Supporting Information

Hierarchical hollow TiO_2/In_2S_3 heterojunction photocatalyst decorated with spatially separated dual co-catalysts for enhanced photocatalytic H_2 evolution

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1. Experimental Section

1.1. Synthesis of TiO_2/In_2S_3 (TO/IS), TiO_2/In_2S_3/PdS (TO/IS/PdS) and TiO_2/In_2S_3/Pt+PdS (TO/IS/Pt+PdS) nanocomposites

The TO/IS sample was obtained under a similar process as the Pt/TO/IS nanocomposite with an initial addition of SiO_2 nanospheres instead of the SiO_2/Pt nanospheres. The TO/IS/PdS nanocomposite were synthesized using a similar photo-deposition process as the Pt/TO/IS/PdS composite, with the addition of TO/IS instead of the Pt/TO/IS. The TO/IS/Pt+PdS nanocomposite were also synthesized using a subsequent photo-deposition process. In detail, 50 mg of the as-fabricated TO/IS powder was ultrasonically dispersed into a 50 mL of 0.1 M Na_2S-Na_2SO_3 aqueous solution. Subsequently, a certain volume of H_2PtCl_6 aqueous solution was added and then the resultant suspension was irradiated under visible light for an hour. Then the obtained product was redispersed into a 50 mL of 0.1 M Na_2S-Na_2SO_3 aqueous solution, a certain volume of $PdCl_2$ aqueous solution was added and then the resultant suspension was irradiated under the visible light for 30 min. The product was collected and washed with deionized water, and then dried at 60 °C to obtain the TO/IS/Pt+PdS nanocomposite.

1.2. Photocatalytic H_2 evolution test

The photocatalytic H_2 evolution activity was measured in a Pyrex top-irradiation quartz reactor. For a typical reaction, 10 mg of the photocatalyst powder was uniformly dispersed into a 50 mL aqueous solution containing 5 mL TEOA as the sacrificial agent. Before the reaction began, the reactant system was evacuated for 30 min to remove the residual air completely. The reaction temperature was maintained at 10 °C with a cooling water system. A 300 W Xe lamp ($\lambda > 420$ nm) was utilized as the light source and the amount of generated gas was monitored by an online TCD gas chromatograph (GC-7920, Ar carrier). In addition, the wavelength-dependent H_2 production tests were measured by using a 300 W Xe lamp equipped with different band-pass filters of 420, 450, 475, 500, 550 and 600 nm.

1.3. Photoelectrochemical measurements

The photoelectronchemical measurements were analyzed using an electrochemical working station (CHI660E Shanghai Chenhua Co.) and carried out in a three-electrode cell system, in which Ag/AgCl electrode was as a reference electrode, Pt foil as a counter electrode and photocatalyst-coated ITO conducting glass as the working electrode. For preparing the working electrodes, 5 mg of photocatalyst powder was mixed with 10 μL of Nafion and 2 mL of ethanol completely, and then the suspension was coated on an ITO conducting glass and dried in air. All the photoelectronchemical measurements were carried out in a 0.1 M Na_2SO_4 aqueous solution as an electrolyte. A 300 W Xe lamp ($\lambda > 420$ nm) was utilized as the light source.

1.4. Characterizations

The crystal phase and structure of the as-prepared samples were examined by powder X-ray diffraction (XRD) on a Siemens D5005 diffractometer (Cu Kα radiation, λ = 1.5418 Å) with an operating voltage and operating current of 40 kV and 40 mA, respectively. Scanning electron microscopy (SEM) images were obtained on Hitachi SU8010. Transmission electron microscopic (TEM), high-resolution transmission electron microscopy (HRTEM) and elemental mapping images were obtained on a JEM-2100F microscope with an accelerating voltage of 200 kV. The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were recorded using an Agilent Cary 7000 spectrophotometer. The Brunauer-EmmettTeller (BET) specific surface areas were obtained on a Micromeritics Tristar 3000 analyzer. Chemical compositions and chemical valence of the samples were analyzed by using X-ray photoelectron spectroscopy (XPS) on a Thermo ESCALAB 250 instrument with a monochromatic source: Al Kα hv = 1486.6 eV.

2. Results

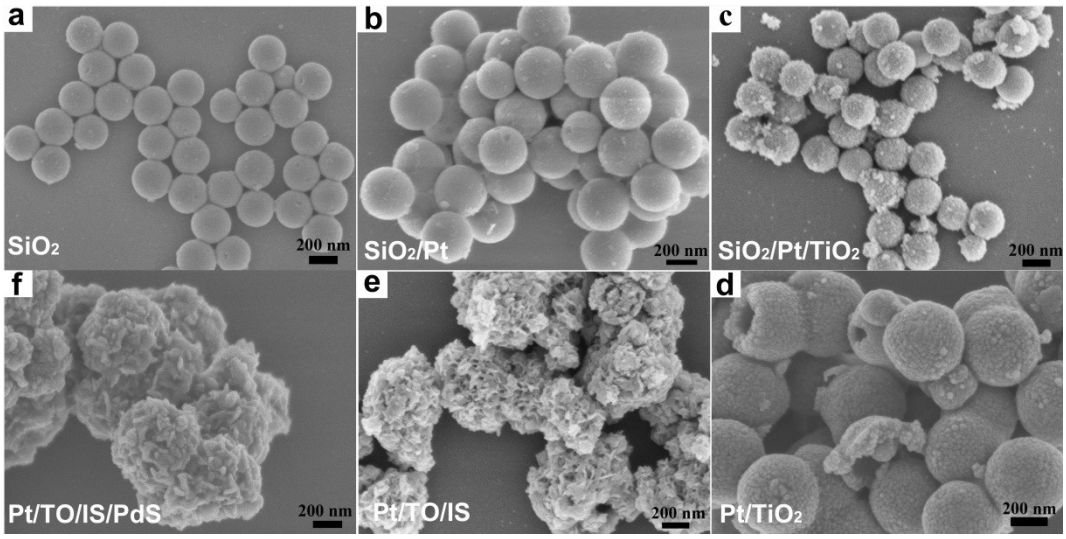

Fig. S1. SEM images of (a) SiO_2, (b) SiO_2/Pt, (c) SiO_2/Pt/TiO_2, (d) Pt/TiO_2, (e) Pt/TO/IS and (f) Pt/TO/IS/PdS nanocomposites.

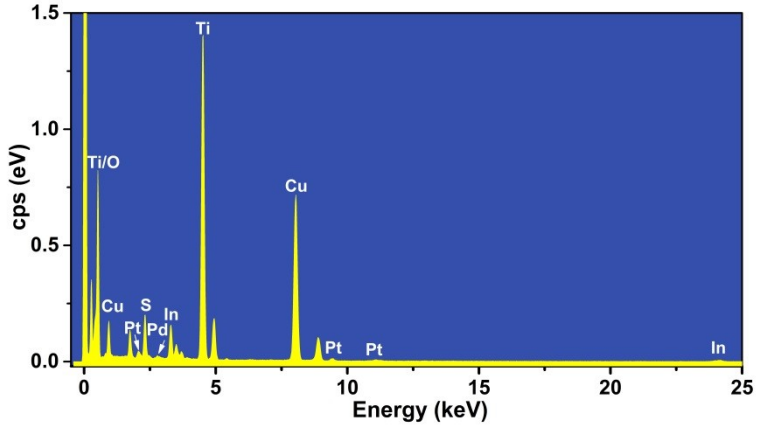

Fig. S2. TEM-EDX image of the as-prepared Pt/TO/IS/PdS nanocomposite.

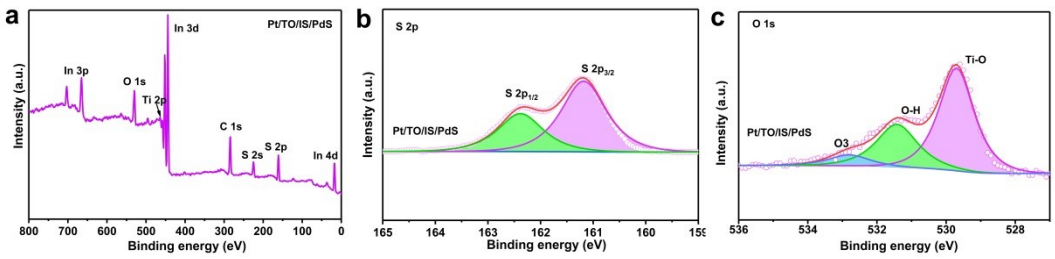

Fig. S3. (a) XPS survey spectrum and high resolution spectra for (b)S 2p and O 1s of Pt/TO/IS/PdS.

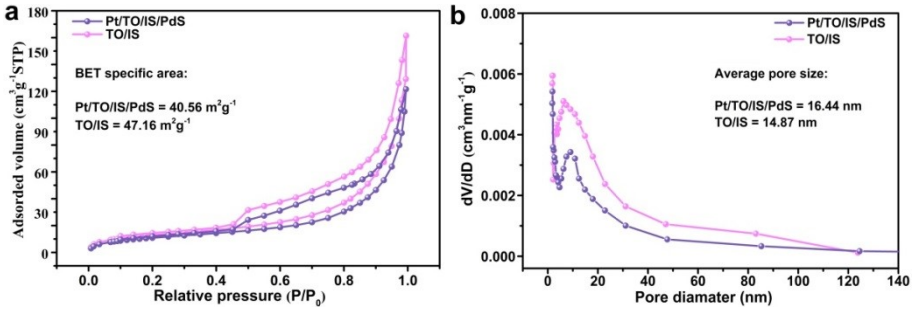

Fig. S4. (a) BET adsorption-desorption isotherms and (b) the pore sizes distribution curves of TO/IS and Pt/TO/IS/PdS.

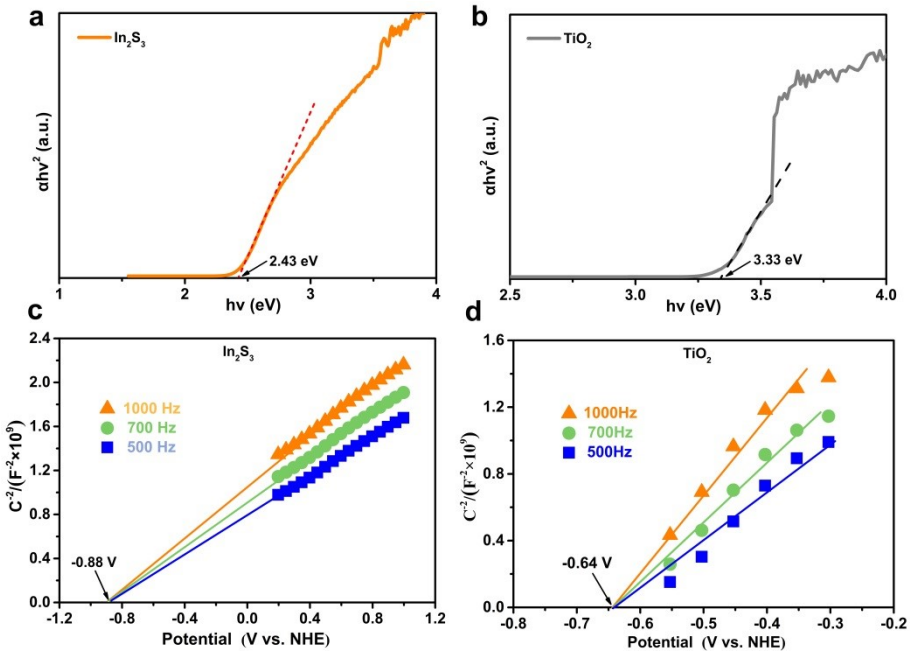

Fig. S5. (a) Tauc plots for pristine In_2S_3 and TiO_2 and (b) Mott-Schottky plots for pristine In_2S_3 and TiO_2.

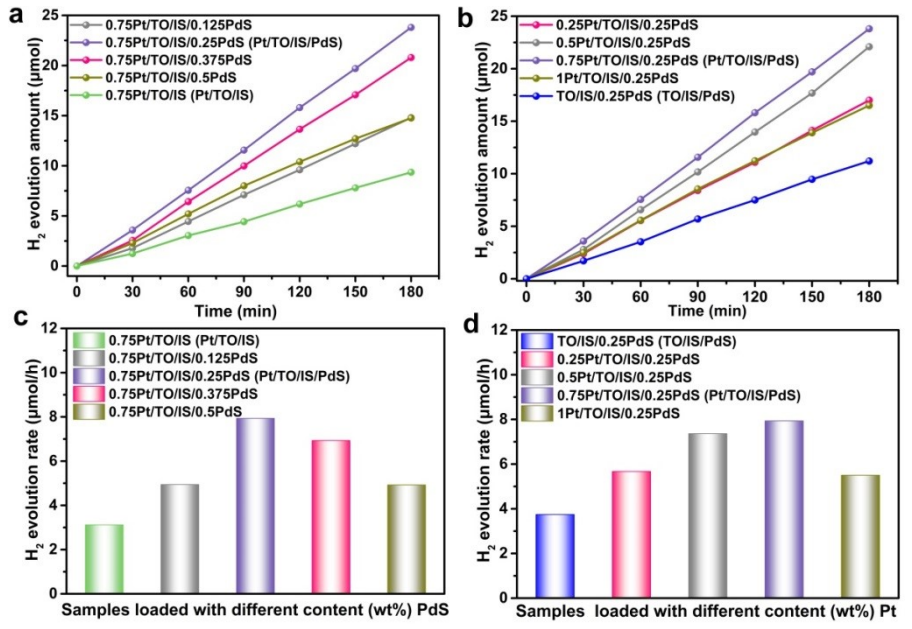

Fig. S6. (a) H_2 evolution amount of Pt/TO/IS loaded with different weight percentage of PdS, (b) H_2 evolution amount of TO/IS/PdS loaded with different weight percent of Pt, (c) H_2 evolution rate of Pt/TO/IS loaded with different weight percent of PdS and (d) H_2 evolution rate of TO/IS/PdS loaded with different weight percent of Pt.

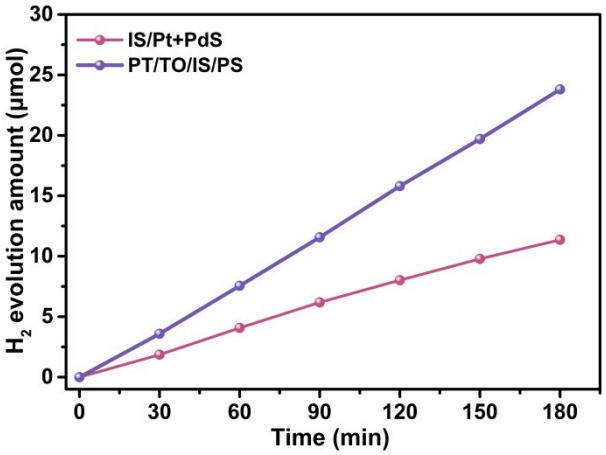

Fig. S7. H_2 evolution rate of IS/Pt+PdS and Pt/TO/IS/PdS samples.

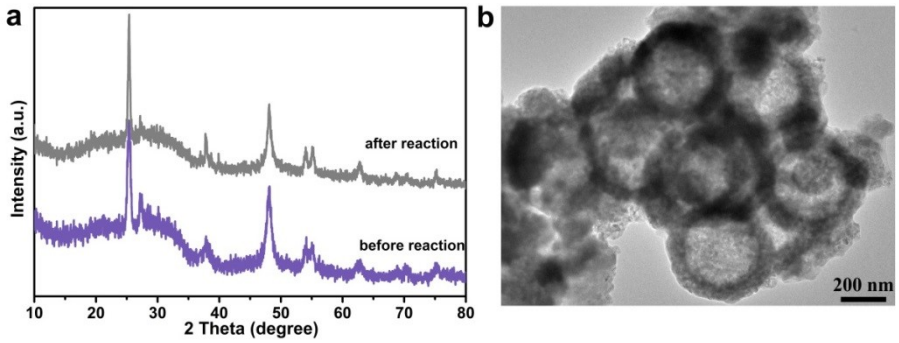

Fig. S8. (a) XRD pattern and (b) TEM image of Pt/TO/IS/PdS after the photocatalytic H_2 evolution cycle reaction.

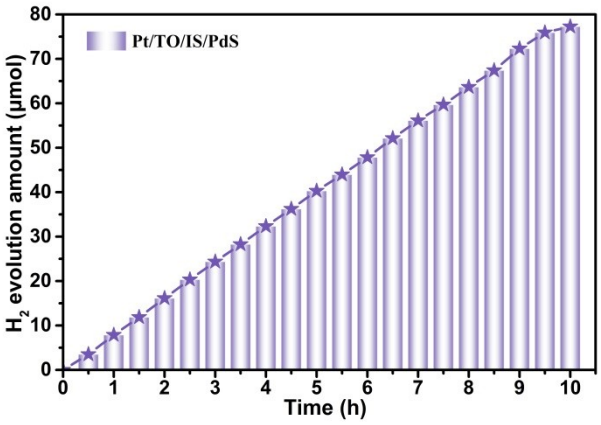

Fig. S9. Long-time H_2 production performance of Pt/TO/IS/PdS.