Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Enhancement of photocatalytic hydrogen formation under visible illumination by integrating plasmonic Au nanoparticles with strongly catalytic Ni_3S_2/carbon nanotube composite

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The theoretical calculation of loading amount of AuNPs in AuNPs@NiS@CNT

The loading amount of AuNPs in the composite can be approximated by the following equation.

AuNP wt% in the photocatalyst= $\frac{C \times V \times M_{Au}}{M_c} \times 100\%$

where C is the concentration of a $HAuCl_4$ solution (0.5 M), V is the volume extracted from AuNP colloid (1, 5 or 10 mL), M_{Au} and M_c are the atomic mass of gold and the mass of composite photocatalyst, respectively.

The calculation of apparent quantum yield (AQY)

AQY value, which is widely used to evaluate the performance of photocatalysts for water splitting, is defined by the following equation:[1]

$$\text{AQY (\%)} = \frac{2 \times number\ of\ evolved\ hydrogen\ molecules}{number\ of\ incident\ photons} \times 100\% =$$

$$\frac{2 \times 1.85 \times 10^{-2}\ mol\ g^{-1} h^{-1} \times 0.02\ g}{5.02 \times 10^{-8} mol\ cm^{-2} s^{-1} \times 3600 \frac{s}{h} \times 50.3\ cm^2} \times 100\% = 8.1\ \%$$

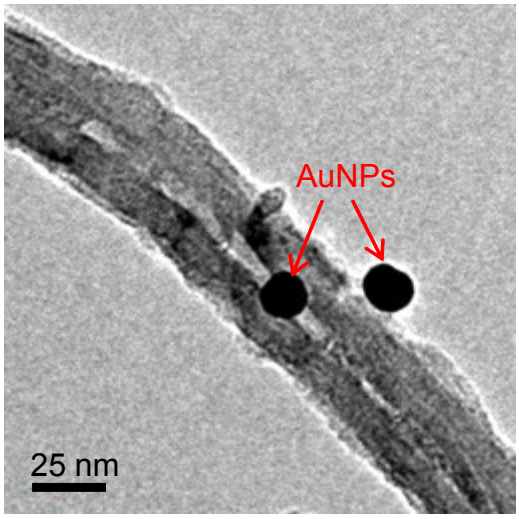

Figure S1 TEM image of AuNPs@CNT.

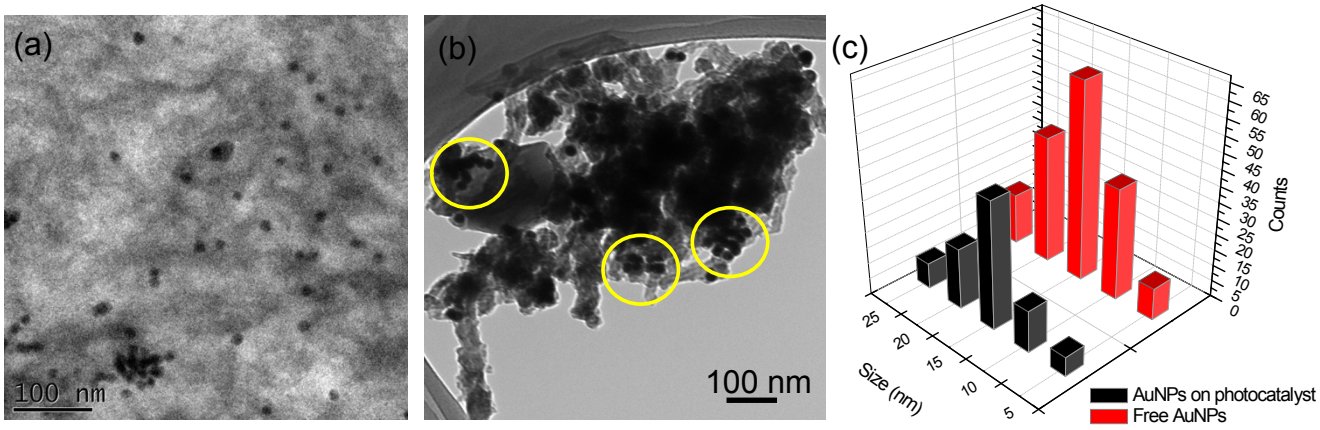

Figure S2 TEM images of (a) as-synthesized AuNPs on the carbon support and (b) AuNPs@NiS@CNT. The yellow circles in Figrure (b) indicate the locations of AuNPs in the photocatalyst. (c) Size distributions of free AuNPs and the AuNPs loaded on the photocatalyst. The average diameters of free AuNPs and the loaded AuNPs are 15.8 and 15.3 nm, respectively.

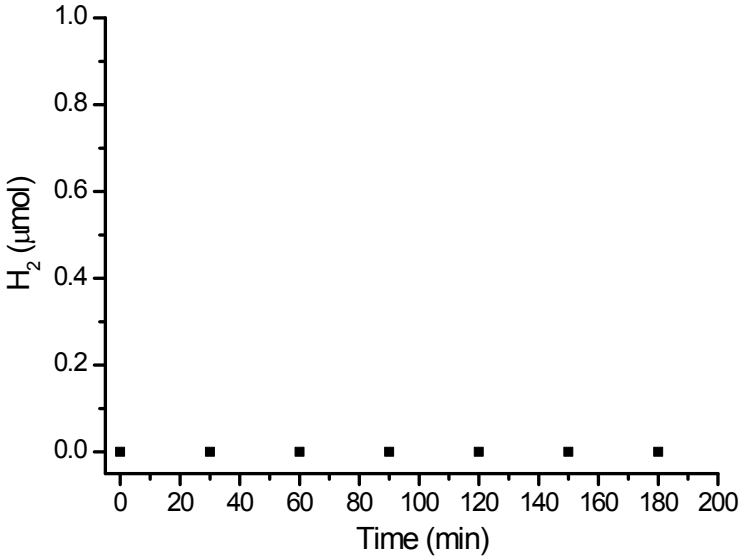

Figure S3 Time courses of hydrogen evolution over ErY-free NiS@CNT.

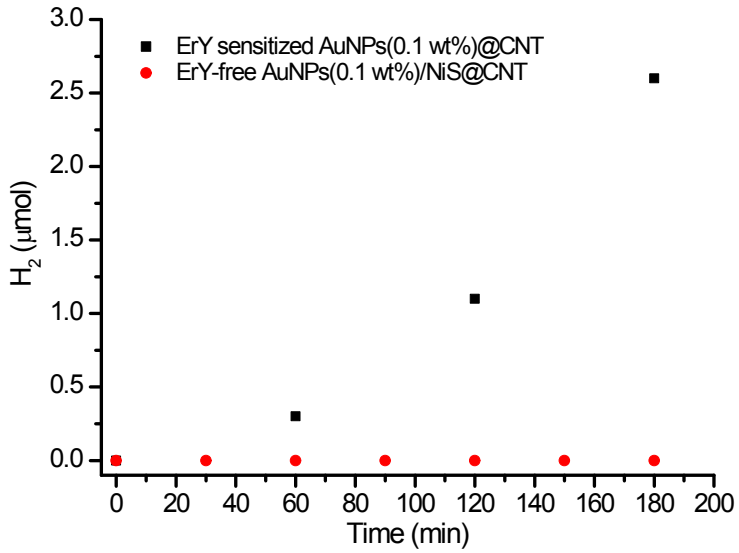

Figure S4 Time courses of hydrogen evolution over ErY sensitized AuNPs(0.1 wt%)@CNT and ErY-free AuNPs(0.1 wt%)@NiS@CNT under visible light irradiation.

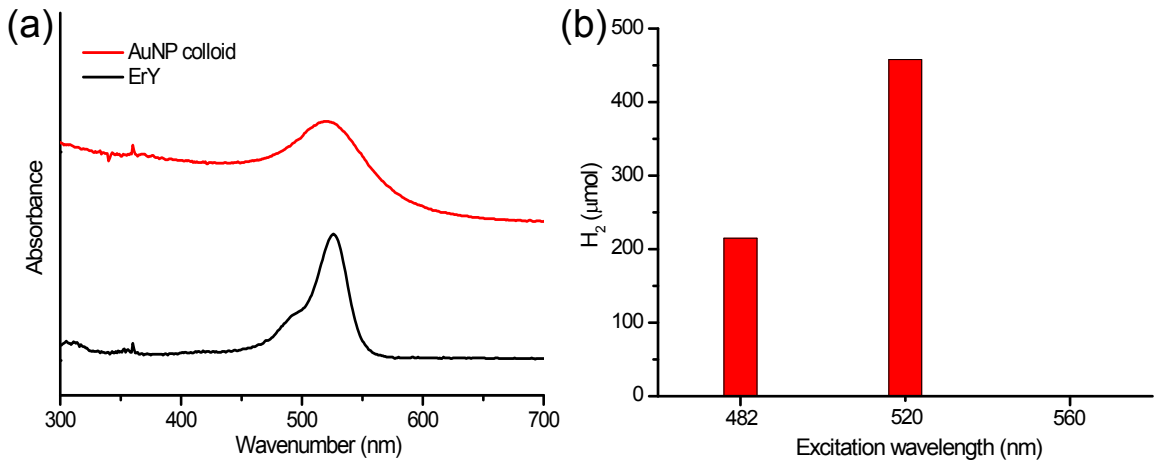

Figure S5 (a) Absorption spectra of AuNP colloid and ErY sensitizer. The UV/Vis–near-infrared absorption spectra were obtained using a UV-1800 Shimadzu spectrophotometer. (b) The effect of the illumination wavelength on photocatalytic hydrogen evolution. At the illumination wavelength of 560 nm, no hydrogen evolution is observed. In each photocatalytic experiment, the AuNPs(1 wt%)@NiS@CNT of 55 mg in the mixed solution of ErY and TEA was irradiated with a 300 W Xe

lamp equipped with a cutoff filter of 400 nm and a bandpass filter for 5 h.

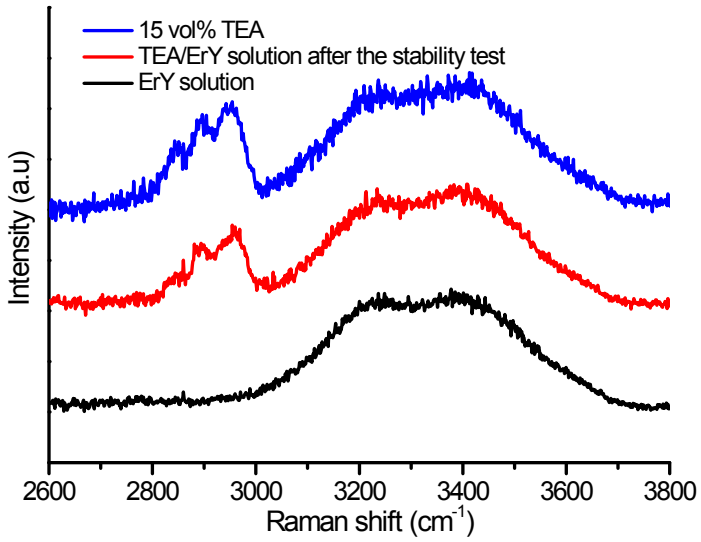

Figure S6 Raman spectrum of the mixed solution of TEA and ErY after the stability test. These Raman spectra were measured using 633 nm laser excitation with a laser power of 1 mW.

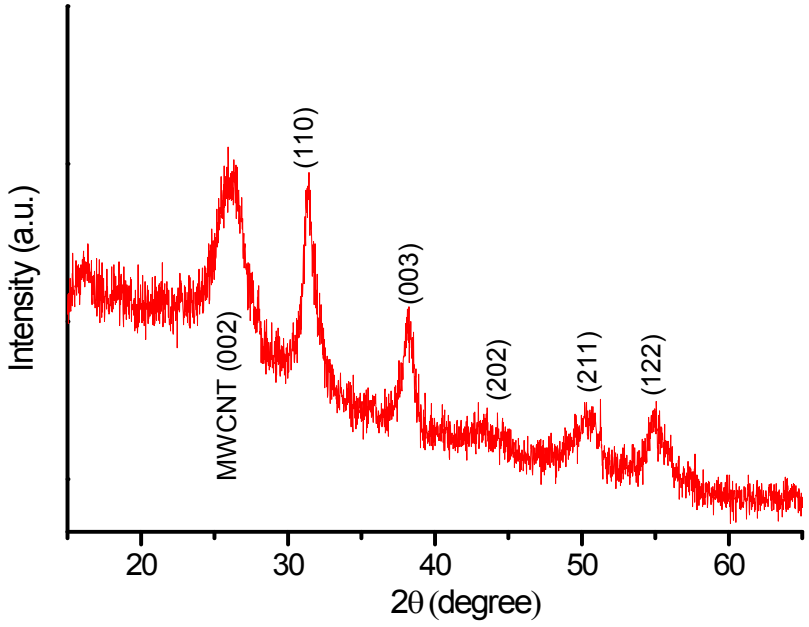

Figure S7 XRD pattern of KOH-treated AuNPs(1 wt%)@NiS@CNT after the stability test.

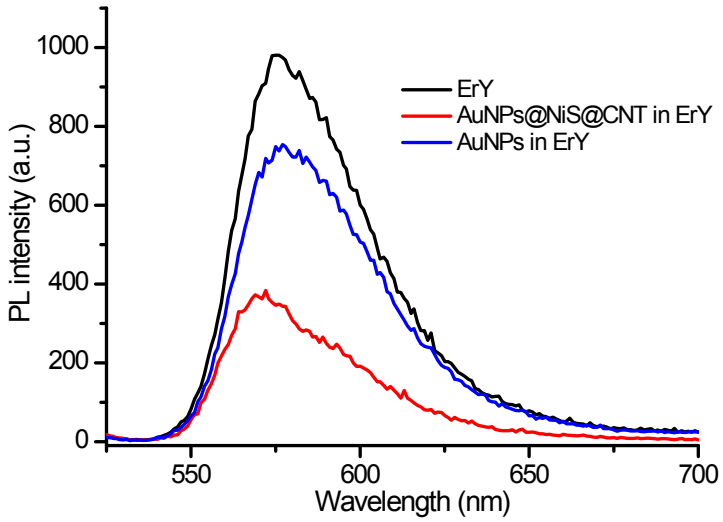

Figure S8 Photoluminescence (PL) spectra of the various ErY solutions. In each PL measurement, ErY solution of 0.4 mM is excited by the wavelength of 520 nm. The amount of AuNPs added in ErY solution is the same as that (1 wt%) used in the hydrothermal reaction. Furthermore, the amount of AuNPs(1 wt%)@NiS@CNT in ErY is 1 mg. When 1wt% AuNPs are added to ErY solution, the PL intensity of ErY decreases due to the fact that a large fraction of the excited dye undergoes deactivation as it interacts with AuNPs.[2] Furthermore, the PL intensity of ErY decreases more significantly when the photocatalyst is added to the ErY solution. Compared with AuNPs in ErY solution, the amount of AuNPs in the ErY solution containing the photocatalyst is much less. Therefore, the decreased PL intensity may be attributed to both the quenching effect from AuNPs loaded on the photocatalyst and the efficient transfer of photoexcited electron from ErY to the catalyst through conducting CNTs.

References

1. Z. Jin, X. Zhang, Y. Li, S. Li and G. X. Lu, *Catal. Commun.*, 2007, **8**, 1267–1273.

2. M. Jebb, P. K. Sudeep, P. Pramod, K. G. Thomas, and P. V. Kamat, *J. Phys. Chem. B*, 2007, **111**, 6839.