Supporting Information

Dual S-scheme TiO$_2$@In$_2$Se$_3$@Ag$_3$PO$_4$ heterojunction for efficient photocatalytic CO$_2$ reduction

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Synthesis of hollow TiO$_2$@Ag$_3$PO$_4$

The as prepared TiO$_2$ was then dispersed in 30 mL of absolute ethanol, and 0.1 g of HPC and 0.5 mL of deionized water were added to it and stirred for 30 min. The ethanolic suspension of Ag$_3$PO$_4$ was added to the above solution and the mixed solution was transferred to an autoclave with a Teflon liner and kept at 100°C for 8 h to obtain TiO$_2$@Ag$_3$PO$_4$.

Photocatalytic CO$_2$ reduction test

A 200 mL self-made Pyrex reactor with a silicone rubber septum was used to evaluate the photocatalytic CO$_2$ reduction efficiency of the samples. 10 mL of deionized water and 25 mg of photocatalyst were added to the Pyrex reactor and sonicated for 10 min. The reactor was placed in a vacuum oven so that the photocatalyst was deposited uniformly onto the bottom of the reactor. In the photocatalytic reaction, the air in the Pyrex reactor was flushed with N$_2$ and then CO$_2$ and H$_2$O were generated *in situ* by the reaction of 84 mg of aqueous NaHCO$_3$ and H$_2$SO$_4$ (0.3 mL, 2 M, introduced by syringe). The reactor was irradiated with a 300 W Xe lamp with a 400 nm filter and a 780 nm reflector, in which the outputting light density was approximately 150 mW/cm^2 by calibrating with an NREL-calibrated Si solar cell. The gases generated were detected at intervals by gas chromatography (GC-2014C, Shimadzu, Japan). After the 1 h of reaction, 1 mL of the gas was collected by a syringe and analyzed by gas chromatograph (GC-2014, Shimadzu, Japan). ^{13}C-isotope tracer experiment was carried out to investigate the carbon source. NaH^{13}CO$_3$ was replaced by NaHCO$_3$ for the *in situ* generation of ^{13}CO$_2$ and H$_2$O and the generated products were analysed by gas chromatography-mass spectrometry (6980N network GC system-5975 inert mass selective detector, Agilent Technologies, USA).

The calculation of the apparent quantum efficiency (*AQE*): The *AQE* was performed under a 300 W Xe lamp with certain monochromatic light filter. In this paper, the *AQE* is defined as the ratio of the photocatalytic electron consumption ($N_{electron}$) to the induced photons flux per hour (N_{photon}) within a specialized wavelength range, which can be illustrate as the followed formula:

2

$$AQE(\%) = \frac{N_{electron}}{N_{photon}}$$

The N_{photon} is calculated using the following equation:

$$N_{photon} = \frac{Light\ intensity \times Illumination\ area \times Time}{N_A \times Average\ single\ photon\ energy\ (E_{Photon})}$$

Where the illumination area is controlled to 1 cm², N_A is the Avogadro constant. The E_{Photon} at a certain wavelength is calculated using the following equation:

$$E_{photon} = \frac{hc}{\lambda}$$

Where h is the Plank constant, c indicates speed of light, and λ is the wavelength.

The calculation of the bandgaps (E_g): The bandgaps (E_g) of the sample is calculated by the following equation:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

Where α is the absorbance index, $h\nu$ is the photon energy, n is the nature of the electronic transition (equal to 1/2 in this case) and A is a constant.
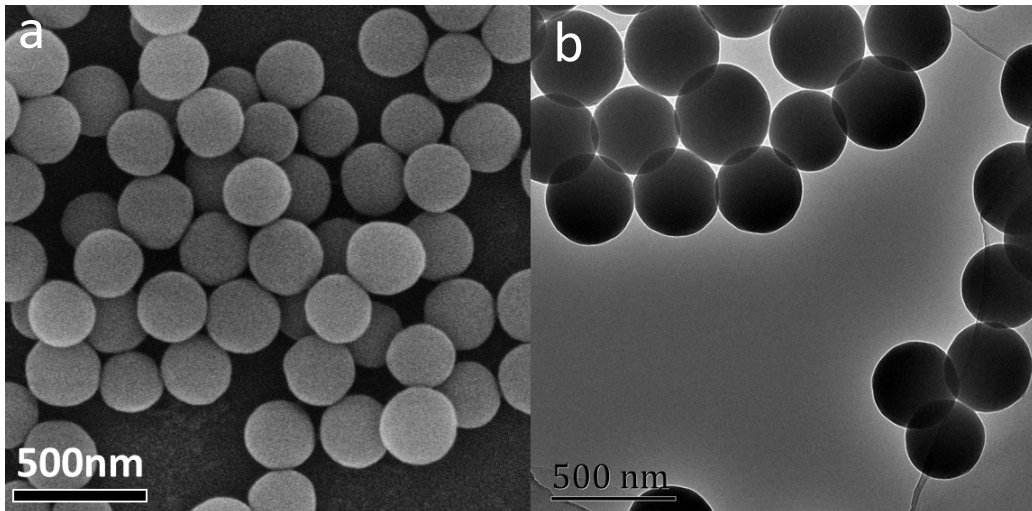
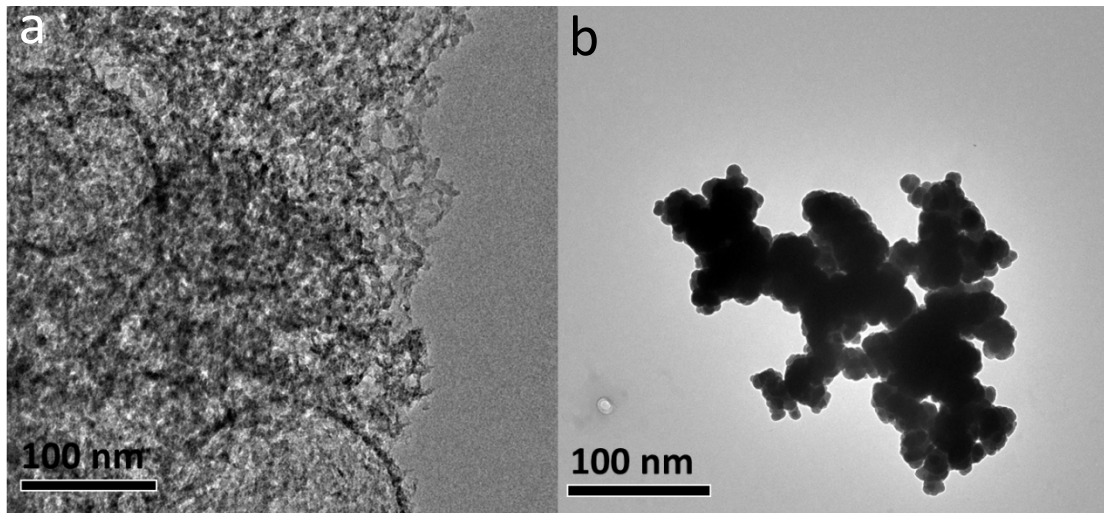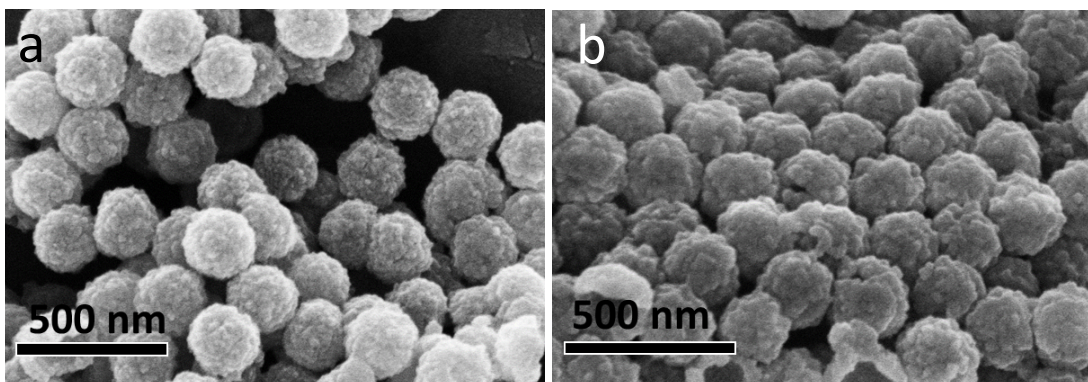Fig. S1. (a) SEM image and (b) TEM image of SiO_2.
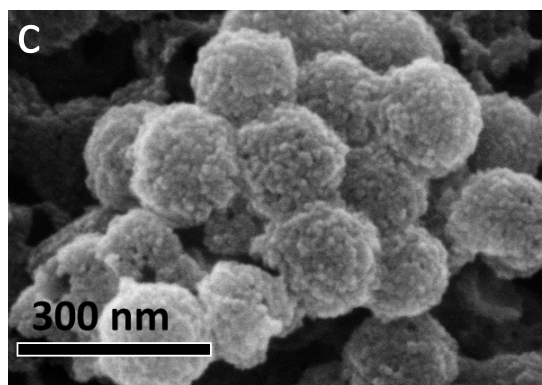

Fig. S2. TEM images of (a) In_2Se_3 and (b) Ag_3PO_4.

Fig. S3. SEM images of (a) hollow TiO_2, (b) $TiO_2@In_2Se_3$ and (c) $TiO_2@In_2Se_3@Ag_3PO_4$.
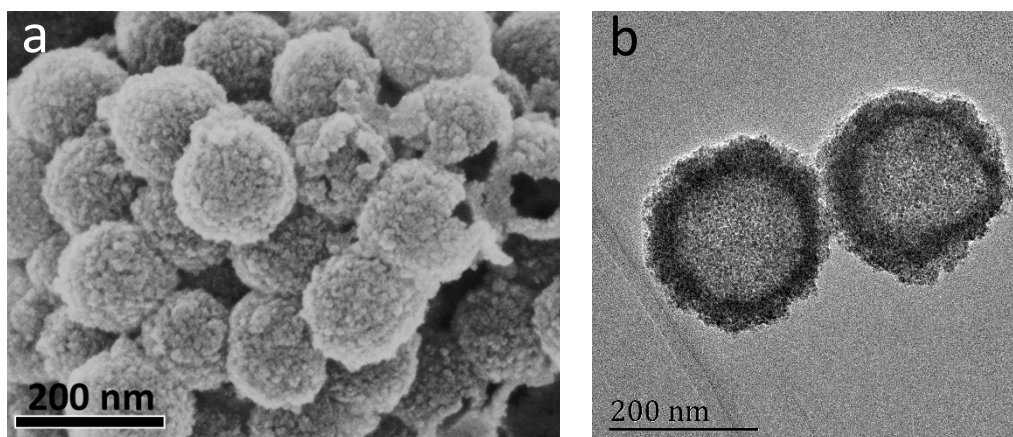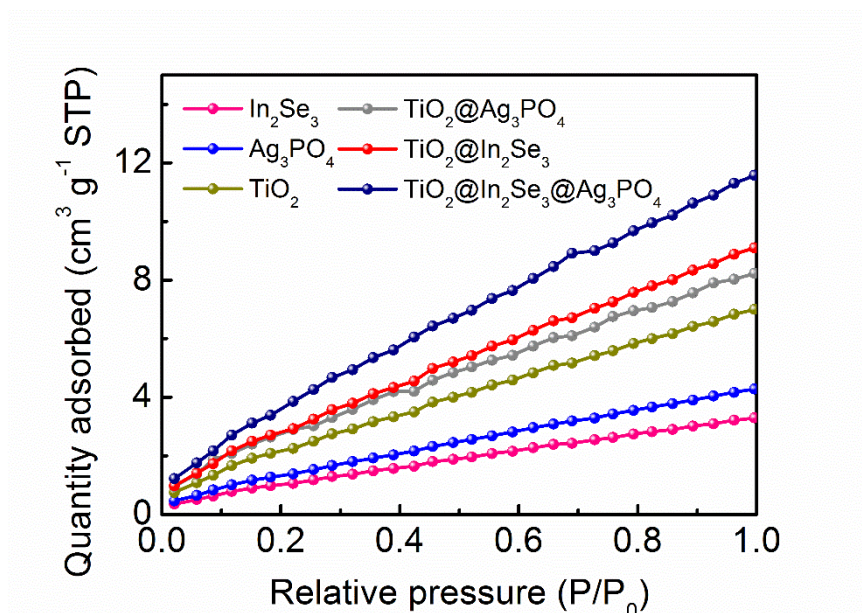

Fig. S4. (a) SEM and (b) TEM images of $TiO_2@Ag_3PO_4$.

Fig. S5. CO_2 adsorption isotherms of TiO_2, In_2Se_3, Ag_3PO_4, $TiO_2@Ag_3PO_4$, $TiO_2@In_2Se_3$ and $TiO_2@In_2Se_3@Ag_3PO_4$.

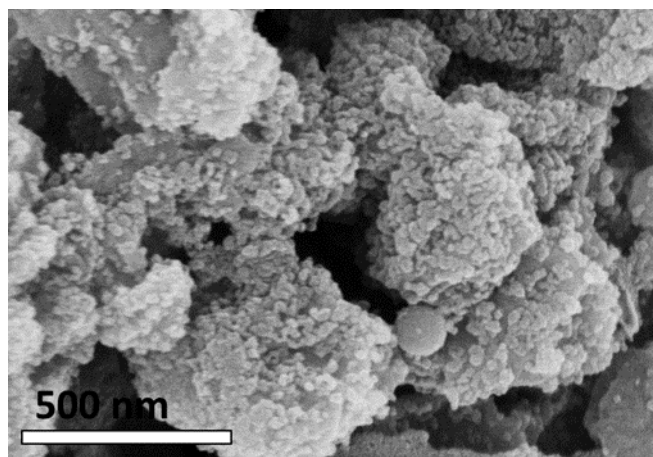Fig. S6. SEM image of bulk-TiO$_2$.

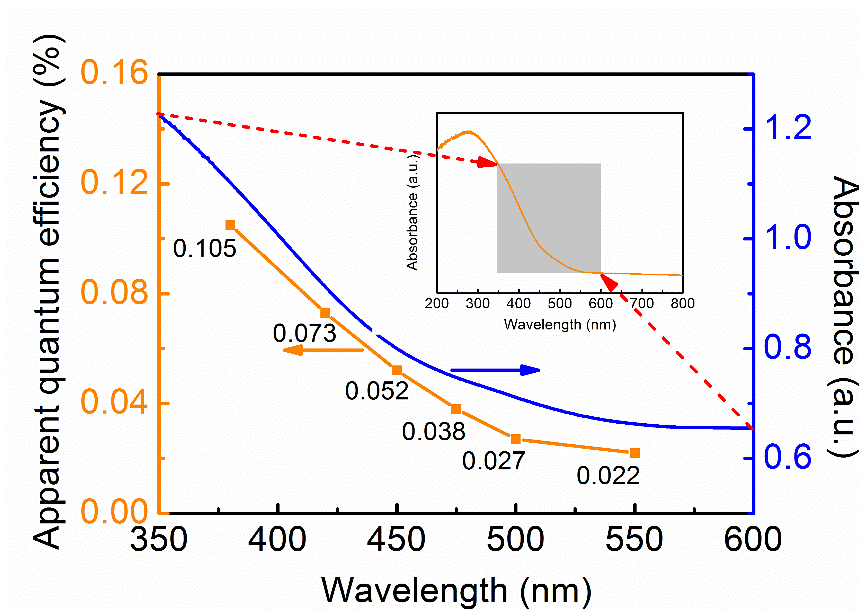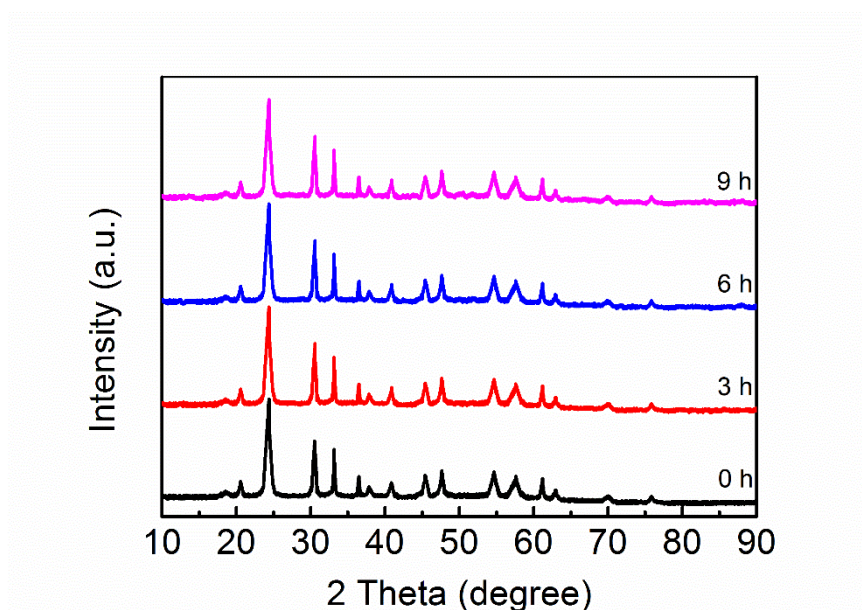Fig. S7. Apparent quantum efficiency (AQE) and UV-vis spectra of TiO$_2$@In$_2$Se$_3$@Ag$_3$PO$_4$.

Fig. S8. XRD spectra of $TiO_2@In_2Se_3@Ag_3PO_4$ after testing for 6 h.
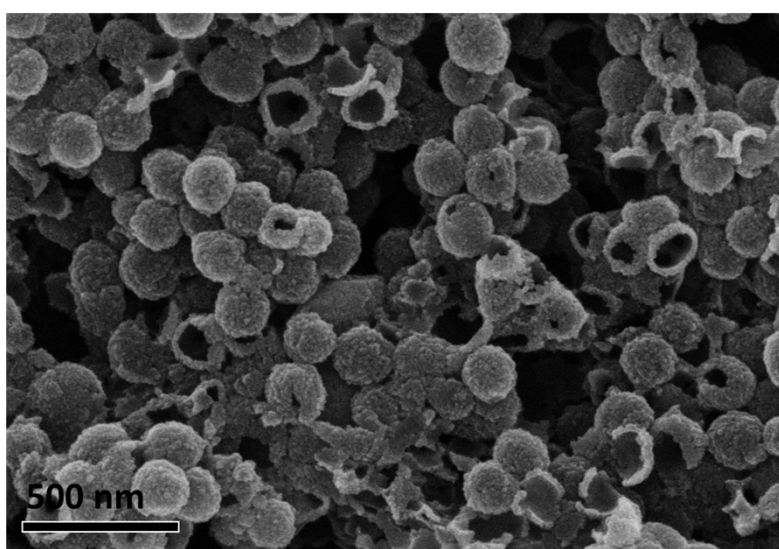

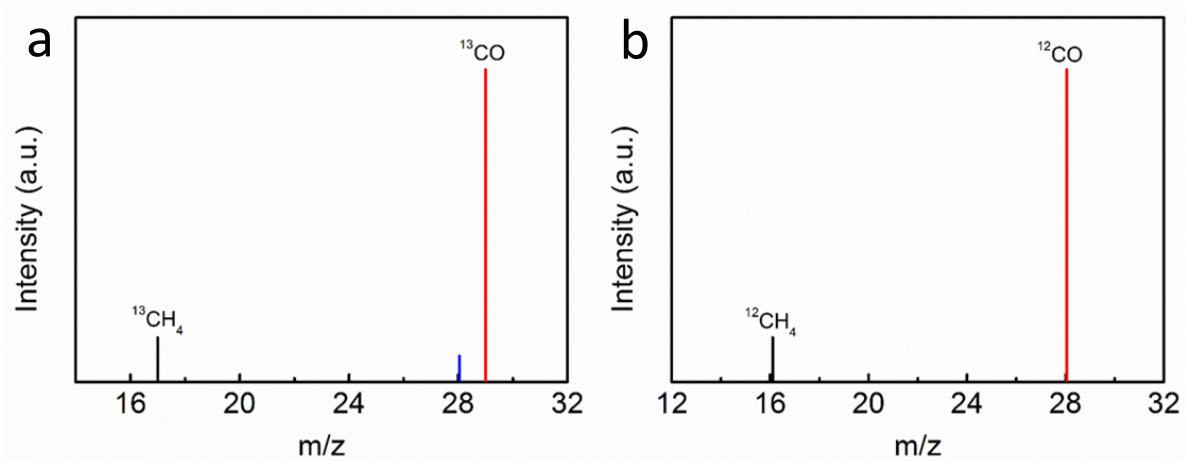Fig. S9. SEM image of $TiO_2@In_2Se_3@Ag_3PO_4$ after testing for 6 h.

Fig. S10. GC-MS spectra of the isotope labeled catalytic products: (a) $^{13}CO_2$ and H_2O (vapor, m/z = 18) atmosphere and (b) CO_2 (m/z = 44) and H_2O atmosphere.
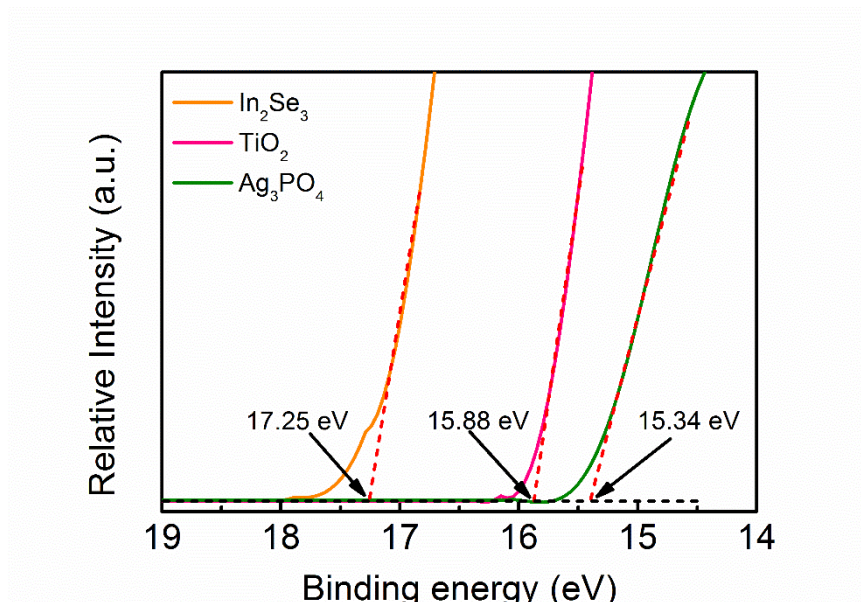

Fig. S11. UPS plots of TiO_2, In_2Se_3 and Ag_3PO_4.

Table S1. Comparison of the measured evolution rates of O_2 with its theoretical ones in terms of the amount of photoreduction products.

	Photoreduction product rate ($\mu mol\ h^{-1}\ g^{-1}$)			Photooxidation product rate ($\mu mol\ h^{-1}\ g^{-1}$)	
	CH_4	CH_3OH	CO	O_2 (Theoretical)	O_2 (Measured)
bulk-TiO_2	0.21	0.51	1.69	2.03	1.92
TiO_2	0.38	0.87	2.59	3.36	2.97
In_2Se_3	1.03	1.97	3.32	6.68	6.04
Ag_3PO_4	0.01	0.02	0.015	0.05	0.01
$TiO_2@Ag_3PO_4$	2.58	3.87	5.03	13.48	12.85
$TiO_2@In_2Se_3$	2.72	4.03	5.52	14.25	13.27
$TiO_2@In_2Se_3@Ag_3PO_4$	3.98	4.32	7.14	18.01	16.92

Theoretical amount of O_2 = (amount of $CH_4\times8$ + amount of $CH_3OH\times6$ + amount of $CO\times2$)/4.

Table S2. The fitted parameters obtained from decay curves of samples in TRPL spectra.

Sample	A_1 (%)	τ_1	A_2 (%)	τ_2	τ_a
TiO_2	57.64	1.47	42.63	5.02	4.01
In_2Se_3	63.21	1.38	36.79	4.79	3.66
Ag_3PO_4	48.73	1.69	51.27	6.23	5.30
$TiO_2@Ag_3PO_4$	40.21	1.13	59.79	3.87	3.42
$TiO_2@In_2Se_3$	36.47	1.03	63.53	3.29	2.94
$TiO_2@In_2Se_3@Ag_3PO_4$	23.18	0.83	76.82	2.57	2.42