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

Supporting Information

Bioinspired spiky-like double yolk-shell structured TiO_2@$ZnIn_2S_4$ for efficient photocatalytic CO_2 reduction

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Keywords: bioinspired; double yolk-shell; photocatalytic CO_2 reduction; titanium dioxide; $ZnIn_2S_4$

The flat band potential of semiconductor film in a liquid junction can be estimated from the Mott–Schottky equation 1:

$$\frac{1}{C_{SC}^2} = (2/e\varepsilon\varepsilon_0 N_D)(E - E_{fb} - kT/e)$$ equation 1

where Csc is the space charge capacitance in F cm^{-2}; e is the electronic charge in C; ε is the dielectric constant of the semiconductor; ε_0 is the permittivity of free space; N_D is the carrier density in cm^{-3}; E is the applied potential in V; E_{fb} is the flat band potential in V; k is the Boltzmann constant; and T represents the temperature in K. The temperature related term (kT/e) in eq 1 is negligible, 0.0257, at room temperature. The flat band potential is obtained from the x-intercept of the tangent line of the Mott–Schottky curve on potential axis (vs. Ag/AgCl). According to the equation that E (NHE) = E (Ag/AgCl) + 0.197 V, the flat band potentials (VS. NHE) of the obtained materials were calculated to be E (Ag/AgCl) plus 0.197 V. In this way, the flat band potential of the prepared materials was determined.

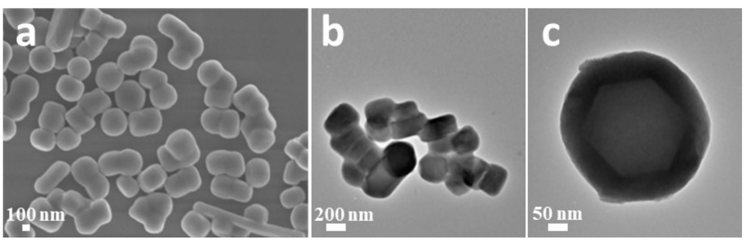

Figure S1. SEM (a) and TEM images (b, c) of S1@TiO_2

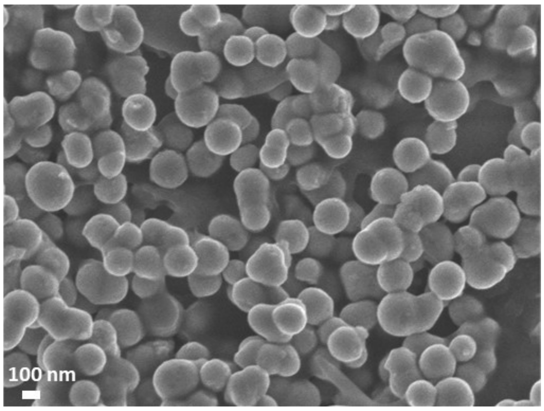

Figure S2. SEM of TiO_2 NPs

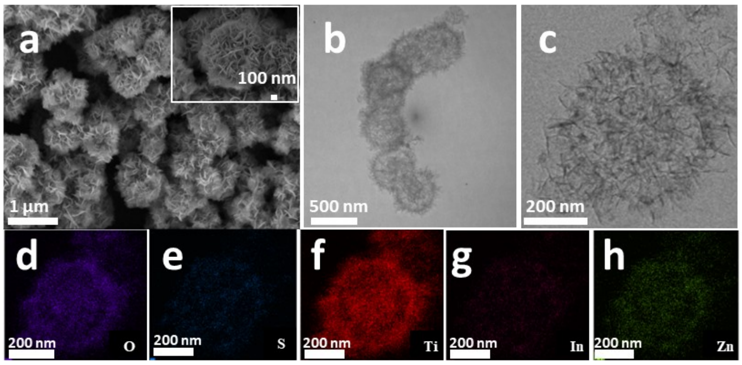

Figure S3. SEM (a), TEM (b, c) and EDS mapping images (d-h) of D-Y-TiO_2@$ZnIn_2S_4$-1

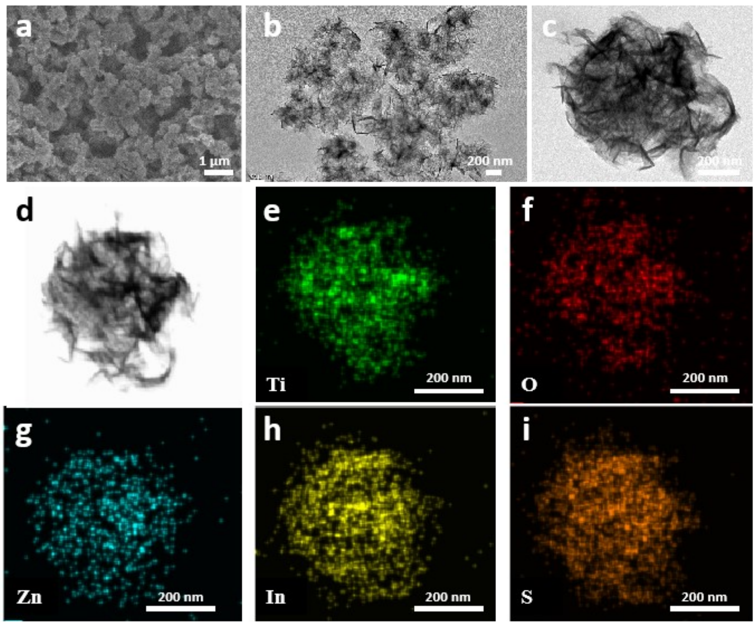

Figure S4. SEM (a),TEM (b, c) and EDS mapping images (d-i) of D-Y-TiO_2@$ZnIn_2S_4$-2

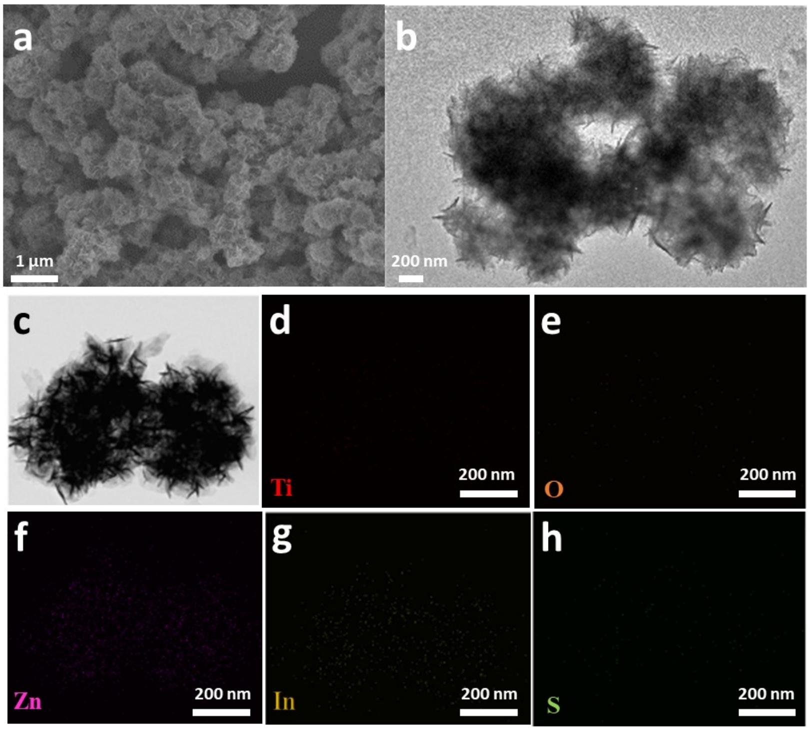

Figure S5. SEM (a), TEM (b, c) and EDS mapping images (d-h) of D-Y-TiO_2@$ZnIn_2S_4$-4

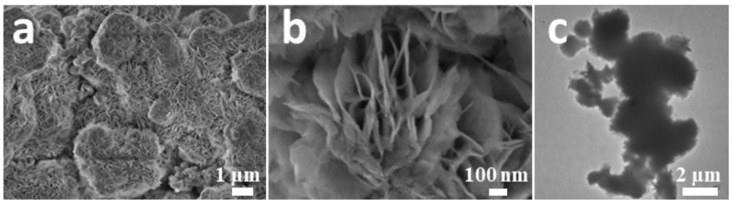

Figure S6. SEM (a, b) and TEM images (c) of $ZnIn_2S_4$ only

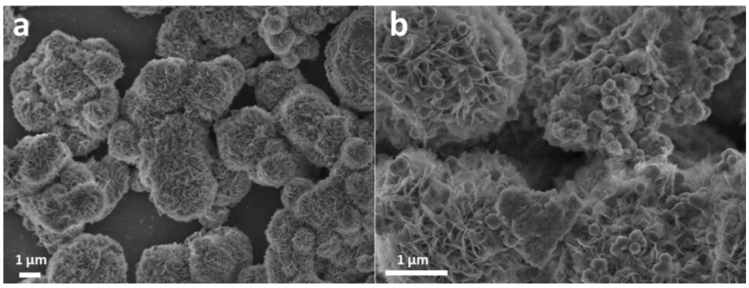

Figure S7. SEM images of TiO_2 NPs@$ZnIn_2S_4$-3, (b) is the enlarged image of (a).

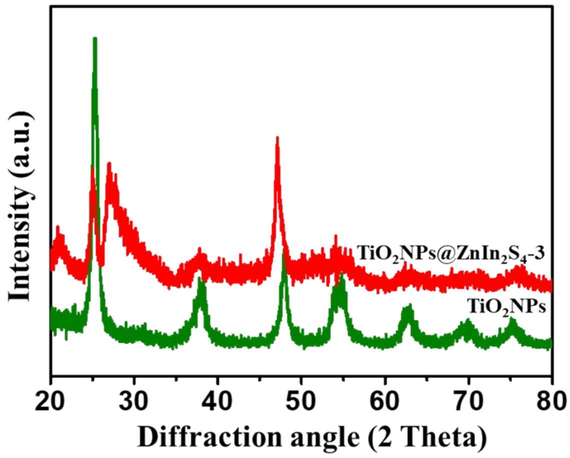

Figure S8. XRD of TiO_2 NPs and TiO_2 NPs@$ZnIn_2S_4$-3.

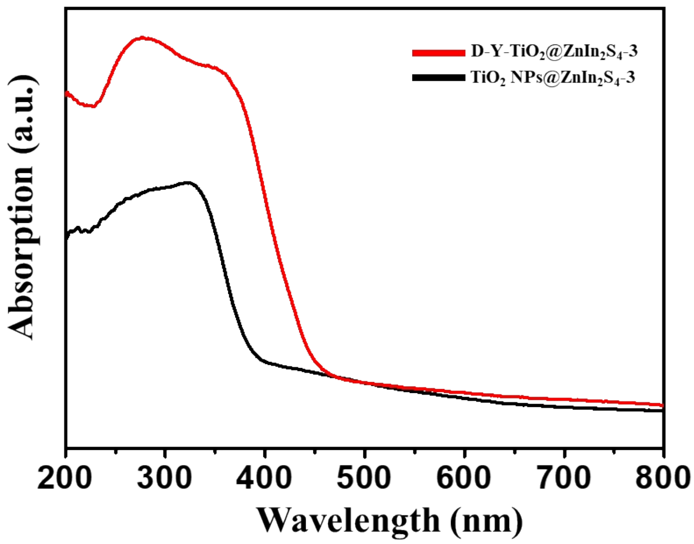

Figure S9. UV-Vis spectra of D-Y-TiO_2@$ZnIn_2S_4$-3 and TiO_2 NPs@$ZnIn_2S_4$-3.

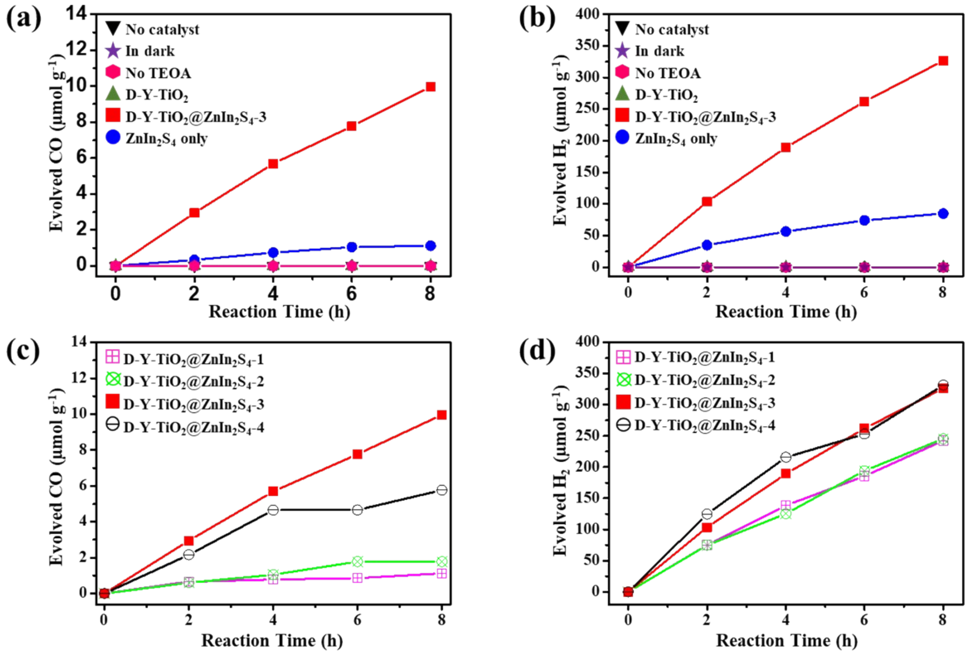

Figure S10. PCR of different samples under LED irradiation (λ=420 nm). Amounts of CO (a, c) and H_2 (b, d) generation of D-Y-TiO_2, $ZnIn_2S_4$ only, and D-Y-TiO_2@$ZnIn_2S_4$ with different loading amount of $ZnIn_2S_4$.

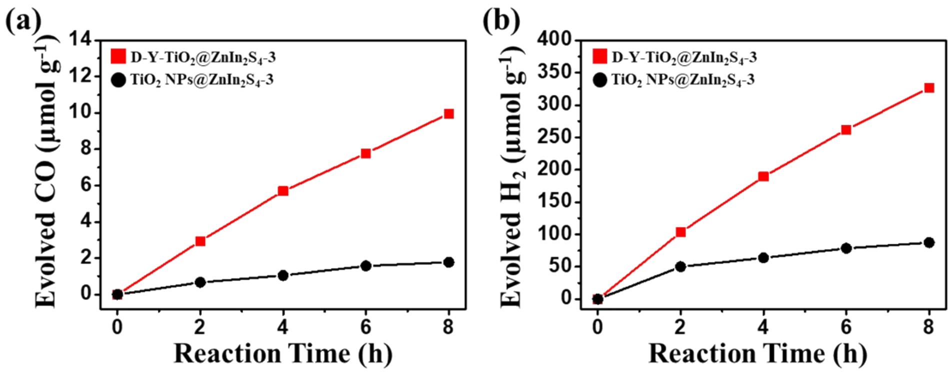

Figure S11. CO_2 photocatalytic reduction of D-Y-TiO_2@$ZnIn_2S_4$-3 and TiO_2 NPs@$ZnIn_2S_4$-3 under LED irradiation (λ=420 nm). (a) Amounts of CO generation; (b) Amounts of H_2 generation.

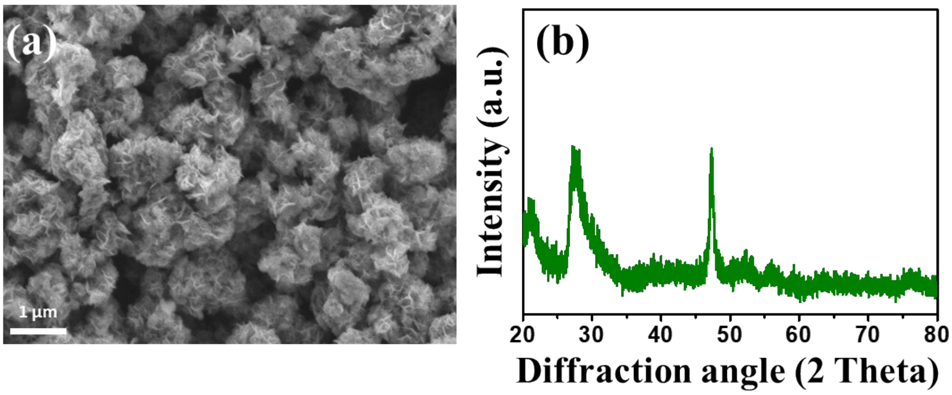

Figure S12. SEM (a) and XRD (b) of D-Y-TiO_2@$ZnIn_2S_4$-3 after the photocatalytic reaction.

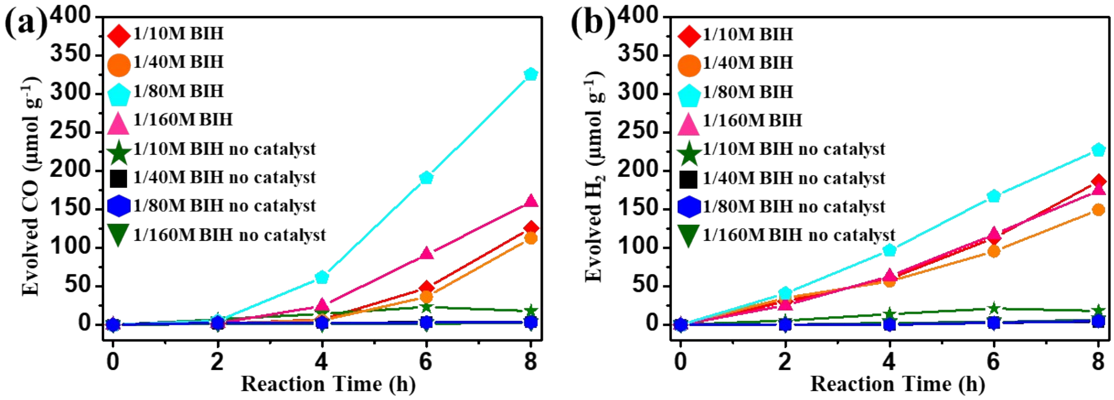

Figure S13. Time courses of CO (a) and H_2 (b) generation of D-Y-TiO_2@$ZnIn_2S_4$ with various sacrificial reagents.

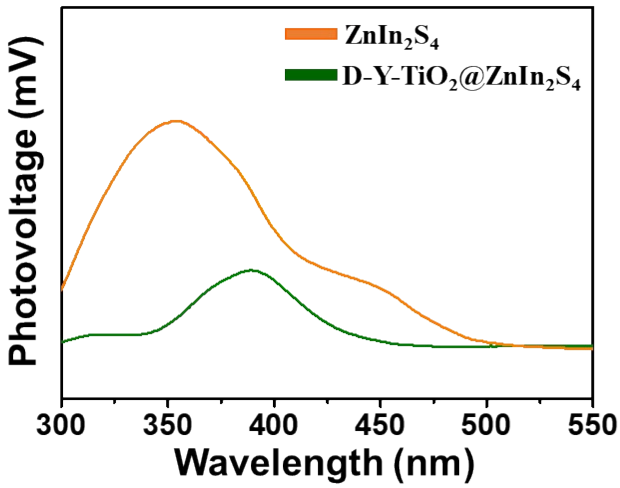

Figure S14. The surface photovoltage of $ZnIn_2S_4$ and D-Y-TiO_2@$ZnIn_2S_4$.

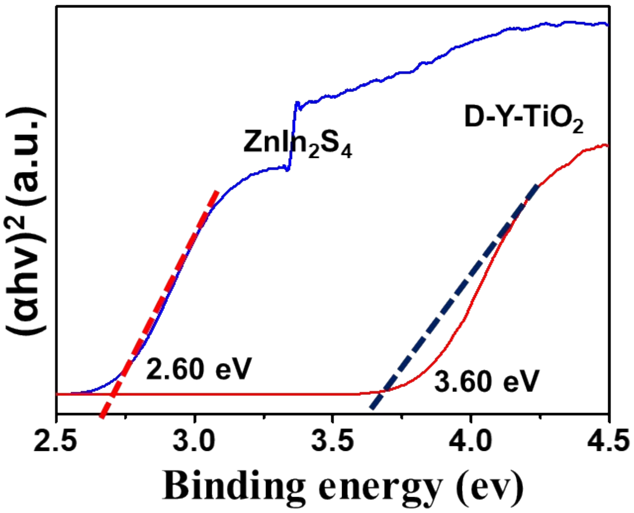

Figure S15. Tauc plots of $(\alpha h\nu)^2$ vs photon energy of $ZnIn_2S_4$ and D-Y-TiO_2 corresponding to the UV-vis spectra in Figure 4b.

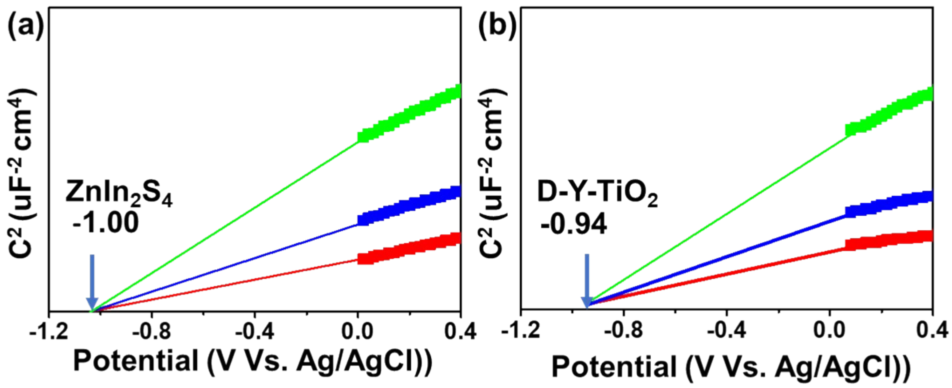

Figure S16. Mott–Schottky plots of $ZnIn_2S_4$ and D-Y-TiO_2.

Table S1. The detailed parameters for PL decay lifetime.

T_{total}=t1*R1+t2*R2 (ns)	t1 (ns)	t1 (ns)	R 1 (%)	R 2 (%)
D-Y-TiO_2@$ZnIn_2S_4$-3 (7.9)	0.57	2.15	85.98	14.02
$ZnIn_2S_4$ (2.0)	0.04	1.99	91.98	8.02

Reference

1. N. Wang, Q.M. Sun, R.S. Bai, X. Li, G.Q. Guo, J.H. Yu, In Situ Confinement of Ultrasmall Pd Clusters within Nanosized Silicalite-1 Zeolite for Highly Efficient Catalysis of Hydrogen Generation, J Am Chem Soc, 138 (2016) 7484-7487.