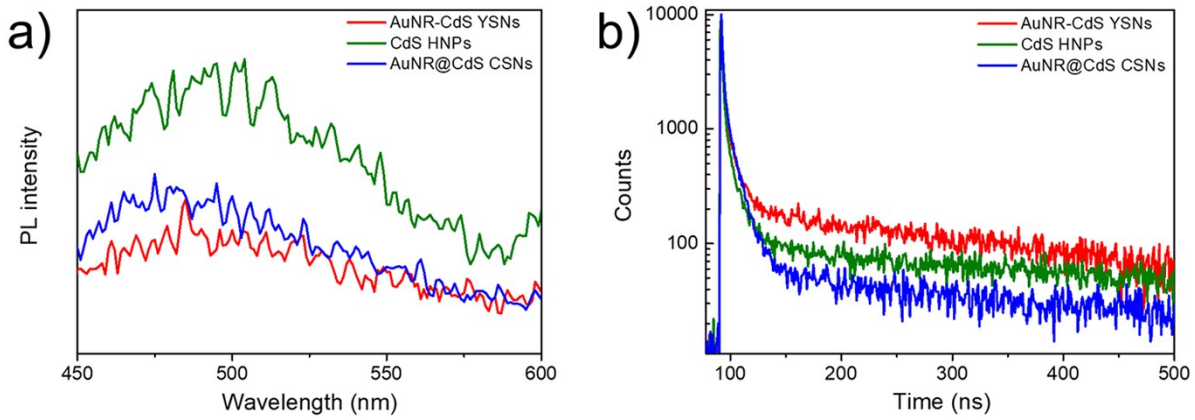

Fig. S11 (a) Steady-state PL spectra and (b) time-resolved PL decays of AuNR-CdS YSNs, CdS HNPs, and AuNR@CdS CSNs in an aqueous solution containing Na_2S (0.25 M) and Na_2SO3 (0.35M). The excitation wavelength was 375 nm.

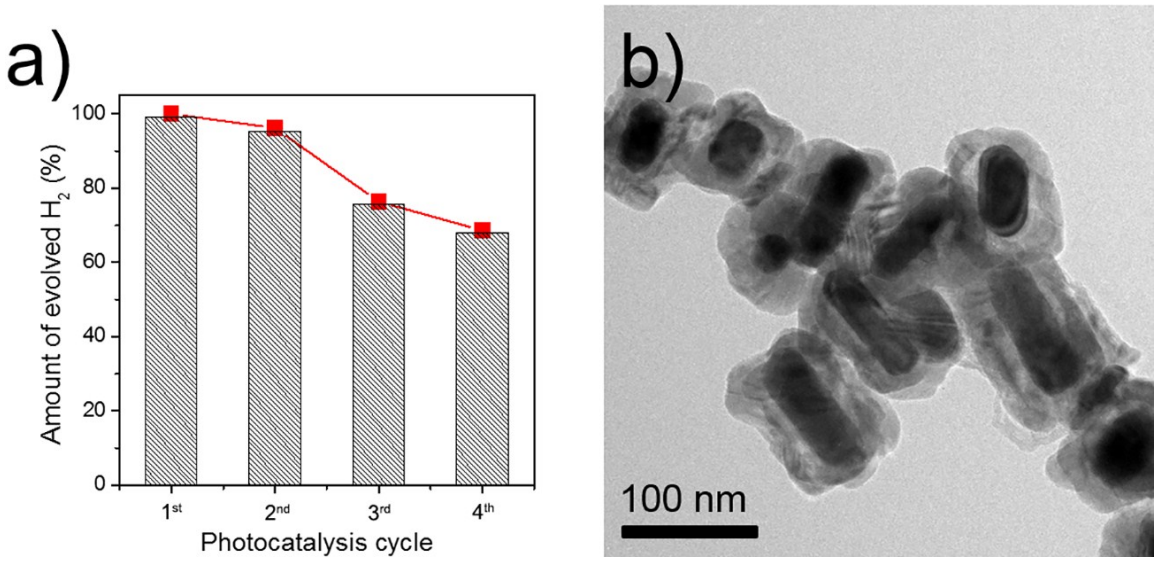

Fig. S12 (a) Recyclability of AuNR-CdS YSNs for photocatalytic hydrogen evolution. Each photocatalysis cycle was conducted for 2 h. After each photocatalysis run, the catalysts were collected from the reaction solution by centrifuging (8,000 rpm for 7 min), and then subjected to the next photocatalytic reaction. (b) TEM image of AuNR-CdS YSNs after the fourth cycle of photocatalysis, revealing that most of the nanostructures maintained their original morphology.

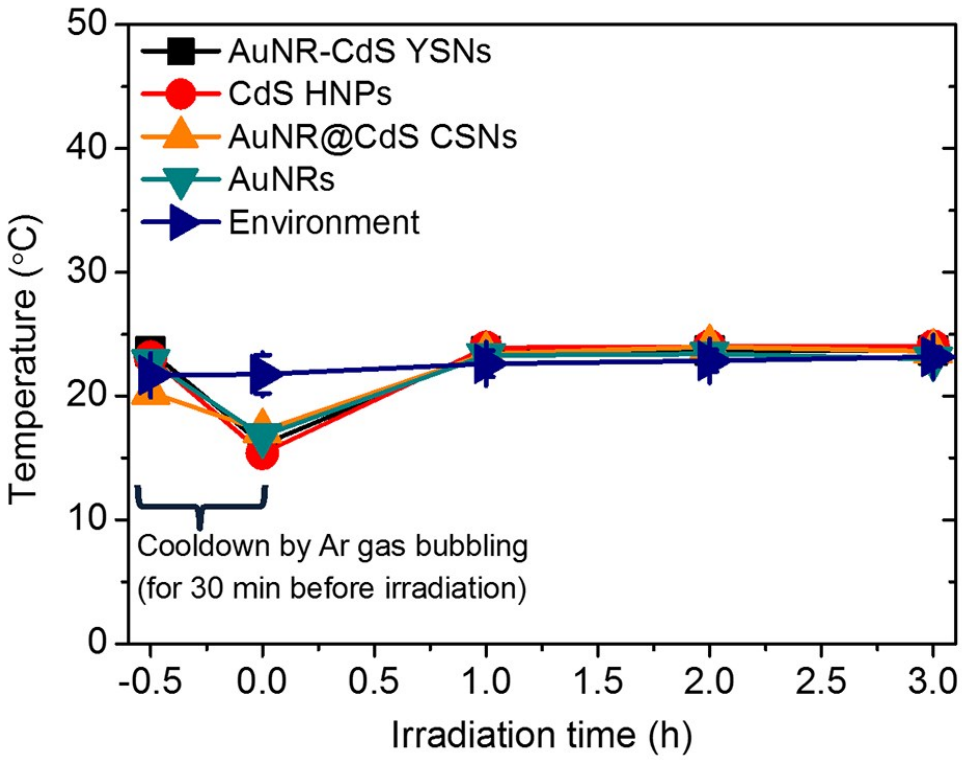

Fig. S13 Plots of the temperature of the reaction mixture under visible light irradiation as a function of time for different catalysts. Environmental temperature was increased by 1.5 °C after 3 h visible light irradiation. The initial decrease in the temperature is due to the 30 min Ar gas bubbling for establishing an anaerobic condition. When the Ar gas bubbling was stopped and the visible light started to be irradiated, the temperature of the reaction mixture reached to the same level of the environmental temperature within 1 h.

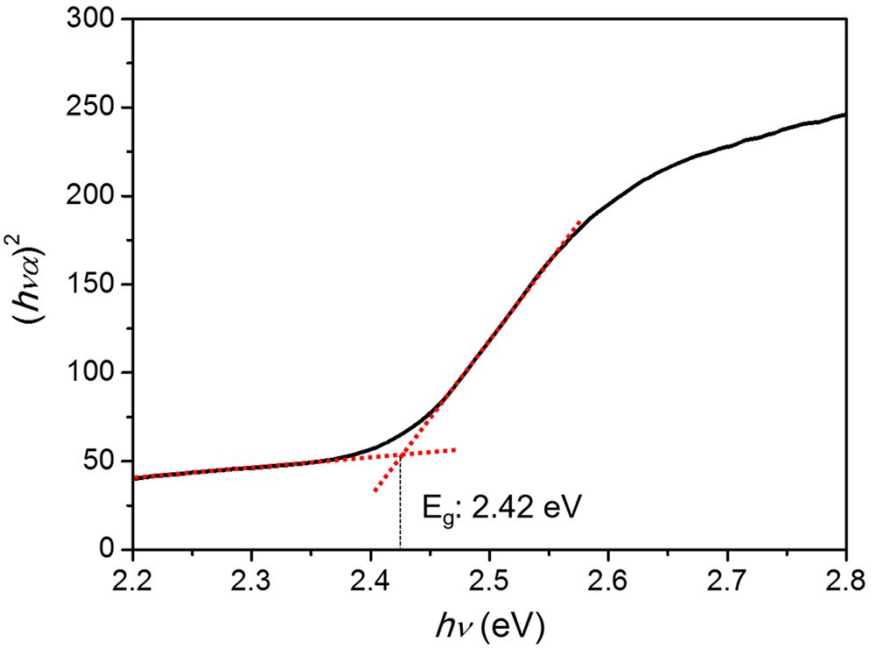

Fig. S14 Tauc plot for calculating the band gap energy (E_g) of CdS HNPs. The E_g of CdS HNPs was calculated to be 2.42 eV.

Table S1 PL lifetimes of various catalysts determined by fitting PL decay curves with the following triple exponential function:

$$I(t) = A + B_1\exp\left(-\frac{t}{\tau_1}\right) + B_2\exp\left(-\frac{t}{\tau_2}\right) + B_3\exp\left(-\frac{t}{\tau_3}\right)$$

Photocatalyst	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_A (ns)*	χ^2
AuNR-CdS YSNs	1.455	9.162	429.5	339.8	1.013
CdS HNPs	1.492	9.532	375.1	226.2	1.076
AuNR@CdS CSNs	1.446	9.473	364.5	146.5	1.020

*The average PL lifetime calculated from the following equation:

$$\tau_A = \sum_{i=1}^{3}(B_i\tau_i^2)/\sum_{i=1}^{3}(B_i\tau_i)$$

Table S2 Quantum efficiencies of various catalysts for photocatalytic H_2 evolution.

Photocatalyst	Light source	Quantum efficiency (%)	Reference
Au/CdSe	300 W Xe lamp (λ = 400 nm)	0.8	S1
Au/SiO_2/CdS	300 W Xe lamp (λ = 350 nm)	0.3	S2
Au/TiO_2/CdS	300 W Xe lamp (λ = 420 nm)	0.55	S3
$Cd_{1-x}Zn_xS$	300 W Hg lamp (λ > 400 nm)	0.60	S4
Au-CdS YSNs	300 W Xe lamp (λ = 450 nm)	0.32	this work

References

(S1) R. Shi, Y. Cao, Y. Bao, Y. Zhao, H. I. N. Waterhouse, Z. Fang, L.-Z. Wu, C.-H. Tung, Y. Yin, T. Zhang, *Adv. Mater.*, 2017, **29**, 1700803.

(S2) T. Torimoto, H. Horibe, T. Kameyama, K. Okazaki, S. Ikeda, M. Matsumura, A. Ishikawa, H. Ishihara, *J. Phys. Chem. Lett.*, 2011, **2**, 2057-2062.

(S3) J. Fang, L. Xu, Z. Zhang, Y. Yuan, S. Cao, Z. Wang, L. Yin, Y. Liao, C. Xue, *ACS Appl. Mater. Interfaces*, 2013, **5**, 8088-8092.

(S4) C. Xing, Y. Zhang, W. Yan, L. Guo, *Int. J. Hydrogen Energy*, 2006, **31**, 2018-2024.