Electronic Supplementary Information

Asymmetric synthesis of Au-CdSe core-semishell nanorods for plasmonenhanced visible-light-driven hydrogen evolution

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Fig. S1 TEM image of pristine Au nanorods. The average sizes of the initial Au nanorods are 63.1 $(\pm 2.4) \times 19.1 (\pm 1.1) \times 19.1 (\pm 1.1) \text{ nm}^3$.



Fig. S2 TEM image of the Au-Ag nanorods. The Ag overgrows at both tips of the Au nanorods.



Fig. S3 The corresponding XRD pattern of lateral Au-CdSe NRs. The cubic phase Au and hexagonal phase CdSe pattern were detected.



Fig. S4 TEM of intermediate products shows that the Au-CdSe heterorods change from lateral growth mode to the head growth one.



Fig. S5 The time-dependent extinction spectra of the Au-CdSe heterorods grows at $pH_0 = 8.0$. The LSPR gradually red shifts as the reaction time of growth increases.



Fig.S6 The TEM morphology of the lateral Au-CdSe heterorods with one hour overgrowth of CdSe on the Au nanorods.



Fig. S7 The extinction spectra of the heterorods varied with the concentration of Cd^{2+} at $pH_0 = 7.5$ and $pH_0 = 9.0$. The change pattern is the same as when pH = 8.0. (a) The turning point from red-shift to blue-shift is at Cd^{2+} concentration of 60 µL when $pH_0 = 7.5$. (b) The turning point from red-shift to blue-shift is at Cd^{2+} concentration of 300 µL when $pH_0 = 9.0$.



Fig. S8 TEM images Au-CdSe heterorods in the turning point ($V_{Cd}^{2+} = 60 \ \mu L$ at $pH_0 = 7.5$, $V_{Cd}^{2+} = 300 \ \mu L$ at $pH_0 = 9.0$) and end point ($V_{Cd}^{2+} = 300 \ \mu L$ at $pH_0 = 7.5$, $V_{Cd}^{2+} = 460 \ \mu L$ at $pH_0 = 9.0$). CdSe grows on the side of Au nanorods at the turning point and grows on the tip of Au nanorods at the end point.



Fig. S9 TEM images of the lateral Au-CdSe heterorods at the tuning points of Cd^{2+} concentrations of 60 µL at pH₀ = 7.5, 180 µL at pH₀ = 8.0, and 300 µL at pH₀ = 9.0. A higher pH₀ value in the solution leads to a larger amount of CdSe overgrowth in the lateral Au-CdSe heterorods.



Fig. S10 H_2 evolution of the lateral Au-CdSe NRs as a function of time measured for evacuation every 4 hours without renewal of the sacrificial agents.



Fig. S11 The hydrogen production efficiency of pure Au NRs and lateral Au-CdSe heterorods in different condition. The lateral Au-CdSe heterorods does not have hydrogen production performance under dark conditions and the pure Au nanorods have very low hydrogen production capacity.



Fig. S12 The EDX measurements of the longitudinal and lateral Au-CdSe heterorods. The atom ratio of Cd to Au is 0.028 in the lateral Au-CdSe heterorods and 0.056 in the longitudinal ones.



Fig. S13 The IPCE spectrum of the lateral Au-CdSe heterorods. The IPCE enhanced by T-SPR at 520 nm is larger than the one enhanced by L-SPR at 810 nm.

Apparent quantum efficiency:

The apparent quantum efficiency (AQE) of lateral Au-CdSe heterorods was

measured under the same photocatalytic reaction condition except that the incident light was supplied by a 300 W Xe short arc lamp with specific band-pass filters to get the desired incident wavelength (420 nm). The catalyst solution was irradiated for 10 hours. The total amount of H₂ molecules produced in 10 h is 534.3 μ mol. The average intensity of irradiation was determined to be 5.2 mW·cm⁻² and the irradiation area was 14.2 cm².

$$AQE[\%] = \frac{Number of reacted electrons}{Number of incident photos} \times 100$$
$$= \frac{Number of evolved H_2 molecules \times 2}{Number of incident photos} \times 100$$

Number of evolved H₂ molecules = $6.02 \times 10^{23} \times 534.3 \times 10^{-6} = 3.216 \times 10^{20}$

Number of incident photons = $E\lambda / hc$

 $= (5.2 \times 10^{-3} \times 14.2 \times 3600 \times 10 \times 420 \times 10^{-9}) / (6.626 \times 10^{-34} \times 3 \times 10^{8})$

$$= 5.617 \times 10^{21}$$

The calculated AQE at 420 nm was 11.5%.