Supporting Information

Boosting Photocatalytic Hydrogen Evolution Reaction Using Dual Plasmonic Antennas

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Experiment Section:

Synthesis of Au and Ag nanoparticles. Au seeds of 45 nm were prepared according to the Frens method.[1] 1.5 mL (1 wt%) sodium citrate solution was added into the 200 mL ultrapure water, and the solution was heated to boiling. Then, 2.4 mL (1 wt%) of $HAuCl_4$ was added rapidly. Au nanoparticles with a mean size of 45 nm were obtained after 40 minutes of continuous boiling. The 45-nm Au nanoparticles were used as seeds to prepare 120-nm Au nanoparticles. 10 mL of 45-nm Au seeds was added into 60 mL water. 0.3 mL (1 wt%) sodium citrate and 1.2 mL (1 wt%) ascorbic acid were added. The mixture was stirred at 4 ^oC, into which 1.964 mL (0.01 wt%) $HAuCl_4$ was slowly dropped in 50 minutes. After adding the solution, the mixtures were kept in a 70 ^oC water bath for 15 min to complete the preparation. The Ag nanoparticles with a mean diameter of 120 nm were prepared via a similar method. 60 mL water, 10 mL of 45 nm Au seeds, 0.41 mL (1 wt%) sodium citrate, and 0.41 mL (1 wt%) ascorbic acid were mixed together. Then, 10 mL (1.2 mM) $AgNO_3$ was slowly dropped in 50 minutes. The mixture was kept stirring for another 20 min to complete the preparation.

Synthesis of $Ag@SiO_2$ and $Au@SiO_2$ SHINs. Au and Ag nanoparticles with a mean diameter of ~120 nm were prepared via a seed-mediated method. 2-3 nm SiO_2 shells were then coated on then to prepare the $Ag@SiO_2$ and $Au@SiO_2$ SHINs.[2-3] Typically, 1 mL 3-aminopropyltrimethoxysilane (1 mM) were added into 40 mL Ag (120 nm) solutions. The obtained mixture was stirred for 30 min. Then, 2 mL $NaBH_4$ (5.5 mM) and 3.2 mL sodium silicate (0.54 wt%) were added. The pH value of the mixture was tuned to 10.2 by H_2SO_4. The mixture was stirred at 99 ^oC for 30 min. Au SHINs were synthesized via a similar procedure but using Au colloids and no $NaBH_4$.

Synthesis of Au@CdS with and without of pinhole. Au@CdS with pinholes was prepared as follows.[4] 1 mL (20 mM) cadmium nitrate and 10 mL (20 mM) L-Cysteine were mixed in 9 mL water. The resulting mixture was stirred in an autoclave for 20 min, into which 30 mL Au sols (~15 nm) were then added. The pH value of the mixed solution was tuned by ammonia to 10.2. After sealed, the autoclave was heated and maintained at 130 ^oC for 6 h and then cooled to room temperature. For pinhole-free Au@CdS, the pH value was adjusted to 11.

Synthesis of SiO_2@CdS. Typically, 1.8 mL hexanol, 7.5 mL cyclohexane, 1.75 mL tralatone, 0.24 mL ammonia, and 1.5 mL water were vigorously stirred for 1 h. Then, 0.1 mL tetraethyl orthosilicate was added and stirred for 12 h. 3 mL 0.1 M sodium citrate and 5 mL 0.05 M $CdCl_2$ were added to 200 mL as-prepared SiO_2. After adjusting pH with ammonia solution to 10.2, 1.3 mL 0.2 M thiourea was added. The mixture was reacted at 70 ^oC for 5 h to generate SiO_2@CdS nanoparticles.

Self-assembly SHIN-Au@CdS dual-antenna nanocomposites. The Au@CdS nanoparticles were self-assembled on the surface of Ag or Au SHINs using PAH as a coupling reagent. 1 mL of PAH (1 mM) was added into 200 mL Ag or Au SHINs colloids under vigorous stirring for 30 min. Then, the modified Ag or Au SHINs were separated via centrifugation and washed for three times. This modified Ag or Au SHINs was mixed with a proper amount of Au@CdS colloids to obtain the Ag or Au SHIN-Au@CdS nanocomposites. SiO_2-Au@CdS nanocomposites were prepared via a similar method.

Numerical simulations. The electromagnetic field distribution of Ag SHIN-Au@CdS, Au SHIN-Au@CdS, and SiO_2-Au@CdS was calculated using commercially available Lumerical 3D-FDTD Solutions software (version 7.5). The structure of the simulation model consisted of 15 nm Au cores with 5 nm CdS shells. The diameter of the SiO_2 nanoparticles and Ag or Au cores in SHINs is 120 nm, while the SiO_2 shell thickness is 2 nm. The wavelength of the incident laser is 400 nm or 590 nm, and the refined structure is $1\times1\times1$ nm^3. The dielectric function of Au was derived from Johnson and Christy, and the refractive index of CdS was set as 2.5.

Characterizations: SEM and TEM images of the nanomaterials were collected on HITACHI S-4800 and F30, respectively. The UV–Vis absorption spectra were obtained using a UV–Vis spectrophotometer (Shimadzu, UV 2550).

Photocatalytic measurement. The photocatalytic hydrogen evolution reaction was carried out on a commercial photocatalytic reaction system (PerfectLight, PCX-50C) equipped with various LED lights using 1 mM Na_2SO_3 and 1 mM Na_2S as sacrificial reagents. The reaction temperature is controlled at 15 ^oC, and the reaction mixtures

contain 30 mL solutions and 1.6 mg catalyst. A gas chromatograph (Shimadzu, GC-2018, TCD, argon as carrier gas and 5 A molecular sieve column) was applied to detect the amount of the hydrogen produced from the reaction.

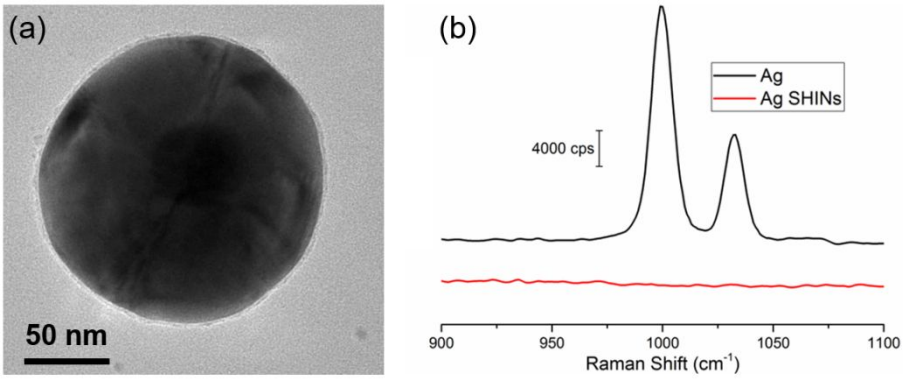

Figure S1. TEM image of Ag SHINs. (b) SERS spectra of pyridine on bare Ag nanoparticles and Ag SHINs.

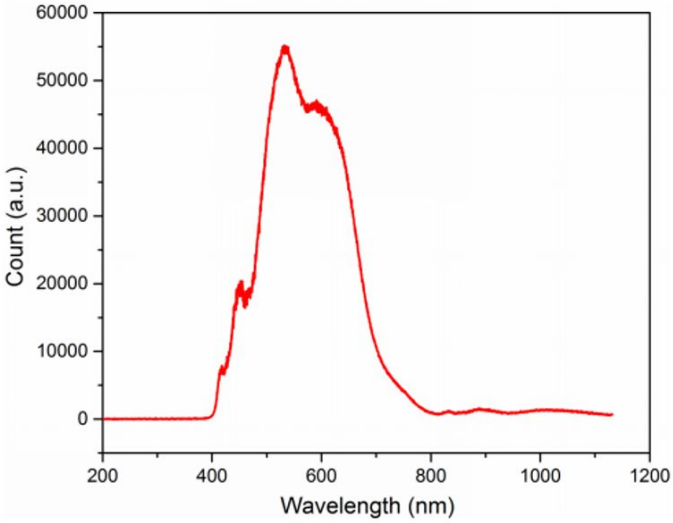

Figure S2. Spectrum for the white light LED.

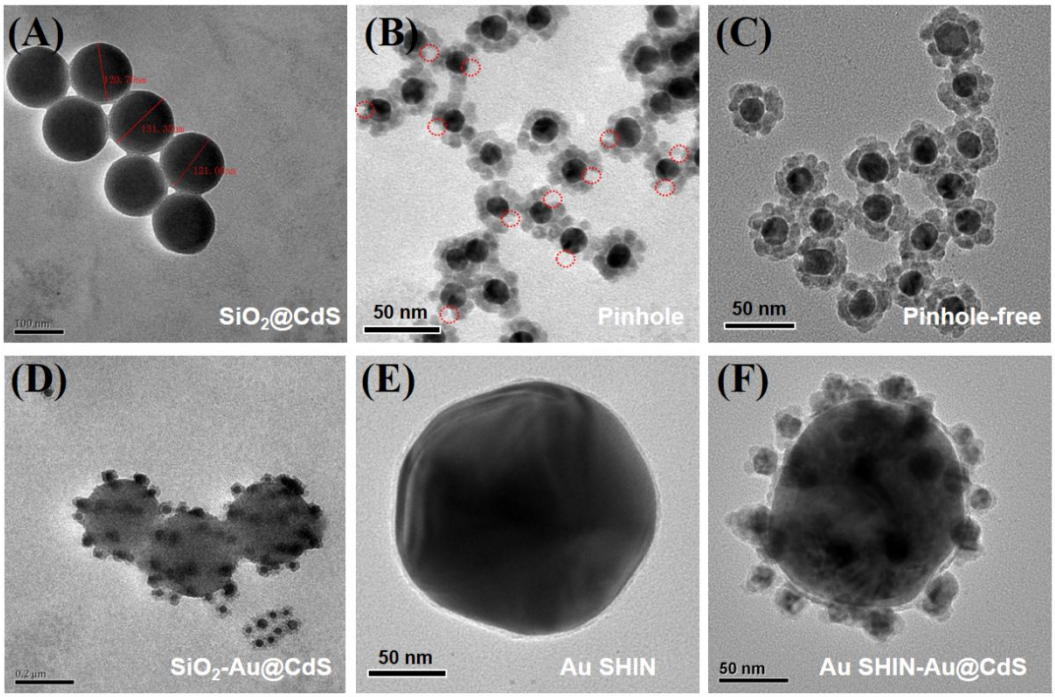

Figure S3. TEM characterization of (a) SiO_2@CdS, (b) Au@CdS with pinholes, (c) (c) pinhole-free Au@CdS, (d) SiO_2-Au@CdS, (e) Au SHIN, (f) Au SHIN-Au@CdS.

Table S1. Comparison of the catalytic performance of Ag SHINs-Au@CdS with previously reported CdS-based catalysts.

Sample	***HER (mmol/g*h)***	***Power (W)***	***Wavelength (nm)***	***Reference***	***Sacrificial agent***
Ag SHINs-Au@CdS	191.2	0.35	≥ 400 nm	this work	Na_2S/Na_2SO_3
Ni-decorated CdS nanorods	63	0.2	447 nm	5	C_2H_6O
Au-chain@$Zn_{0.67}Cd_{0.33}S$	16.42	300	≥ 420 nm	6	Na_2S/Na_2SO_3
10%CdS/Ti^{3+}/N-TiO_2	11.12	300	≥ 420 nm	7	Na_2S/Na_2SO_3
CdS/5% NC@Mo_2N	7.43	300	≥ 400 nm	8	Na_2S/Na_2SO_3
15%CdS/PI	0.61	300	≥ 420 nm	9	$C_3H_6O_3$
MoO_2-C/CdS	16.08	300	≥ 420 nm	10	$C_3H_6O_3$

L-CdS	0.77	300	≥ 420 nm	11	Na_2S/Na_2SO_3
CD/CdS@MIL-101(50)	14.66	300	≥ 420 nm	12	$C_3H_6O_3$
CdS-MoS_2	9.68	300	≥ 420 nm	13	Na_2S/Na_2SO_3
ZnO/CdS	4.13	350	all	14	Na_2S/Na_2SO_3
CDs/CdS	6.7	300	all	15	$C_3H_6O_3$
TiO_2/MoS_2/CdS	8.95	0.086	>400 nm	16	$C_3H_6O_3$
2D-2D MoS_2/CdS	26.32	300	>420 nm	17	Na_2S/Na_2SO_3
TiO_2-Au-CdS	0.67	300	≥ 420 nm	18	Na_2S/Na_2SO_3
MXene@Au@CdS	17.07	300	≥ 420 nm	19	Na_2S/Na_2SO_3
(Au/AgAu)@CdS	4.71	300	>420 nm	20	Na_2S/Na_2SO_3

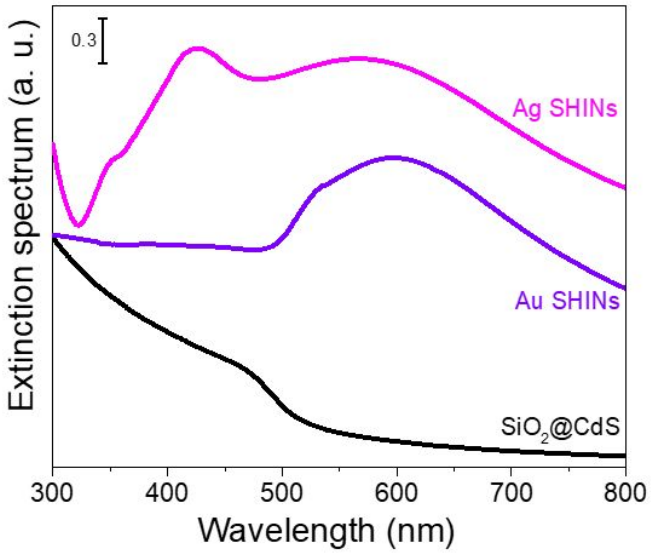

Figure S4. UV-Vis spectra of SiO_2@CdS, Au SHINs, and Ag SHINs.

Table S2. Instrument parameter of PCX-50C photocatalytic reaction system.

Wavelength	***Power***
White light (400 nm ~800 nm)	350 mW
380 nm	400 mW
430 nm	160 mW
475 nm	110 mW
530 nm	40 mW
595 nm	18 mW
633 nm	54 mW

To exclude the influence of the power, the power at all wavelengths is normalized to 110 mW when calculating the HER rates in Figure 2b using the following formula:

$$HER\ rates\ in\ Figure\ 2b = \frac{HER\ rates\ measured\ in\ the\ experiments}{Power\ of\ the\ LED\ used} \times 110$$

Table S3. ICP determined content of Cd.

sample	***Cd content (ppm)[1]***	***Calculated amount of CdS in 30 mL reaction solution***
Ag SHIN-Au@CdS	6.325	1.67 mg
Au SHIN-Au@CdS	6.258	1.65 mg
SiO_2-Au@CdS	6.382	1.68 mg
Au@CdS pinhole-free	5.825	1.53 mg
Au@CdS pinhole	5.725	1.51 mg
SiO_2@CdS	71.04	18.74 mg

[1]To determine the amount of CdS, 1 mL core-shell nanoparticle stock solution (5 times concentrated solutions as described above) was dissolved in 1 mL aqua regia and diluted to 10 mL with water.

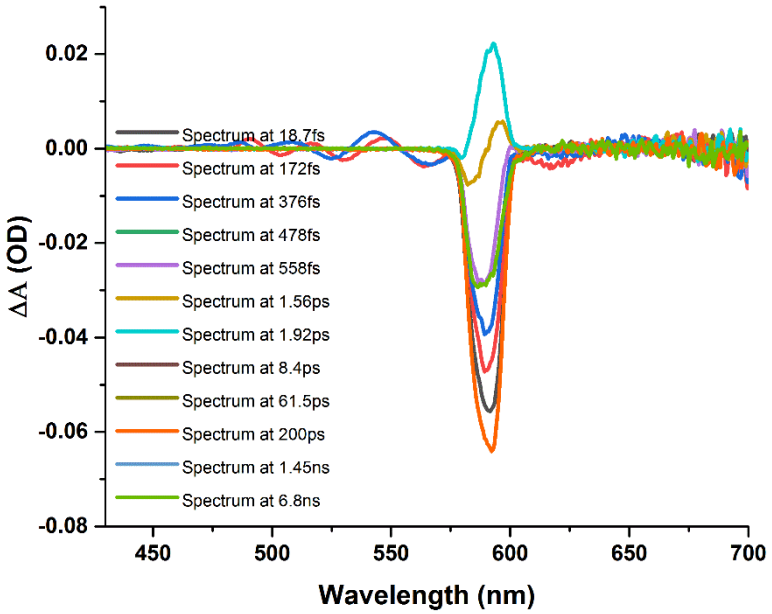

Figure S5. TA spectra of SiO_2@CdS excited by a 590 nm pump.

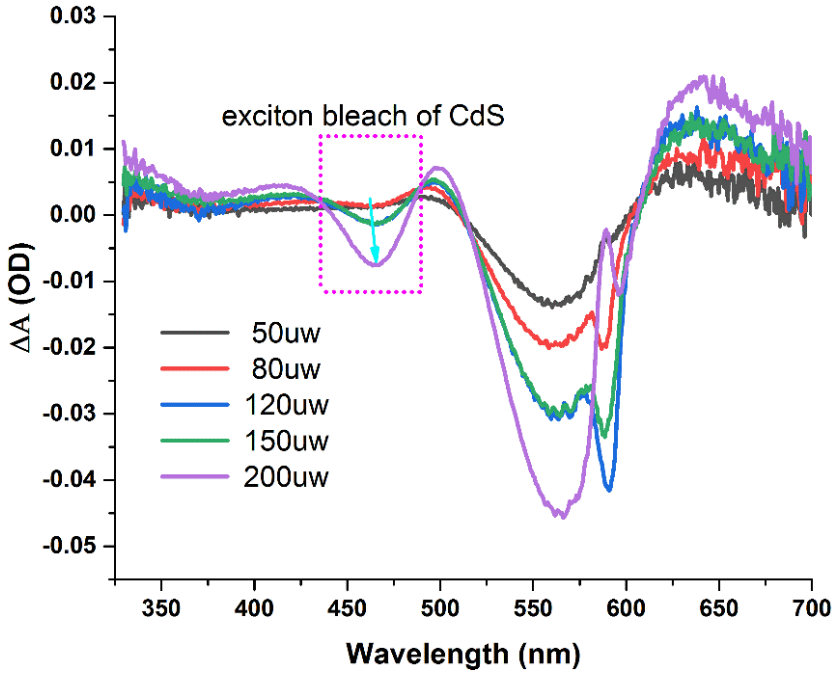

Figure S6. TA spectra of Au@CdS with pinholes excited by a 590 nm pump with different power density.

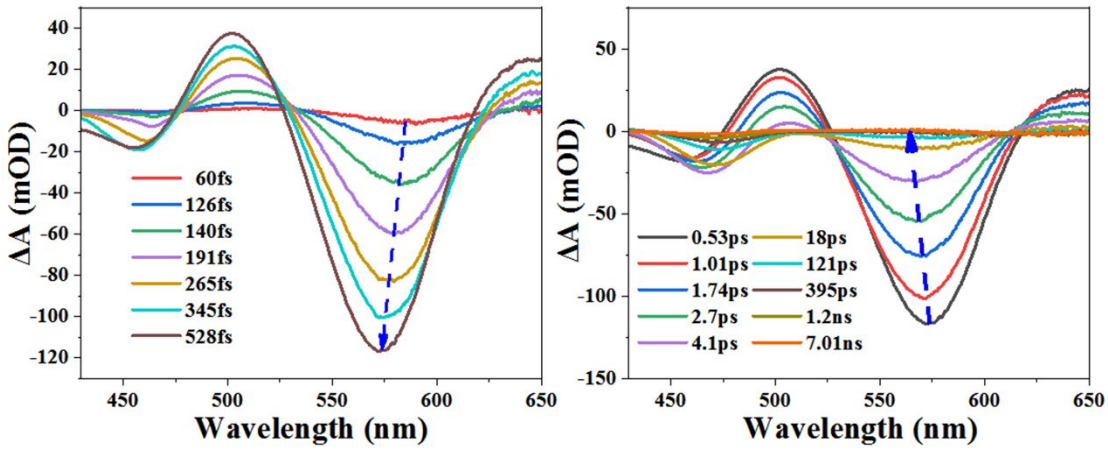

Figure S7. Time-resolved TA spectra of Au@CdS with pinholes excited by a 400 nm pump.

Table S4. Global fitting parameters for TA spectra of SiO_2@CdS and Au@CdS excited by a 400 nm pump.

Decay time	*SiO_2@CdS*	*Au@CdS with pinholes*
τ_1	0.88 ± 0.34 ps	0.27 ± 0.06 ps
τ_2	34.23 ± 18 ps	1.90 ± 0.12 ps
τ_3	207.0 ± 100 ps	60.63 ± 11 ps
τ_4	5.64 ± 0.06 ns	1.24 ± 0.38 ns

In order to explore how the existence of Au affects the lifetime of the carriers of CdS, we need to compare the dynamic data in these two systems. However, as the TA signal at 475 nm is complex and is interfered by the TA signal of Au, the exponential fitting cannot be performed directly. Therefore, we have performed a standard global TA fitting, the corresponding parameters are shown in Table S4. Four kinetic parameters are obtained through the TA fitting, and the parameters of Au@CdS are all significantly smaller than the parameters of SiO_2@CdS. It indicates that the existence of Au significantly shortens the lifetime of carriers of CdS. We believe that this is due to the fact that some of the carriers generated by CdS under the 400 nm excitation

wavelength are transferred from CdS to the Au surface, where the recombination of hot electrons and holes proceeds efficiently.

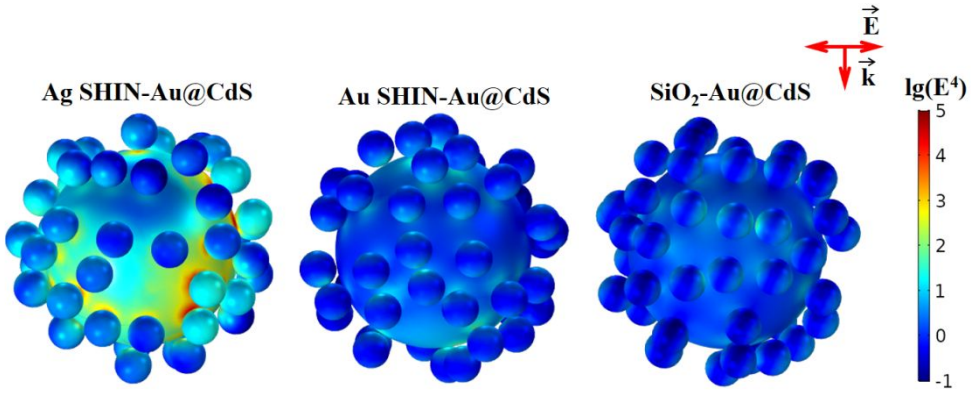

Figure S8. The EM-field distribution and field enhancement of SiO_2-Au@CdS, Au SHIN-Au@CdS, and Ag SHIN-Au@CdS under the excitation of a 400 nm incident light.

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