Electronic Supplementary Material (ESI) for Chemical Communications

Two-step fabrication of porous γ-In_2Se_3 photocatalyst for water splitting

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Experimental Section

The present method of preparing porous γ-In_2Se_3 tetragonums is essentially a two-step process. In a typical synthesis, 1.6 mmol $InCl_3$ was dissolved in 30 ml distilled water. Then, 2.4mmol Se powder was added into the solution under continuous stirring until well dispersed and 30 ml ethylenediamine was added. The mixture was transferred and sealed into an 80 mL Teflon-lined stainless steel autoclave, heated at 180 ℃ in an electric oven for 24 h. The resulting products were centrifuged and washed with distilled water and absolute ethyl alcohol. After drying, all samples were calcined in N_2 at 500 ℃ for 2 h. The In_2Se_3 NPs are obtained by the same method by varying the volume of H_2O and ethylenediamine to be 9∶1. Detailed preparation conditions are summarized in Table S1.

Table S1. Preparation conditions of In_2Se_3 samples.

Amount of starting materials		solvent component	
$InCl_3$[a] / mmol	Se powder[b] / mmol	H_2O /mL	ethylenediamine[c] /mL
1.6	2.4	0	60
1.6	2.4	18	42
1.6	2.4	30	30
1.6	2.4	42	18
1.6	2.4	54	6

[a] Purchased from Sinopharm Chemical Reagent Beijing Co., Ltd, Purity In≥39.5%.

[b,c] Purchased from Wei Si Chemical Company, Beijing, Purity 99.95%.

Commercial In_2Se_3 was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd, Purity $In_2Se_3 \geq 99.99\%$.

Characterization

The composition and phase purity of all samples were analyzed by a Shimadzu XRD-6000 X-ray diffractometer using Cu-Kα (λ = 1.54178 Å) irradiation with a scan rate of 6° per minute, operated at 40 kV voltage and 50 mA current. The morphologies and EDS element mapping images of the samples were characterized by a field-emission scanning electron microscope (JEOL S-4800). Transmission electron microscope (TEM) and SAED images were taken on a H-8100 TEM operating at 200 kV accelerating voltage. FT-IR spectra were recorded on a Nicolet 170SXFT-IR spectrometer (400-4000 cm^{-1}). TGA curves were performed on a Shimadzu DTG-60AH thermal analyzer with a heating rate of 10°C /min under nitrogen atmosphere. UV-vis diffuse reflectance spectra were achieved using Shimadzu UV-vis spectrophotometer (UV-3600). X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250 spectrometer (Perkin-Elmer) to characterize the surface composition. The Brunauer–Emmett–Teller (BET) surface area was measured on a Belsorp-max surface area detecting instrument by N_2 physisorption at 77 K. The impendence spectra were recorded on a CHI-660D potentiostat.

Photocatalytic reactions

The water-splitting experiments were performed with 0.05 g powdered photocatalyst suspended in 100 ml of pure water or triethanolamine aqueous solution (10ml TEA and 90 ml H_2O） in a closed circulation system using an xenon arc lamp (300 W, CEL-HXF300, Jinyuan) with a UV light cutoff filter (420-760 nm). A certain

amount of $H_2PtCl_6 \cdot 6H_2O$ aqueous solution was dripped into the system to load Pt onto the surface of the photocatalyst by a photochemical reduction deposition method. The concentration of H_2 was analyzed by gas chromatography (N2000, Zhejiang University) equipped with a thermal conductivity detector (N_2 carrier), which was connected to the gas circulating line.

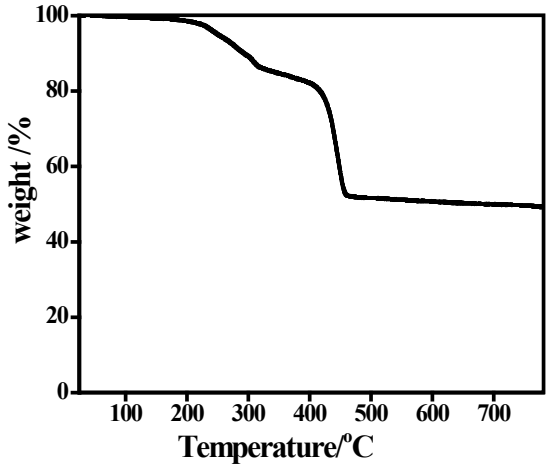

Fig. S1 TGA of the precursor.

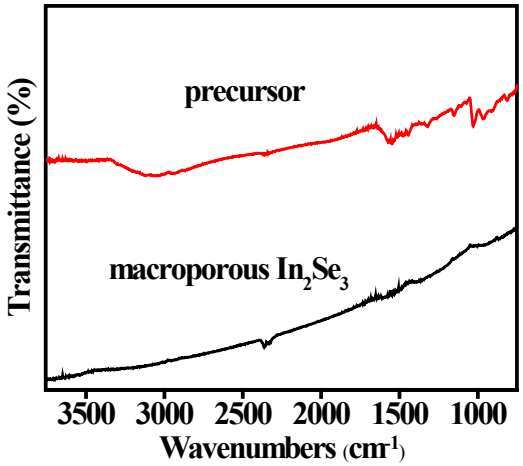

Fig. S2 IR spectra of the precursor and porous In_2Se_3 (after calcination).

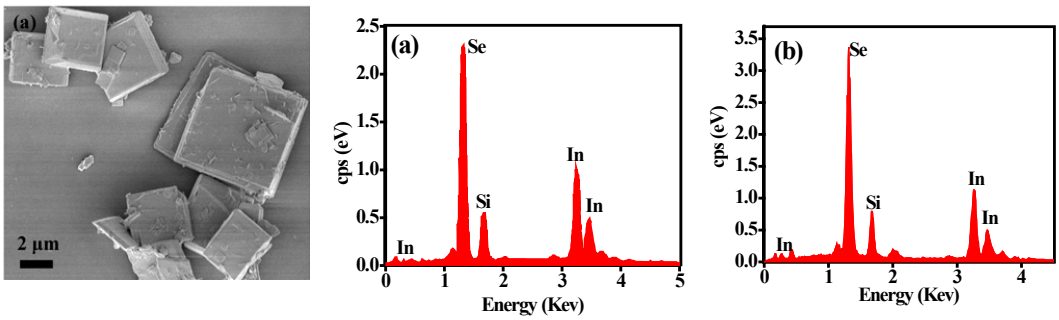

Fig. S3 (a) SEM images of the precursor; EDS spectra for (b) the precursor and (c) porous In_2Se_3 tetragonums.

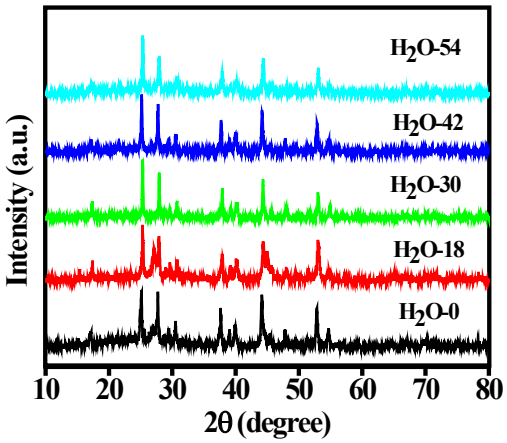

Fig. S4 XRD images of the In_2Se_3 samples obtained by varying the volume of H_2O and ethanediamine, calcined in N_2 at 500 ^oC for 2 h.

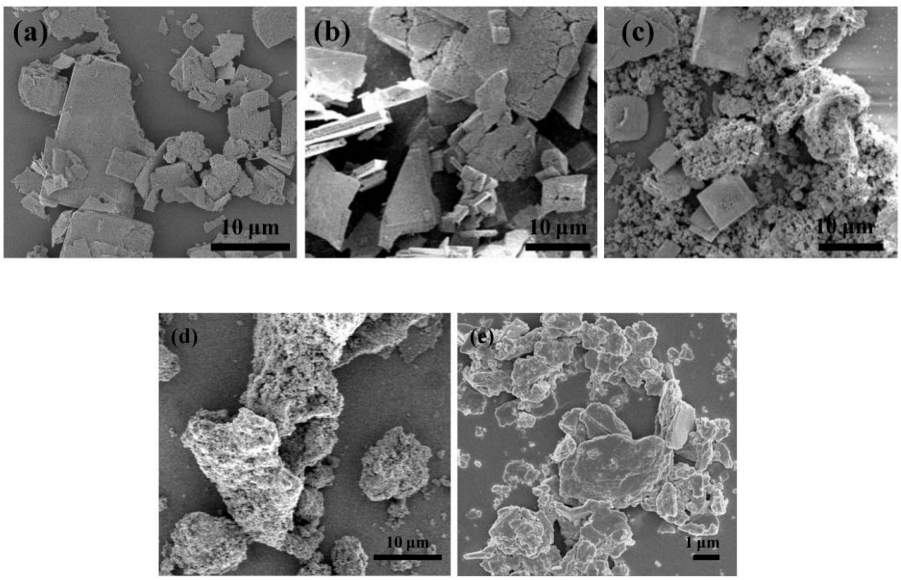

Fig. S5 SEM images of In_2Se_3 samples obtained by varying the volume of H_2O and ethanediamine. (a) 0 mL H_2O, (b) 18 mL H_2O, (c) 42 mL H_2O, (d) 54 mL H_2O. (e) Commercial In_2Se_3.

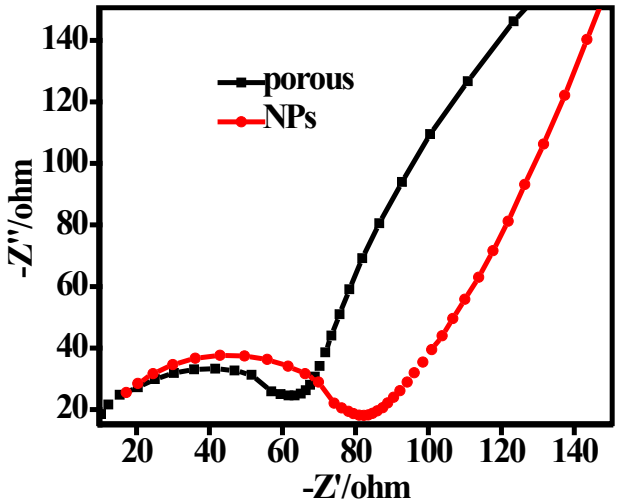

Fig. S6 Electrochemical impedance spectroscopies (EIS) of the as-prepared porous In_2Se_3 and In_2Se_3 NPs under UV light irradiation.

Table S2 The average gas evolution rates under visible light irradiation.

Catalyst	Amount of Pt loaded/wt %	Sacrificial reagent	H_2 production activity /μmol h^{-1}
Porous	0	none	0.10
	2	TEA	1.52
NPs	0	none	0.06
	2	TEA	0.27
Commercial	0	none	0.05
	2	TEA	0.25

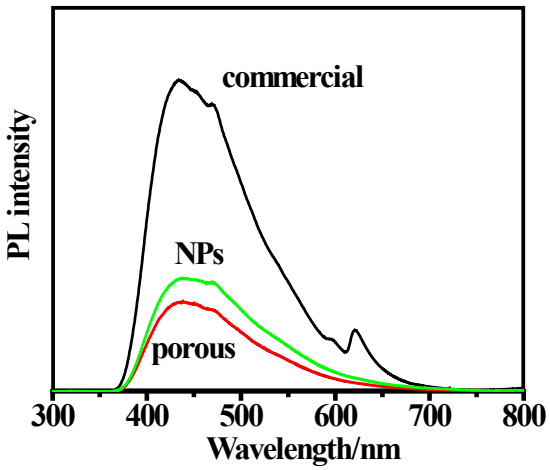

Fig. S7 PL spectra of the as-prepared and commercial In_2Se_3.

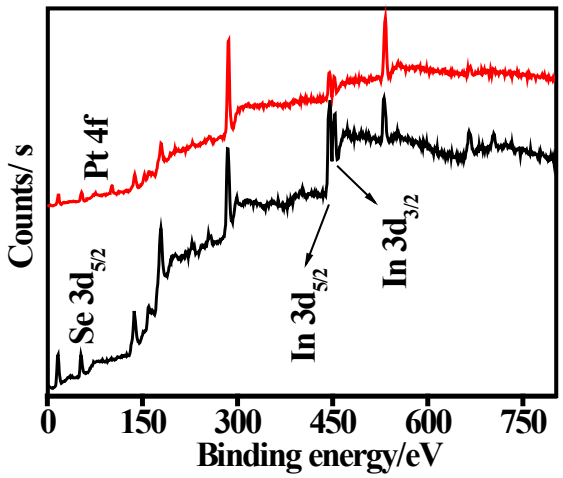

Fig. S8 XPS of the fresh and used porous γ-In_2Se_3 tetragonums recovered after 16h (upper) under UV light irradiation.

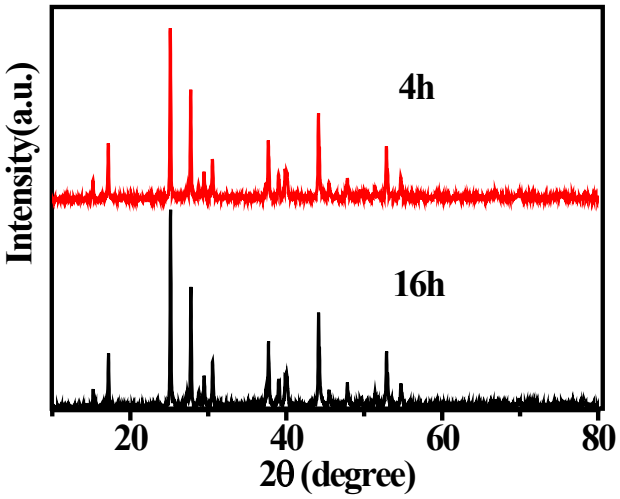

Fig. S9 XRD patterns of the porous In_2Se_3 tetragonums after photoreaction for 4 and 16 h.

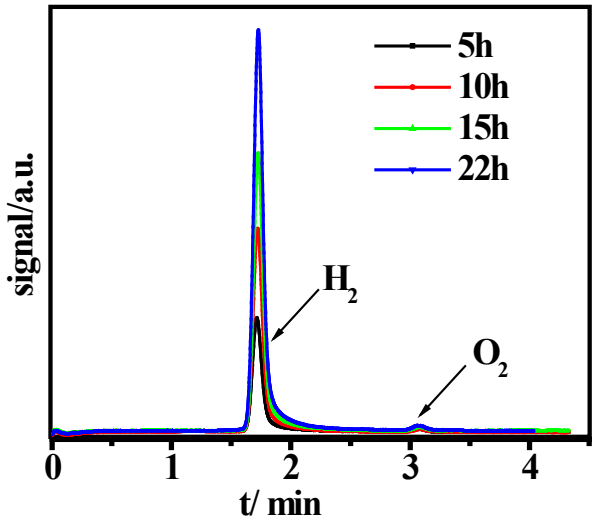

Fig. S10 GC traces of the headspace over continued photodriven reactions of the porous γ-In_2Se_3 tetragonums.

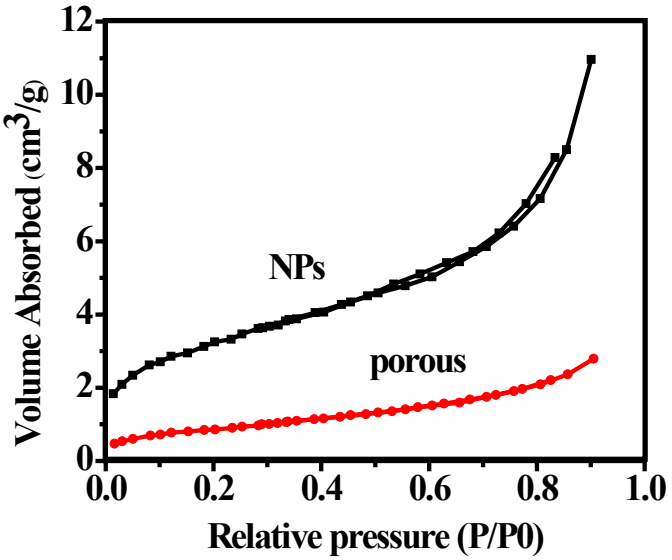

Fig. S11 Nitrogen adsorption–desorption isotherms of the In_2Se_3 samples.