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Facile fabrication of InSe nanosheets: towards efficient visible-light-driven H_2 production by coupling with P25

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Experimental Section

Chemicals and reactants

Indium chloride ($InCl_3$, 99.9% metals basis) was purchased from Aladdin (Shanghai) Chemistry Co., Ltd. Titanium dioxide nanoparticles (P25) were purchased from Alfa Aesar (Tianjin) Chemical Co., Ltd. Selenium dioxide (SeO_2, AR), ethylenediamine, sodium dodecylbenzyl sulfate (SDBS, AR), cetyltrimethylammonium bromide (CTAB, AR), sodium dodecyl sulfate (SDS) and polyvinylpyrrolidone (PVP, AR) were purchased from Wei Si Chemical Company (Beijing). All the chemical reagents were of analytical grade and used without further purification.

Synthesis of InSe nanosheets

In a typical synthesis, 0.1106 g $InCl_3$ was dissolved in 30 mL aqueous solution of SDBS (3 mmol) under stirring for 30 min. Then, 0.0832 g SeO_2 powder was added into the solution until well dissolved under continuous stirring for 30 min. Subsequently, 30 mL ethylenediamine was added into the solution. After stirring for 30 min, the solution was transferred into a 80 mL Teflon-lined autoclave which was then sealed and maintained at 150 ^{o}C for 48 h. After the autoclave was cooled to room temperature naturally, yellow solid product was collected, centrifuged and washed with distilled water and absolute alcohol five times, and dried under vacuum at 60 °C for 24 h to obtain a precursor. Next, the precursor powder was annealed at 250 °C for 2 h under N_2 gas in a tube furnace. The InSe nanosheets were finally obtained after the tube furnace was cooled to room temperature naturally.

As a reference, InSe product was also synthesized without SDBS while other conditions were kept constant. For comparison, three other surfactants (CTAB, SDS and PVP) were also employed in the experiments to prepare InSe.

Synthesis of InSe-TiO_2 heterostructure

The prepare procedure of InSe-TiO_2 heterostructure was the same as that of above InSe nanosheets, and only P25 was added during the hydrothermal step. Different amounts (0.0050, 0.0100, 0.0150, 0.0200, 0.0250, 0.0300, 0.0350, 0.0600, 0.1000, 0.3000 and 0.5000 g) of P25 were used and thus resultant samples were denoted as InSe-TiO_2(0.005), InSe-TiO_2(0.01), InSe-TiO_2(0.015), InSe-TiO_2(0.02), InSe-TiO_2 (0.025), InSe-TiO_2(0.03), InSe-TiO_2(0.035), InSe-TiO_2(0.06), InSe-TiO_2(0.1), InSe-TiO_2 (0.3) and InSe-TiO_2(0.5), respectively.

For comparison, 0.0150 g commercial anatase TiO_2 was employed in the experiment to prepare InSe-TiO_2(A).

A mechanically mixed sample was obtained by grinding the InSe nanosheets and P25 together with the molar ratio of 27:10, which was named as InSe-TiO_2 mixture.

Characterization

The crystal structure and phase purity of the resultant samples were analyzed by X-ray powder diffraction (XRD) recorded on a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation. The structural information for samples was measured by Fourier transform infrared spectrophotometer (FTIR, Thermo IS5) in the range of 4000-400 cm^{-1} using the standard KBr disk method. The morphology and microstructure of the samples were observed by scanning electron microscopy (JEOL S-4800) and transmission electron microscopy (JEOL JEM-2010). The surface composition was analyzed by X-ray photoelectron spectroscopy (XPS) on ESCALAB 250 electron spectrometer. UV-Vis absorption spectra were performed on a UV-vis spectrophotometer (TU-1901) using $BaSO_4$ as the reference. The spectrum of the visible light from Xe lamp was detected on an optical spectrum analyzer Avaspec-NIR256 (avantes, Netherlands). The specific surface area of the resultant was obtained by the Brunauer-Emmett-Teller (BET) method on an adsorption apparatus (Belsorp-max, Netherlands). The relative hydrophobicity/hydrophilicity of material surface was measured by contact angle using a Dataphysics OCA20. The photocurrent performance was performed on a CHI660D electrochemical workstation, where Pt electrode and saturated Ag/AgCl electrode were employed as counter and reference electrode, respectively. A 300-W Xe lamp (CEL-HXF300, Jinyuan, λ= 420-760 nm) was used as light source.

Photocatalytic reactions

The photocatalytic properties of the samples were evaluated by measuring the hydrogen evolution from 50 mL 0.05 M ascorbic acid (AA) aqueous solution under visible light irradiation at 5 °C. The hydrogen production experiment was carried out in a quartz reactor cooled by running water. A xenon arc lamp (300 W, CEL-HXF300, Jinyuan) with a UV light cutoff filter (λ = 420-760 nm) was used as the visible light source to offer photons, where the power density of visible light radiated on the photocatalyst was measured to be 1.5 mW/cm^2. Pt was loaded onto the surface of the photocatalyst by photochemical reduction by adding 1 mL $H_2PtCl_6 \cdot 6H_2O$ (1 mg / mL Pt) aqueous solution into the system. The photocatalytic hydrogen evolution was measured with a Zhejiang University N2000 gas chromatography system by using N_2 as carrier.

The apparent quantum efficiency (QE) was measured under the same photocatalytic reaction condition except that 450 nm xenon arc lamp was used as light source. The QE was calculated according to the following equation:

$$\begin{aligned}\text{QE} &= \text{number of reacted electrons/number of incident photons}\\ &= \text{number of evolved } H_2 \text{ molecules} \times 2/\text{ number of incident photons}\end{aligned}$$

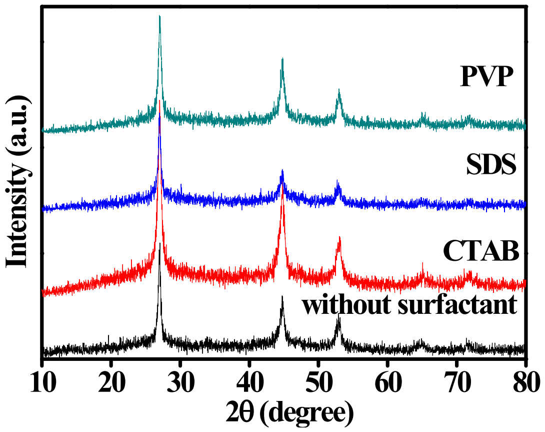

Fig. S1 XRD patterns of InSe samples obtained by using various surfactants.

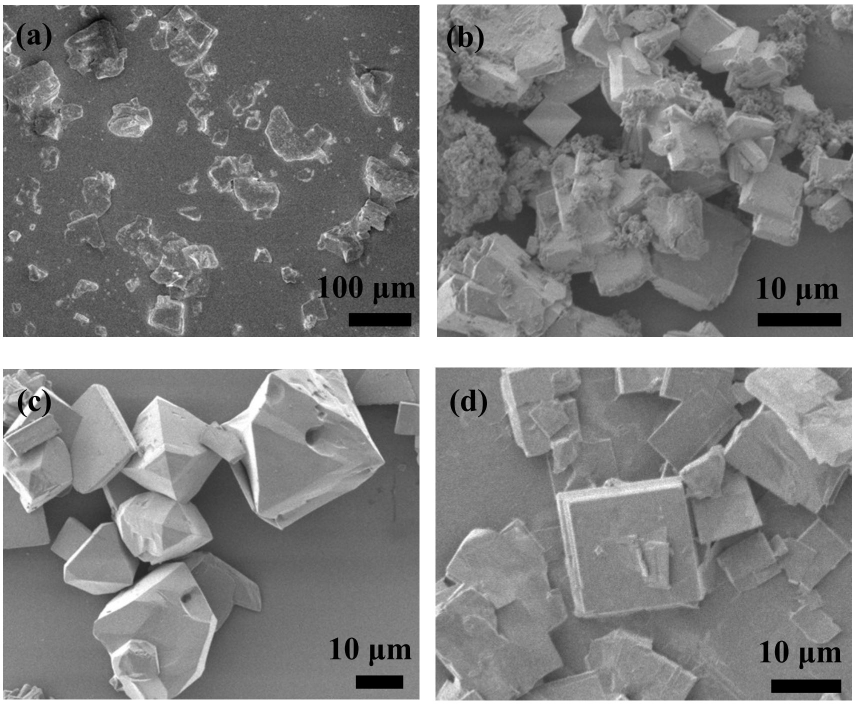

Fig. S2 SEM images of InSe samples obtained by using various surfactants, (a) without surfactant, (b) CTAB, (c) SDS, and (d) PVP.

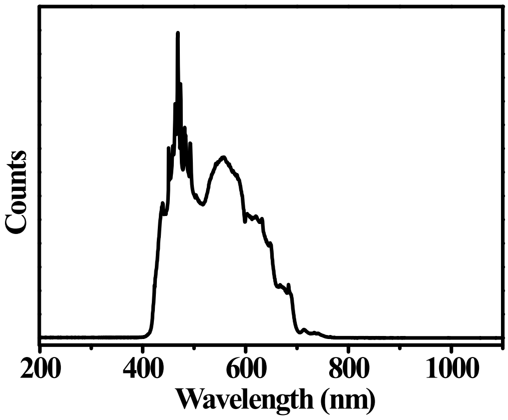

Fig. S3 Emission spectrum of Xe-lamp used in the photocatalytic reaction.

Table S1. Some visible-light-driven photocatalysts for H_2 production under visible light irradiation

Sample	Aqueous reaction solution	Cocatalyst	H_2 production activity / ($\mu mol \cdot g^{-1} \cdot h^{-1}$)
InSe-TiO_2 (0.015)	ascorbic acid	Pt	1100
InSe nanosheets	ascorbic acid	Pt	276
TiO_2:Sb/Cr[1]	methanol	Pt	0.12
CdS[2]	$Na_2S + Na_2SO_3$	Pt-PdS	29233
CdSe[3]	$Na_2S + Na_2SO_3$	none	436
ZnS:C[4]	$Na_2S + Na_2SO_3$	Pt	90
Ta_3N_5[5]	methanol	Pt	12
graphitic C_3N_4[6]	triethanolamine	Pt	107

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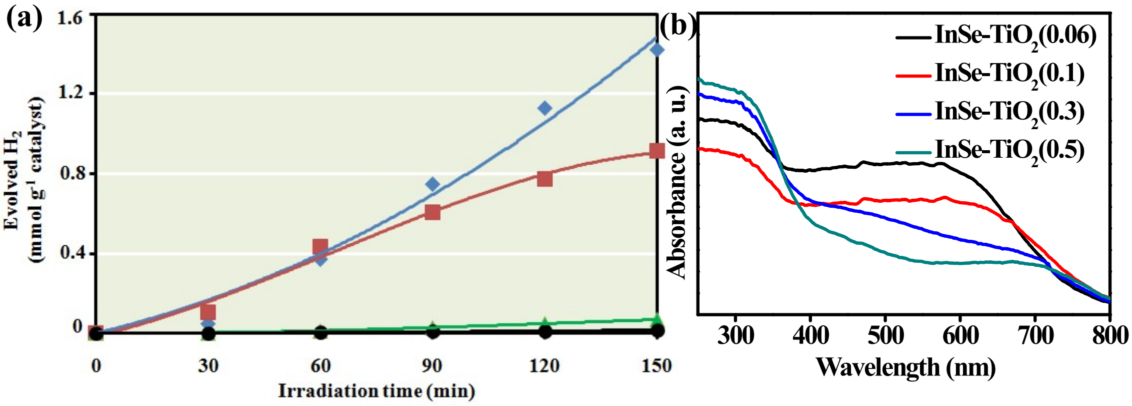

Fig. S4 (a) Photocatalytic hydrogen production rates for —InSe-TiO_2(0.06), —InSe-TiO_2(0.1), —InSe-TiO_2(0.3) and —InSe-TiO_2(0.5), photocatalyst: 0.04 g, cocatalyst: 2.5 % Pt, solvent: 50 mL 0.05M ascorbic acid aqueous solution, Light: Xe-lamp with a 420 nm cut off filter; (b) UV-Vis absorption spectra of InSe-TiO_2(0.06), InSe-TiO_2 (0.1), InSe-TiO_2(0.3) and InSe-TiO_2(0.5).

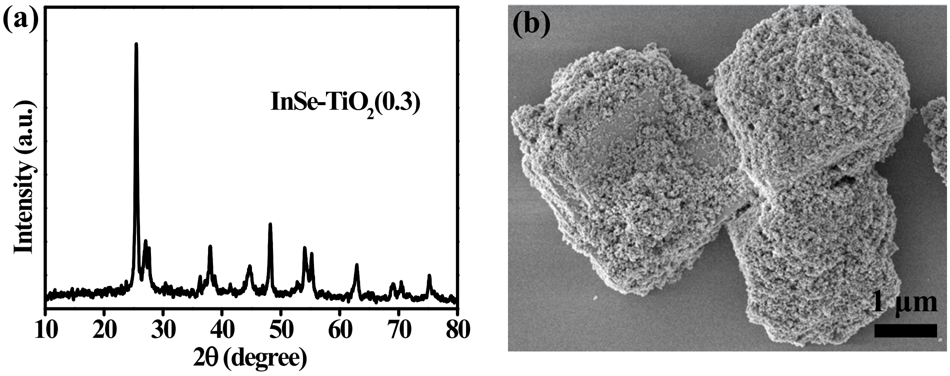

Fig. S5 (a) XRD pattern and (b) SEM image of InSe-TiO_2(0.3).

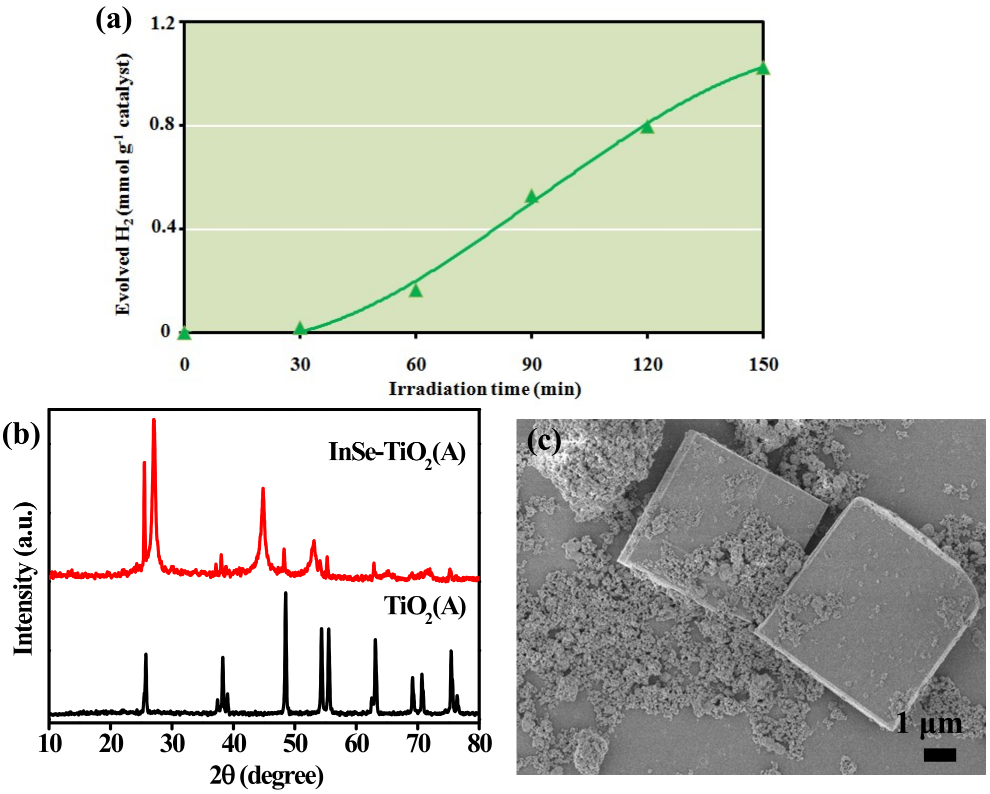

Fig. S6 (a) Photocatalytic hydrogen production rate for InSe-TiO_2(A), photocatalyst: 0.04 g, cocatalyst: 2.5 % Pt, solvent: 50 mL 0.05M ascorbic acid aqueous solution, Light: Xe-lamp with a 420 nm cut off filter; (b) XRD images of commercial anatase TiO_2 and InSe-TiO_2(A) obtained by using anatase TiO_2 as TiO_2 source; (c) SEM image of InSe-TiO_2(A).

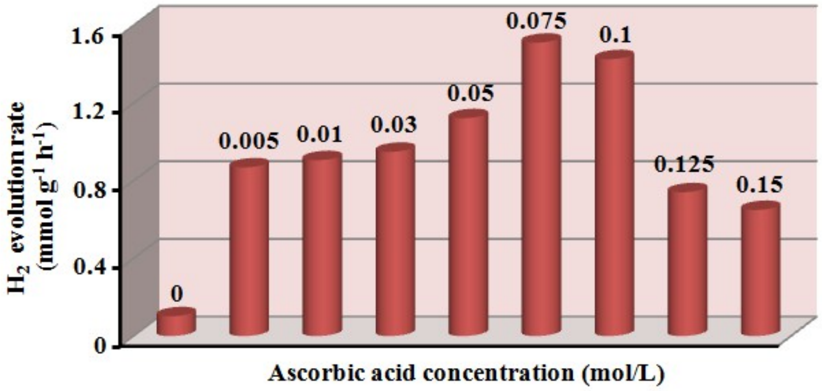

Fig. S7 Dependence of hydrogen production rate of InSe-TiO_2(0.015) on ascorbic acid concentration under visible light. Photocatalyst: 0.04 g, cocatalyst: 2.5 % Pt, solvent: 50 mL ascorbic acid aqueous solution, Light: Xe-lamp with a 420 nm cut off filter.

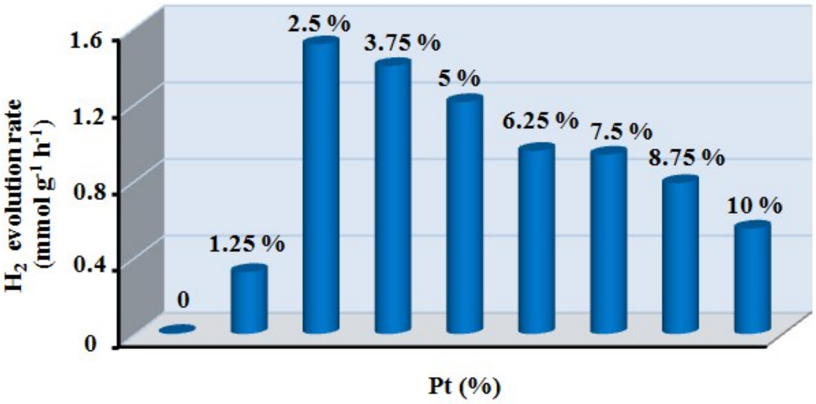

Fig. S8 Dependence of hydrogen production rate of InSe-TiO_2(0.015) on Pt concentration under visible light irradiation. Photocatalyst: 0.04 g, cocatalyst: Pt, solvent: 50 mL 0.075 mol/L ascorbic acid aqueous solution, Light: Xe-lamp with a 420 nm cut off filter.