Electronic Supplementary Information (ESI)

Grain boundary engineering in organic-inorganic hybrid semiconductor $ZnS(en)_{0.5}$ for visible-light photocatalytic hydrogen production

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Experimental Section

Materials :

Zinc acetate dihydrate ($Zn(CH_3COO)_2•2H_2O$) Thiourea (CH_4N_2S) and ethylenediamine ($H_2NCH_2CH_2NH_2$) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All materials were analytical grade and used without any purification process. Deionized (DI) water used in the synthesis came from local sources.

Synthesis of D-$ZnS(en)_{0.5}$ and $ZnS(en)_{0.5}$:

D-$ZnS(en)_{0.5}$ NSs were synthesized by a solvothermal procedure. Typically, 2.6 mmol Zinc acetate dihydrate and 7.8 mmol Thiourea were dispersed into 20 mL DI water. Subsequently, the obtained solution was poured into 60 mL ethylenediamine under the ceaseless stirring until formation of an homogenous mixture. Then the mixed aqueous solution was transferred to a 100 mL Teflon-lined stainless steel autoclave and placed inside a preheated oven at 160 °C and the reaction was continued for 4 h. After the reaction system cooled down to room temperature naturally, the resulting precipitate was separated by centrifugation, washed with DI water and absolute ethanol for several times. Then the products were dried at 60 °C overnight in vacuum oven. In contrast, low-defect $ZnS(en)_{0.5}$ NSs can be obtained via the similar solvothermal process with longer reaction time of 12 h. In addition, other different $ZnS(en)_{0.5}$ samples can be obtained via the similar solvothermal process with reaction time of 6h, 8h and 10h.

Characterization:

The crystal structures of the as-prepared samples was identified by X-ray diffraction using X-ray powder diffraction (XRD) patterns were carried out on a Bruker D8 ADVANCE X-ray diffractometer, with Cu Ka

radiation (l = 0.15418 nm), which operated at 40 kV and 40 mA. The scan rate was 0.5 ($2\theta \cdot s^{-1}$). Scanning electron microscopy (SEM) images were obtained using a HITACHI SU8000 field-emission scanning electron microscope. Transmission electron microscopy (TEM) images were collected with a TecnaiG2F20 S-TWIN with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) investigation was recorded on a Thermo Scientific ESCA Lab 250 system, with a monochromatic Al Kα as the X-ray source, hemispherical analyzer, and sample stage with multi-axial adjustability to obtain the composition on the surface of samples. UV-vis diffuse reflectance spectroscopy (DRS) was measured by a Carry 500 UV-Vis spectrophotometer, during which $BaSO_4$ was served as the background. The nitrogen adsorption and desorption isotherms were characterized using a Micrometrics ASAP 2020 analyzer at 77K after the as-prepared samples were degassed at 180 °C for 300min in a vacuum. Photoelectrochemical measurements were conducted using a ZENNIUM electrochemical workstation (Zahner, Germany) with a conventional three-electrode system. The reference and counter electrodes were Ag/AgCl and Pt plate, respectively, and 0.2 M Na_2SO_4 (pH = 6.8) aqueous solution served as the electrolyte. 10 mg of the as-prepared sample was dispersed in 0.5 mL N,N-dimethyl formamide (DMF) solution by sonication, and the slurry (40 uL) was then evenly spread onto a indium tin oxide (ITO) conductor glass substrate with an area of 5 mm× 5 mm. Then the glasses covered with samples were dried, and the uncovered parts were painted by insulating epoxy resin. The obtained ITO glass serves as a working electrode. A 300 W xenon lamp was used to provide a visible light source equipped with a cut-off filter (λ> 420 nm).

Photocatalytic activity measurement:

Typically, 20 mg as-prepared samples were dispersed into 50 mL 5% (volume fraction) methanol solution. Then a certain volume of H_2PtCl_6 was added as the precursor for the co-catalyst Pt to ensure weight ratio of Pt and $ZnS(en)_{0.5}$-based sample being 0.5%. The suspension was irradiated by full-solar light for 0.5 h under vacuum. Then a certain volume of DI water and a certain Na_2S and $Na_2SO_3$was added into the above resulting solution to obtain 100 mL solution containing 0.35 M Na_2S and 0.25 M Na_2SO_3, those act as the sacrificial reagents. The suspension was poured into a quartz flask, and vacuumed with a vacuum pump for 2 h to drive away the residual air. The photocatalytic water splitting to produce H_2 was carried out by vertically irradiating the suspension with a 300W xenon lamp coupled with a cut-off filter (λ > 420 nm). The temperature of reaction solution was keep at 4 °C. The gas product composition was analyzed every 1 h by an Techcomp 7900

charomatograph (GC) with TCD detector and Ar as the carrier gas.
The equivalent crystallite diameter (D) can be estimated by the Scherrer's formula:

$$D = (0.89\lambda)/(\beta\cos\theta).$$

Where λ is the X-ray wavelength, θ is the half angle of the diffraction peak on the 2θ scale, and β is the full width at half maximum intensity of the diffraction (radian).

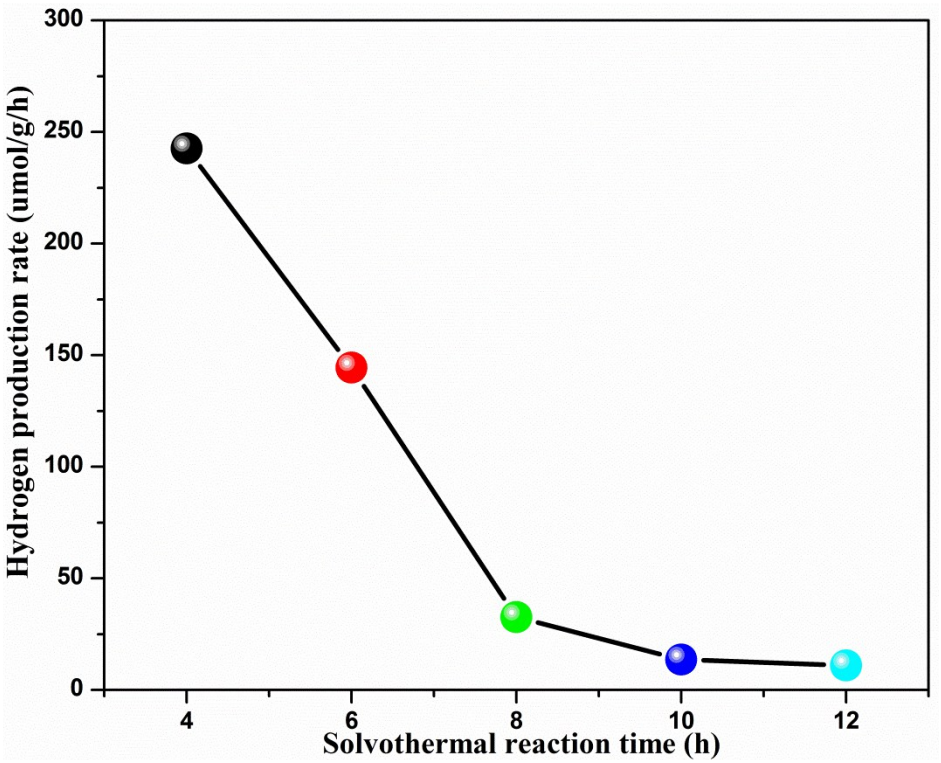

Fig. S1 Photocatalytic H_2 evolution rate over $ZnS(en)_{0.5}$ samples obtained with 4 h, 6h, 8h, 10h and 12 h reaction time under visible light irradiation (λ>420 nm).

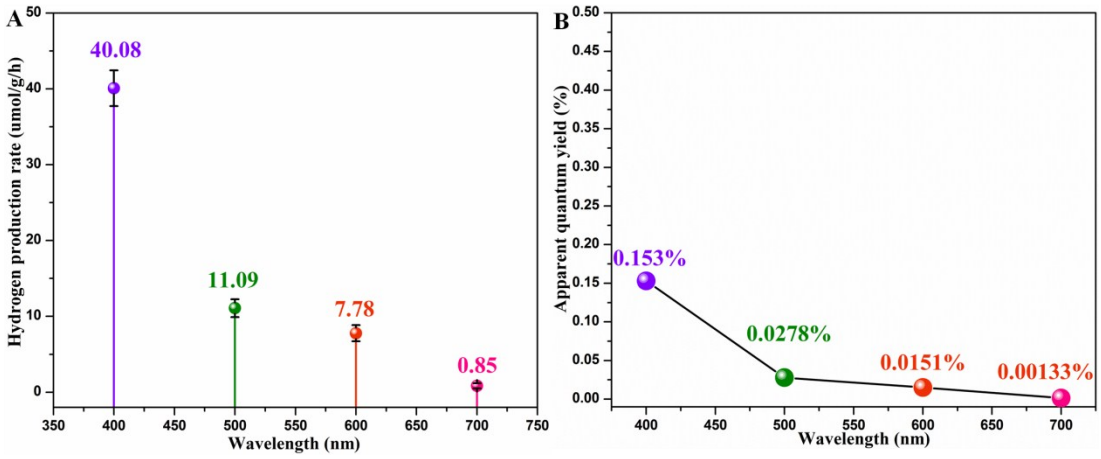

Fig. S2 The hydrogen production rate and apparent quantum yield of D-ZnS$(en)_{0.5}$ under different monochromatic light source.