Supplementary Information

Direct Evidence of Plasmon Enhancement on Photocatalytic Hydrogen Generation over Au/Pt-Decorated TiO_2 Nanofibers

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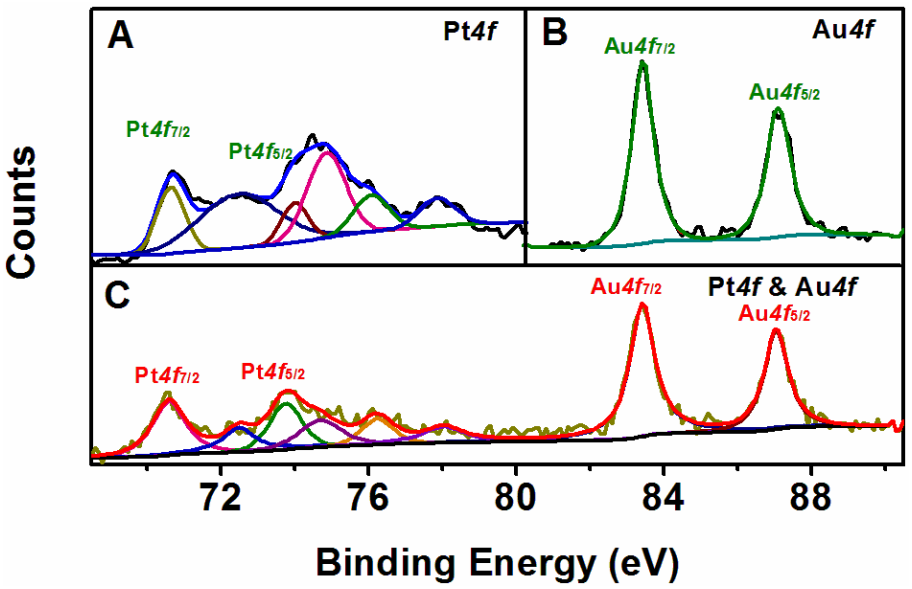

Figure S1. High resolution XPS spectra of Au 4f or/and Pt 4f regions for (A) Pt_1/TiO_2 nanofibers; (B) Au_1/TiO_2 nanofibers; (C) $Au_{0.75}/Pt_{0.25}/TiO_2$ nanofibers.

Elements	Pt_1/TiO_2 nanofibers	Au_1/TiO_2 nanofibers	$Au_{0.75}/Pt_{0.25}/TiO_2$ nanofibers
Pt4f7 Pt (0)	**70.7 eV**	**------**	**70.6 eV**
Pt4f7 Pt (Ⅱ)	**72.5 eV**	**------**	**72.5 eV**
Pt4f7 Pt (Ⅳ)	**74.7 eV**	**------**	**74.7 eV**
Au4f7 Au (0)	**------**	**83.4 eV**	**83.4 eV**

Table S1. Peak position of binding energy of the samples

As observed in Figure 1S, the XPS results shows that the Au species in the Au_1/TiO_2 nanofibers are only metallic Au^0 state, while there are three states of Pt species in the Pt_1/TiO_2 nanofibers, including the metallic Pt^0 state, Pt^{2+} state, and Pt^{4+} state.[1,2] The presence of Pt^{2+} and Pt^{4+} state might be attributed to the formation of Pt-O bond on the surface of Pt nanostructures, which is agreement to the literatures.[3, 4] By comparing the peak positions of binding energy with the Au_1/TiO_2 and Pt_1/TiO_2 nanofibers in table S1, the Au4f7 and Pt4f7 peaks in the $Au_{0.75}/Pt_{0.25}/TiO_2$ nanofibers are nearly unchanged, indicating that the Au and Pt NPs were co-decorated in the TiO_2 nanofibers, and no Au-Pt alloy formation.

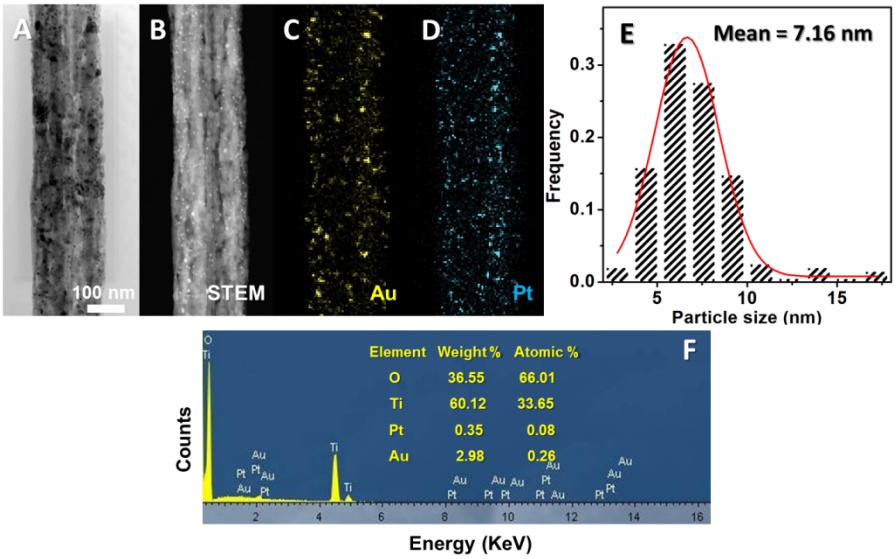

Figure S2. (A) TEM image and (B) dark-field STEM image of the $Au_{0.75}/Pt_{0.25}/TiO_2$ nanofibers; Elemental mapping images from image A: (C) Au element; (D) Pt element; (E) Size distribution histogram of metal NPs in the $Au_{0.75}/Pt_{0.25}/TiO_2$ nanofibers calculated from the above STEM image; (F) EDS spectrum of the $Au_{0.75}/Pt_{0.25}/TiO_2$ nanofibers.

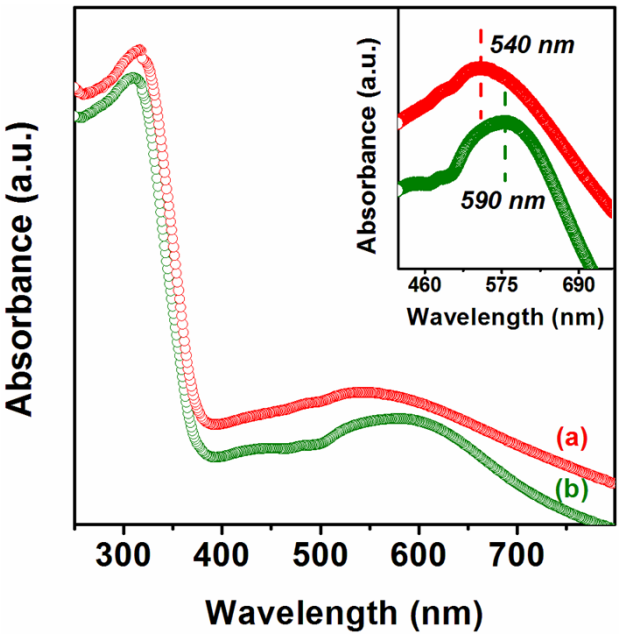

Figure S3. UV-Vis absorption spectra of the (a) $Au_{0.75}/Pt_{0.25}/TiO_2$ and (b) Au_1/TiO_2 nanofibers, which are converted from diffuse reflectance spectra by means of the Kubelka-Munk function.

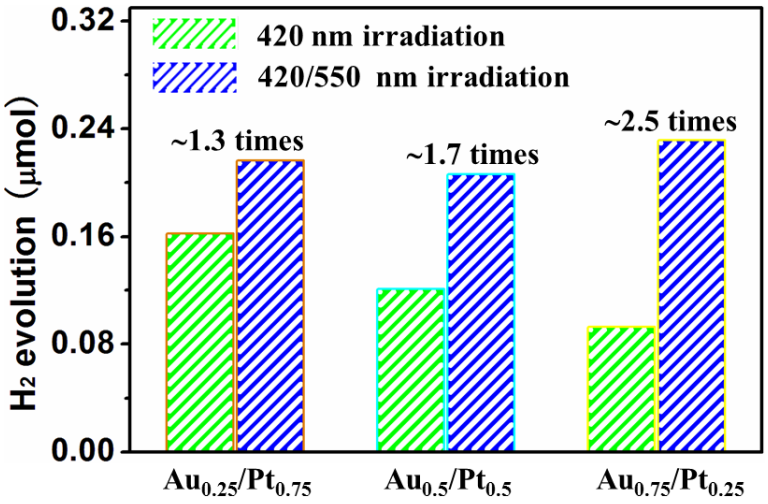

Figure S4. H_2 evolution amount for the Au/Pt/TiO_2 nanofibers with different mole ratios of Au to Pt versus the irradiation wavelength after 2 h irradiation by using L-ascorbic acid (H_2A) as the sacrificial agents in 10 mL aqueous solution.

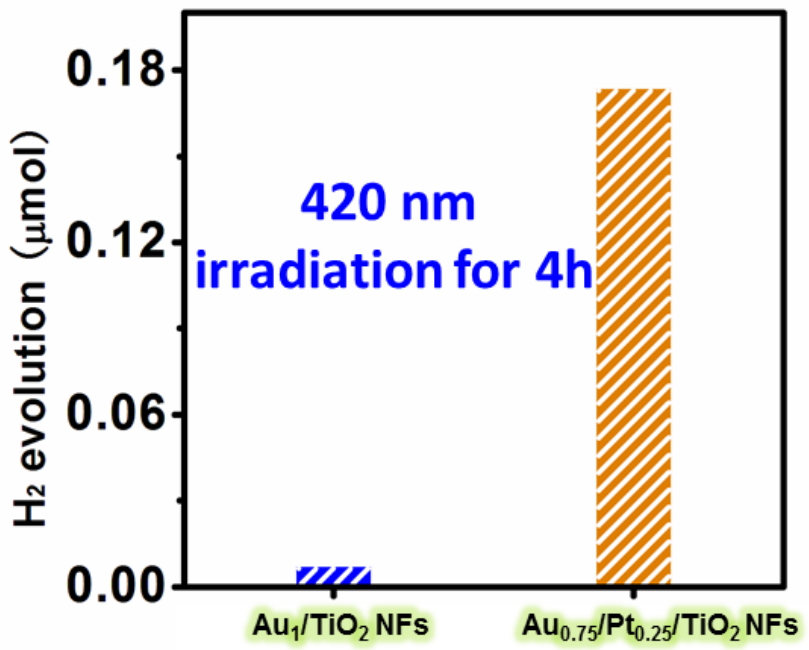

Figure S5. H_2 evolution amount of the Au_1/TiO_2 and $Au_{0.75}/Pt_{0.25}/TiO_2$ nanofibers under irradiation at 420 ±10 nm for 4h.

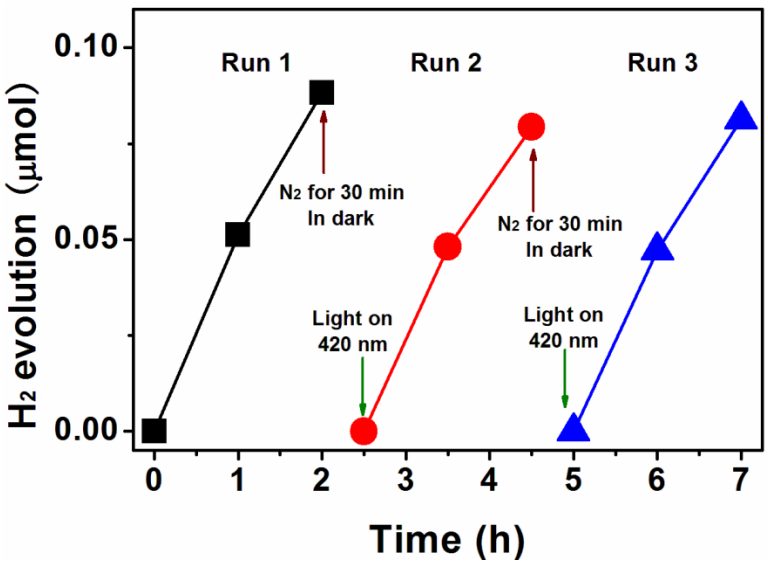

Figure S6. Cycling test of photocatalytic H_2 evolution for the $Au_{0.75}/Pt_{0.25}/TiO_2$ nanofibers under 420 nm irradiation. It demonstrates that the $Au_{0.75}/Pt_{0.25}/TiO_2$ nanofibers have very good stablility in the photocatalytic reaction for H_2 generation.

1. Zhang, P.; Shao, C.; Li, X.; Zhang, M.; Zhang, X.; Sun Y.; Liu, Y. In situ assembly of well-dispersed Au nanoparticles on TiO_2/ZnO nanofibers: A three-way synergistic heterostructure with enhanced photocatalytic activity. *J. Hazard. Mater.* **2013,** *331,* 237-238.
2. Ono, L. K.; Yuan, B.; Heinrich H.; Cuenya, B. R. Formation and Thermal Stability of Platinum Oxides on Size-Selected Platinum Nanoparticles: Support Effects. *J. Phys. Chem. C* **2010**, *114,* 22119-22133.
3. Ding, Y.; Wang, Y.; Zhang, L.; Zhang, H.; Li C. M.; Lei, Y. Preparation of TiO_2-Pt hybrid nanofibers and their application for sensitive hydrazine detection. *Nanoscale* **2011,** *3*, 1149-1157.
4. Bera, P.; Priolkar, K. R.; Gayen, A.; Sarode, P. R.; Hegde, M. S.; Emura, S.; Kumashiro, R.; Jayaram V.; Subbanna, G. N. Ionic Dispersion of Pt over CeO_2 by the Combustion Method: Structural Investigation by XRD, TEM, XPS, and EXAFS. *Chem. Mater.* **2003,** *15*, 2049-2060.