Electronic supplementary information for

Hierarchical metal-semiconductor-graphene ternary heteronanostructures for plasmon-enhanced wide-range visible-light photocatalysis†

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†Electronic supplementary information (ESI) available: Additional data (Fig. S1-S15 and Tables S1 and S2).

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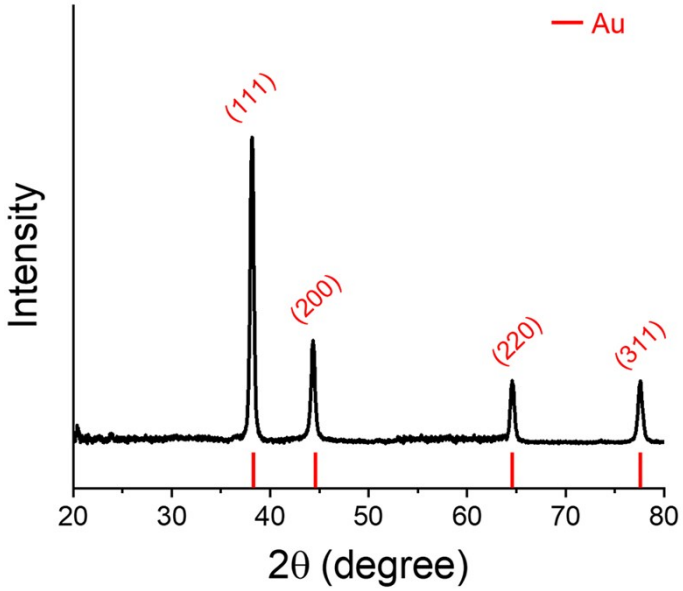

Fig. S1. XRD pattern of Au ONCs. The positions of Au reference were taken from the JCPDS database (Au: 65-2870).

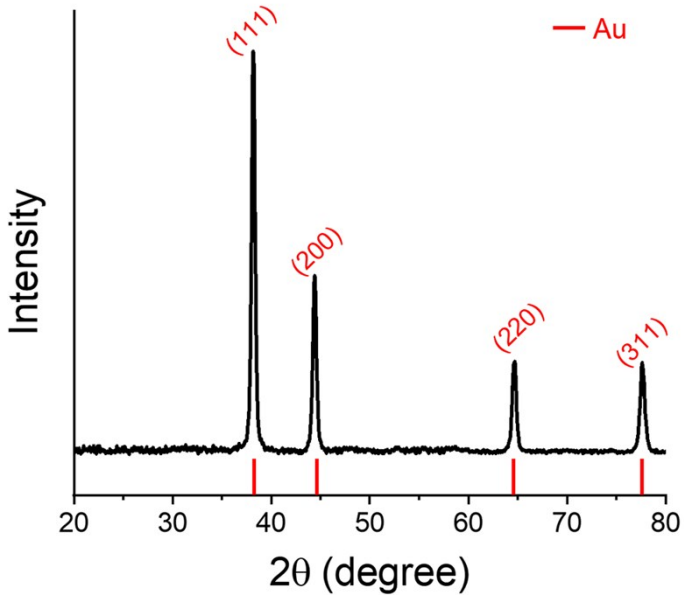

Fig. S2. XRD pattern of Au_{ONC}@aTiO_2 CSNs.

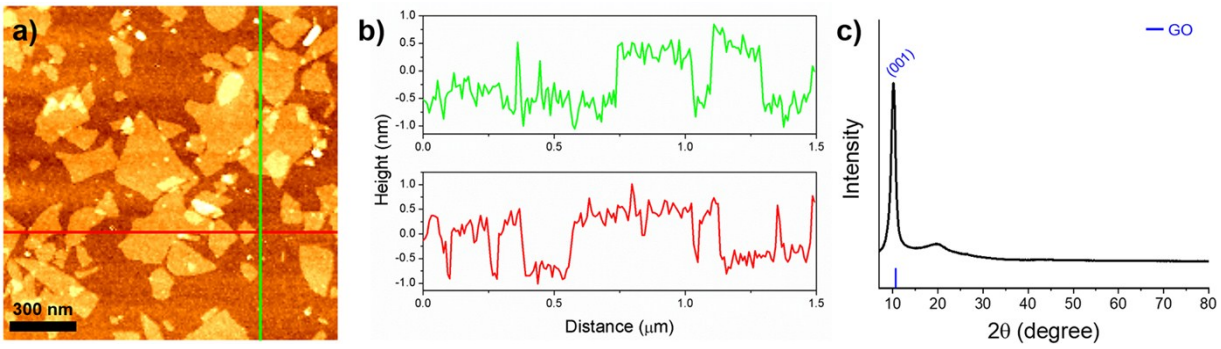

Fig. S3. (a) Tapping mode atomic force microscopy image of GO and (b) corresponding height profiles along the lines in a. (c) XRD pattern of GO.

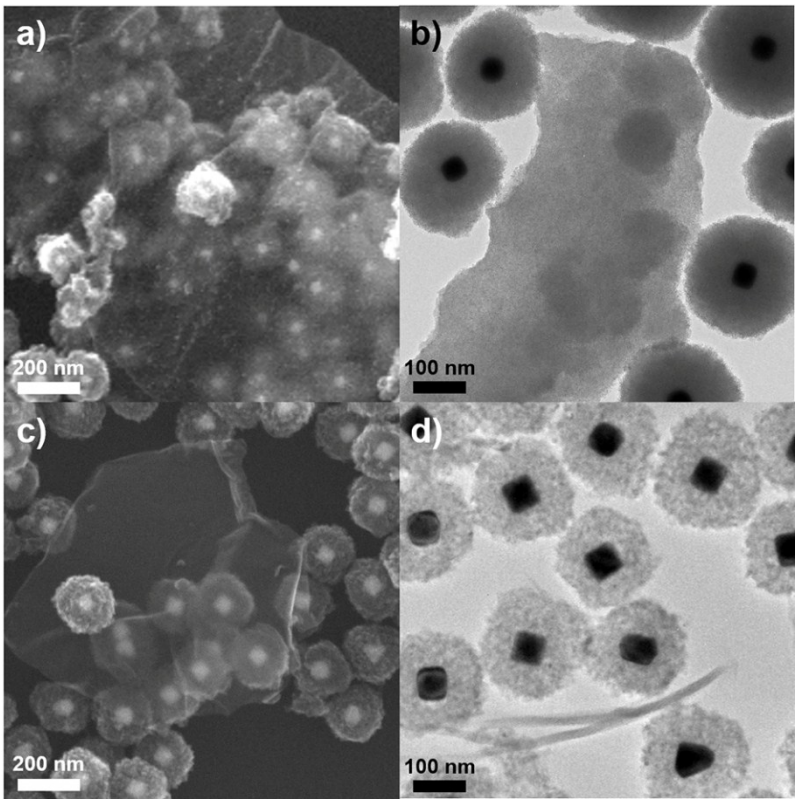

Fig. S4. (a,c) SEM and (b,d) TEM images of Au_{ONC}@aTiO_2 CSNs (a,b) after GO encapsulation and (c,d) calcination without APTMS modification, while keeping other reaction conditions the same as those used in the synthesis of G-Au_{ONC}@TiO_2 CSNs.

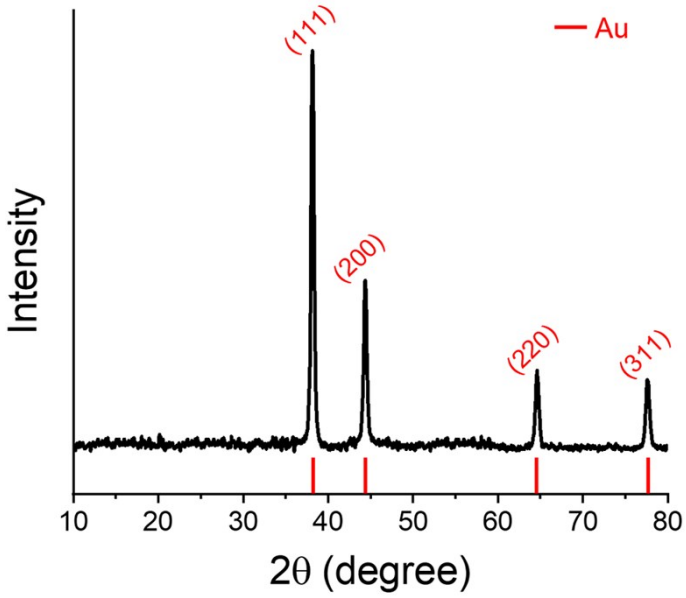

Fig. S5. XRD pattern of GO-Au_{ONC}@aTiO_2 CSNs.

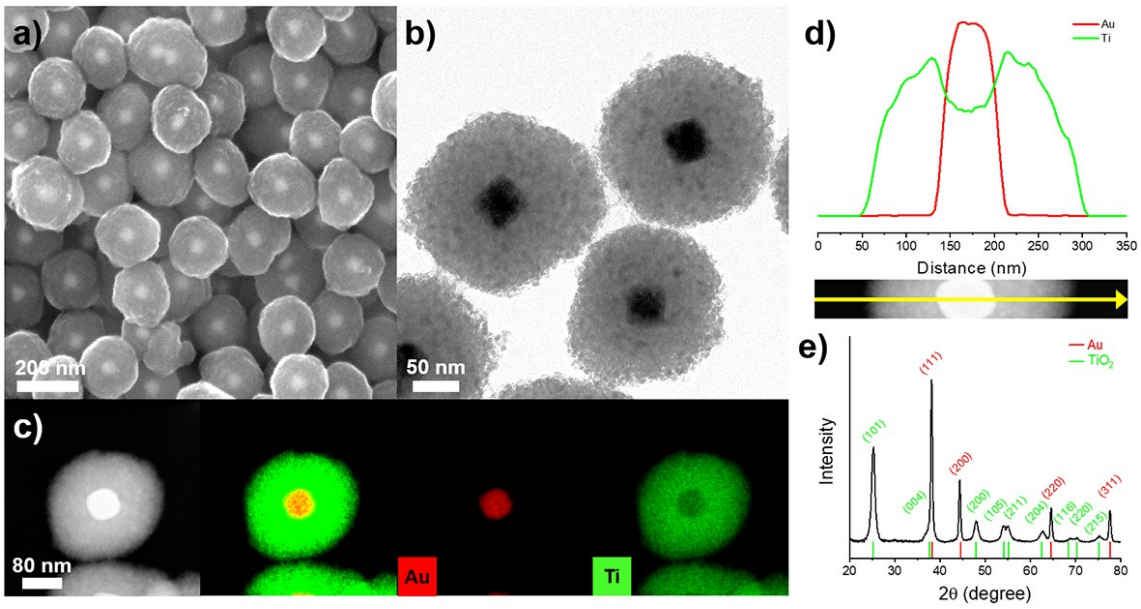

Fig. S6. (a) SEM and (b) TEM image of Au_{ONC}@TiO_2 CSNs. (c) HAADF-STEM image and corresponding EDS elemental mapping images of an Au_{ONC}@TiO_2 CSN. (d) EDS compositional line scanning profiles along the direction marked by a yellow arrow in the HAADF-STEM image of an Au_{ONC}@TiO_2 CSN shown in inset. (e) XRD pattern of Au_{ONC}@TiO_2 CSNs. The positions of anatase TiO_2 reference were taken from the JCPDS database (anatase TiO_2: 21-1272).

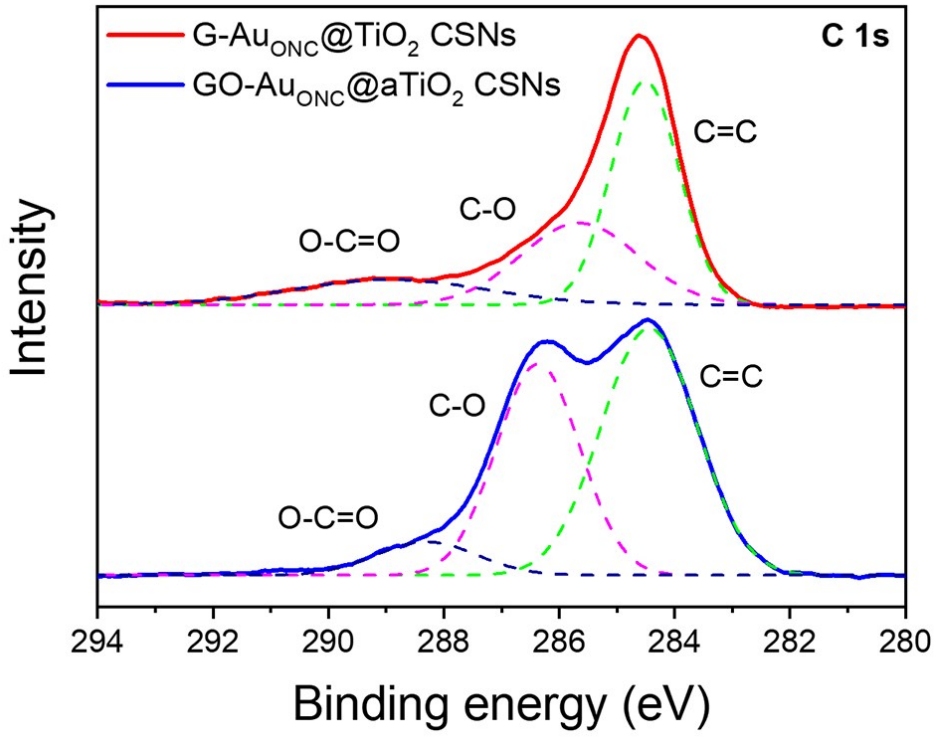

Fig. S7. C 1s XPS spectra of G-Au$_{ONC}$@TiO$_2$ and GO-Au$_{ONC}$@aTiO$_2$ CSNs.

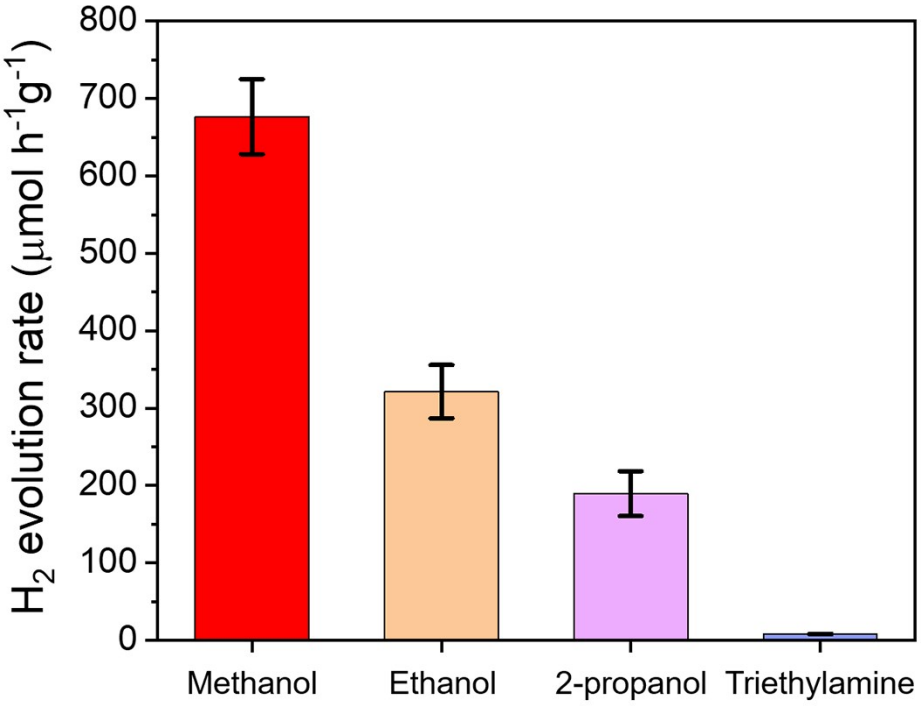

Fig. S8. Hydrogen evolution rate of G-Au_{ONC}@TiO_2 CSNs prepared with 0.5 wt% of GO using different hole scavengers, such as methanol, ethanol, 2-propanol, and triethylamine. The concentration of each hole scavenger was 25 vol%.

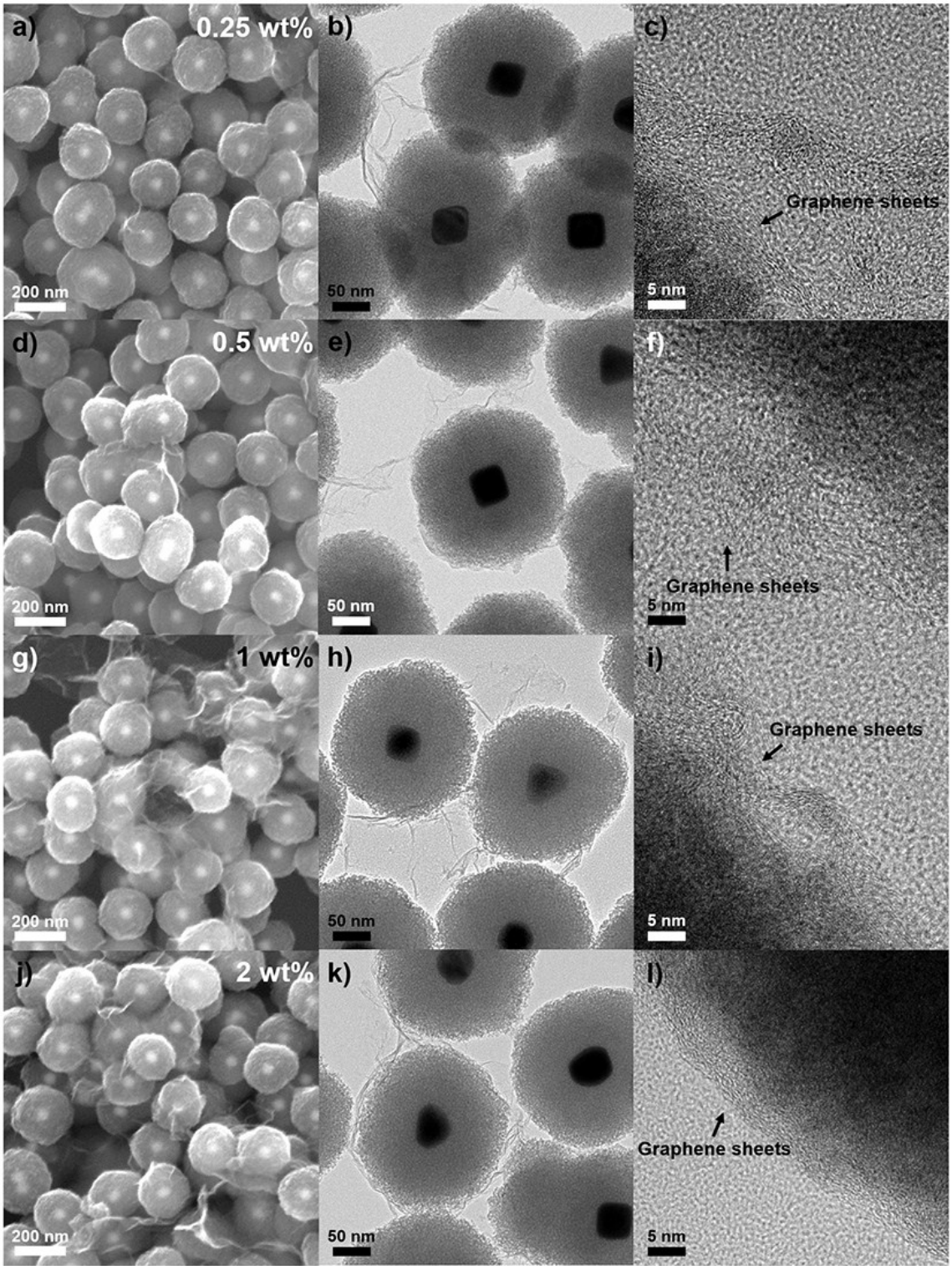

Fig. S9. (a,d,g,j) SEM, (b,e,h,k) TEM, and (c,f,i,l) HRTEM images of G-Au_{ONC}@TiO_2 CSNs prepared with (a-c) 0.25, (d-f) 0.5, (g-i) 1, and (j-l) 2 wt% of GO.

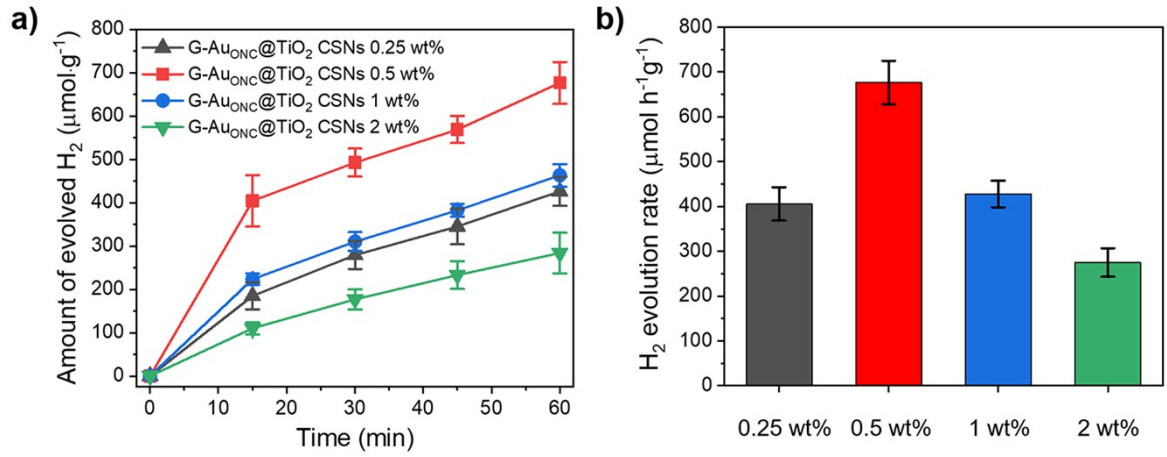

Fig. S10. (a) Amounts of hydrogen evolved during the photocatalysis with G-Au_{ONC}@TiO_2 CSNs prepared with different weight percentages of GO, which are normalized to the total mass of catalysts, and (b) corresponding hydrogen evolution rates.

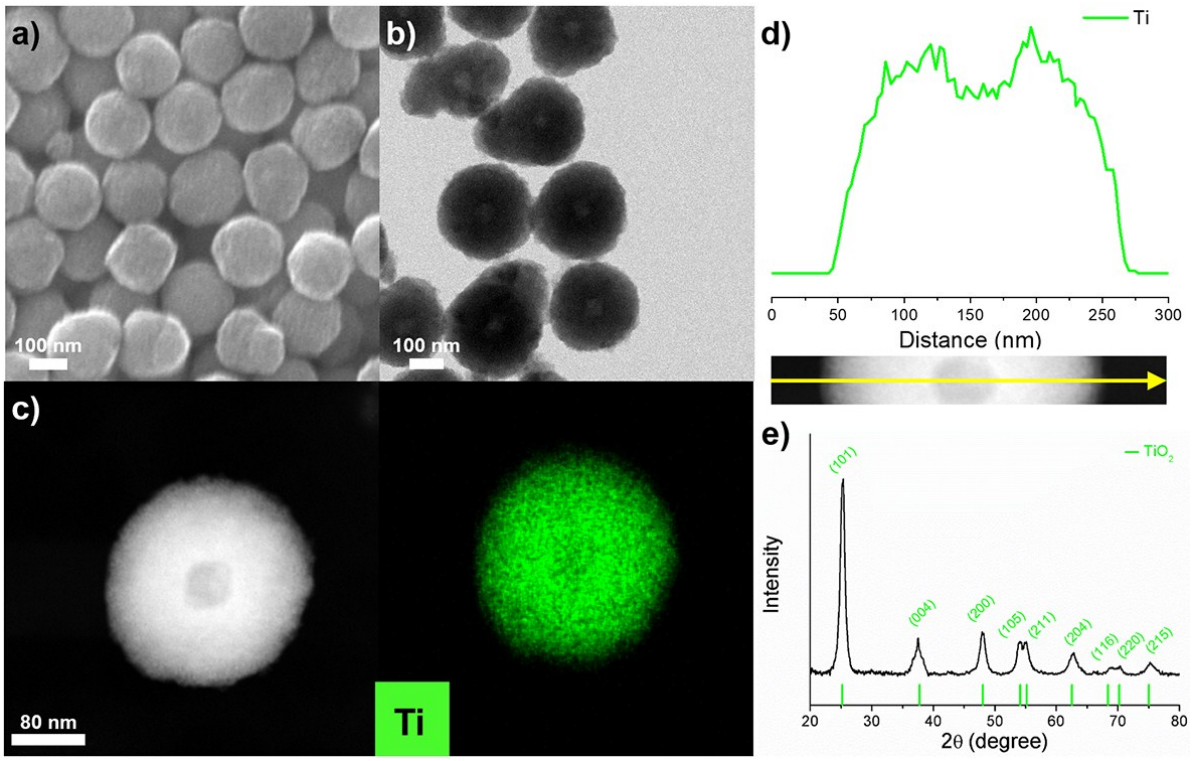

Fig. S11. (a) SEM and (b) TEM image of TiO_2 NPs. (c) HAADF-STEM image and corresponding EDS elemental mapping image of a TiO_2 NP. (d) EDS compositional line scanning profile along the direction marked by a yellow arrow in the HAADF-STEM image of a TiO_2 NP shown in inset. (e) XRD pattern of TiO_2 NPs.

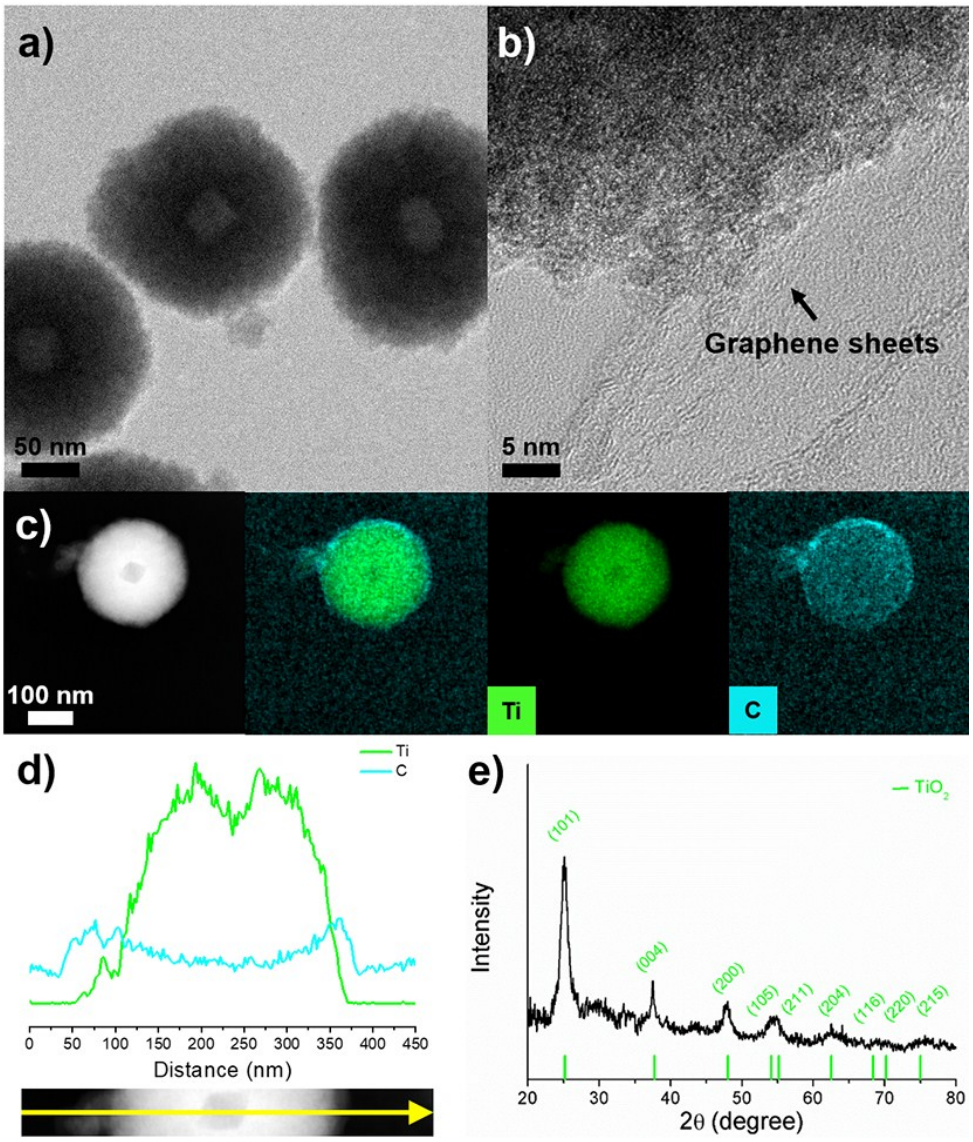

Fig. S12. (a) TEM and (b) HRTEM image of G-TiO_2 NPs. (c) HAADF-STEM image and corresponding EDS elemental mapping images of a G-TiO_2 NP. (d) EDS compositional line scanning profiles along the direction marked by a yellow arrow in the HAADF-STEM image of a G-TiO_2 NP shown in inset. (e) XRD pattern of G-TiO_2 NPs.

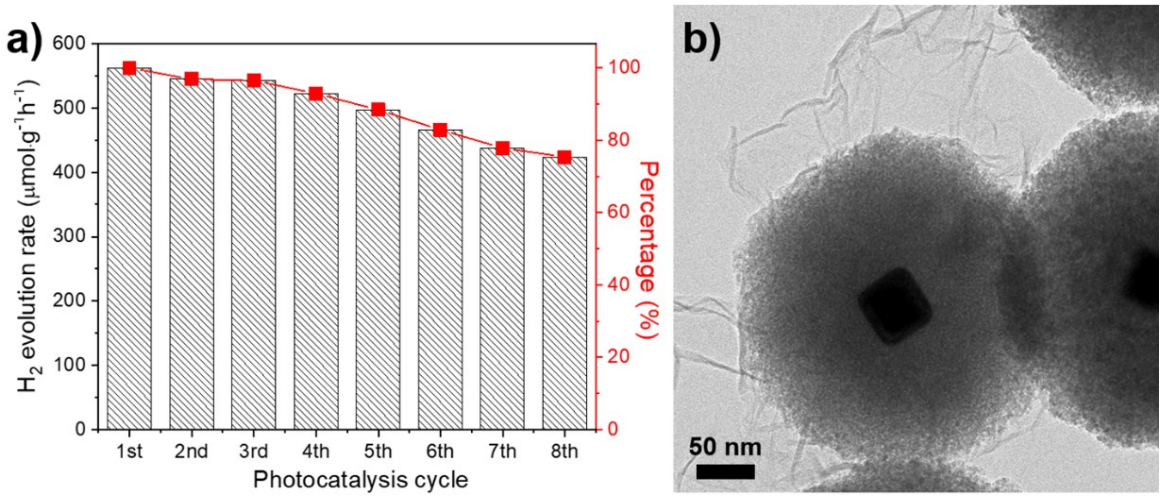

Fig. S13. (a) Recyclability of G-Au_{ONC}@TiO_2 CSNs for photocatalytic hydrogen evolution. Each photocatalysis cycle was conducted for 1 h under visible-light irradiation and the reaction solution containing methanol (37.5 vol%) was purged with Ar for 20 min. After four photocatalysis cycles, the G-Au_{ONC}@TiO_2 CSNs were collected from the reaction solution by centrifugation, and then subjected to the next photocatalytic reaction. (b) TEM image of G-Au_{ONC}@TiO_2 CSNs after repeated photocatalysis cycles.

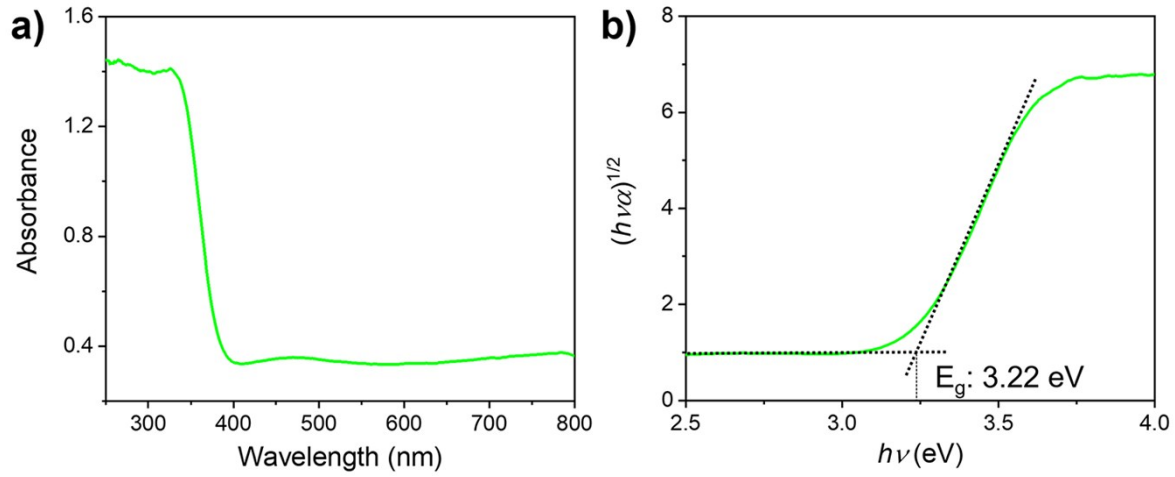

Fig. S14. (a) Diffuse reflectance spectrum and (b) Tauc plot of TiO_2 NPs. The band gap energy (E_g) of TiO_2 NPs was calculated to be 3.22 eV.

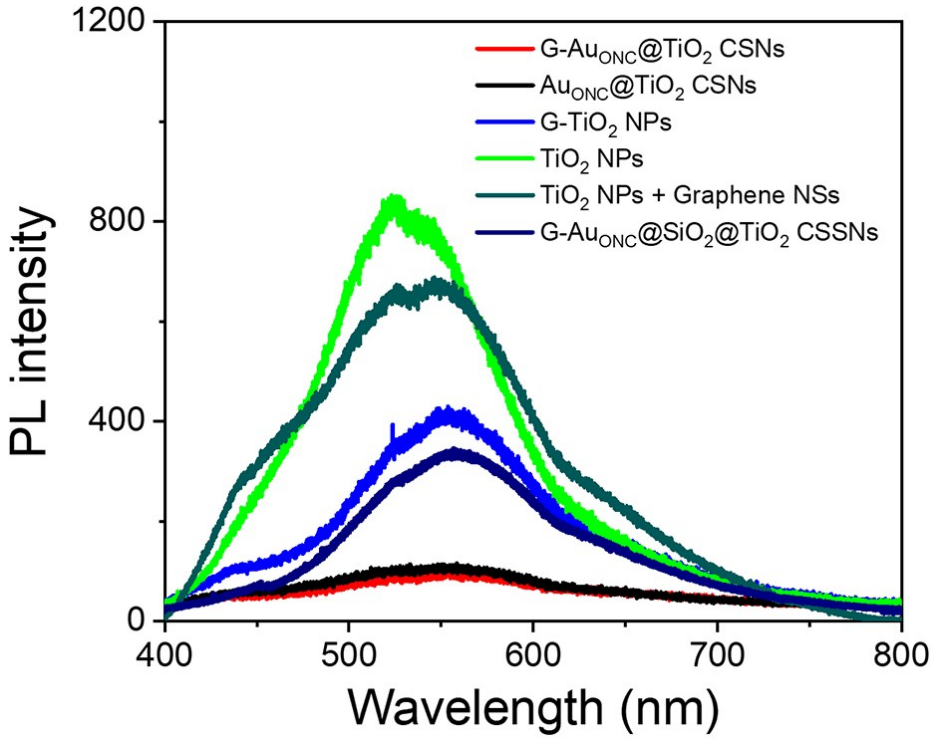

Fig. S15. Steady-state PL spectra of G-Au_{ONC}@TiO_2 CSNs, Au_{ONC}@TiO_2 CSNs, G-TiO_2 NPs, TiO_2 NPs, physical mixture of TiO_2 NPs and graphene NSs, and G-Au_{ONC}@SiO_2@TiO_2 CSSNs.

Table S1. Comparison of the AQEs of G-Au_{ONC}@TiO_2 CSNs with those obtained with other Au-semiconductor hybrids.

Photocatalyst	Light source	AQE (%)	Reference
G-Au_{ONC}@TiO_2 CSNs	450 nm monochromatic (5 mW cm^{-2})	0.53	This work
	700 nm monochromatic (5 mW cm^{-2})	0.31	
Au-TiO_2-NiO_x	590 nm monochromatic (2.9 mW cm^{-2})	0.013	S1
Au@CdS	640 nm-LED (3.4 mW cm^{-2})	0.24	S2
Au-MoS_2	550 nm monochromatic (4.8 mW cm^{-2})	0.04	S3
	780 nm monochromatic (4.8 mW cm^{-2})	0.20	
Au@TiO_2-CdS	420 nm monochromatic	0.55	S4
	550 nm monochromatic	0.0	
Au/$ZnIn_2S_4$/TiO_2	420 nm monochromatic	0.14	S5
	600 nm monochromatic	0.0	
Au/TiO_2-Pt	550 nm monochromatic (0.4 mW cm^{-2})	0.41	S6
	700 nm monochromatic (0.4 mW cm^{-2})	0.075	

References

(S1) A. Tanaka, K. Teramura, S. Hosokawa, H. Kominami and T. Tanaka, *Chem. Sci.*, 2017, **8**, 2574.

(S2) S.-I. Naya, T. Kume, R. Akashi, M. Fujishima and H. Tada, *J. Am. Chem. Soc.*, 2018, **140**, 1251.

(S3) P. Zhang, M. Fujitsuka and T. Majima, *Nanoscale*, 2017, **9**, 1520.

(S4) J. Fang, L. Xu, Z. Zhang, Y. Yuan, S. Cao, Z. Wang, L. Yin, Y. Liao and C. Xue, *ACS Appl. Mater. Interfaces*, 2013, **5**, 8088.

(S5) Z. Zhang, Y. Huang, K. Liu, L. Guo, Q. Yuan and B. Dong, *Adv. Mater.*, 2015, **27**, 5906.

(S6) A. Tanaka, S. Sakaguchi, K. Hashimoto and H. Kominami, *ACS Catal.*, 2013, **3**, 79.

Table S2. PL lifetimes of G-TiO_2 NPs, TiO_2 NPs, and physical mixture of TiO_2 NPs and graphene NSs. The lifetimes were obtained 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
G-TiO_2 NPs	0.7680	12.09	271.4	180.8	1.080
TiO_2 NPs	0.3748	1.783	102.5	25.13	1.090
TiO_2 NPs + Graphene NSs	0.4887	2.759	165.7	28.72	1.073

*The average PL lifetimes were calculated by the following equation:

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