Supporting Information

A simple template-free synthesis of nanoporous ZnS-In_2S_3-Ag_2S solid solutions for highly efficient photocatalytic H_2 evolution under visible light

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Experimental details

The photocatalytic gas evolution was conducted in an outer irradiation quartz cell with a side window, which was connected to a closed gas-circulating system. The photocatalyst powder (0.015 g) was dispersed by ultrasonic for 30 min in an aqueous solution (320 mL) containing 0.6 M Na_2SO_3 − 0.1 M Na_2S as electron donors. The reaction was carried out by irradiating the mixture with light from a Xe lamp (300 W) which is equipped with an optical filter ($\lambda > 400$ nm) to cut off the light in the ultraviolet region. Gas evolution was analyzed by a gas chromatograph (Agilent 6820, TCD, Ar carrier).

Apparent quantum yield (A.Q.Y.) was calculated by the following equation:

$$\text{A.Q.Y. (\%)} = \frac{\text{The number of reacted electrons}}{\text{The total number of incident photons}} \times 100$$

$$= \frac{\text{The number of evolved } H_2 \text{ molecules} \times 2}{\text{The total number of incident photons}} \times 100$$

The total number of incident photons at 420 nm was measured by a 300 W xenon lamp with a cutoff filter and band-pass filter (λ: 420 nm, half width: 15 nm) and light flux meter (1930-C, Newport) with the light sensor.
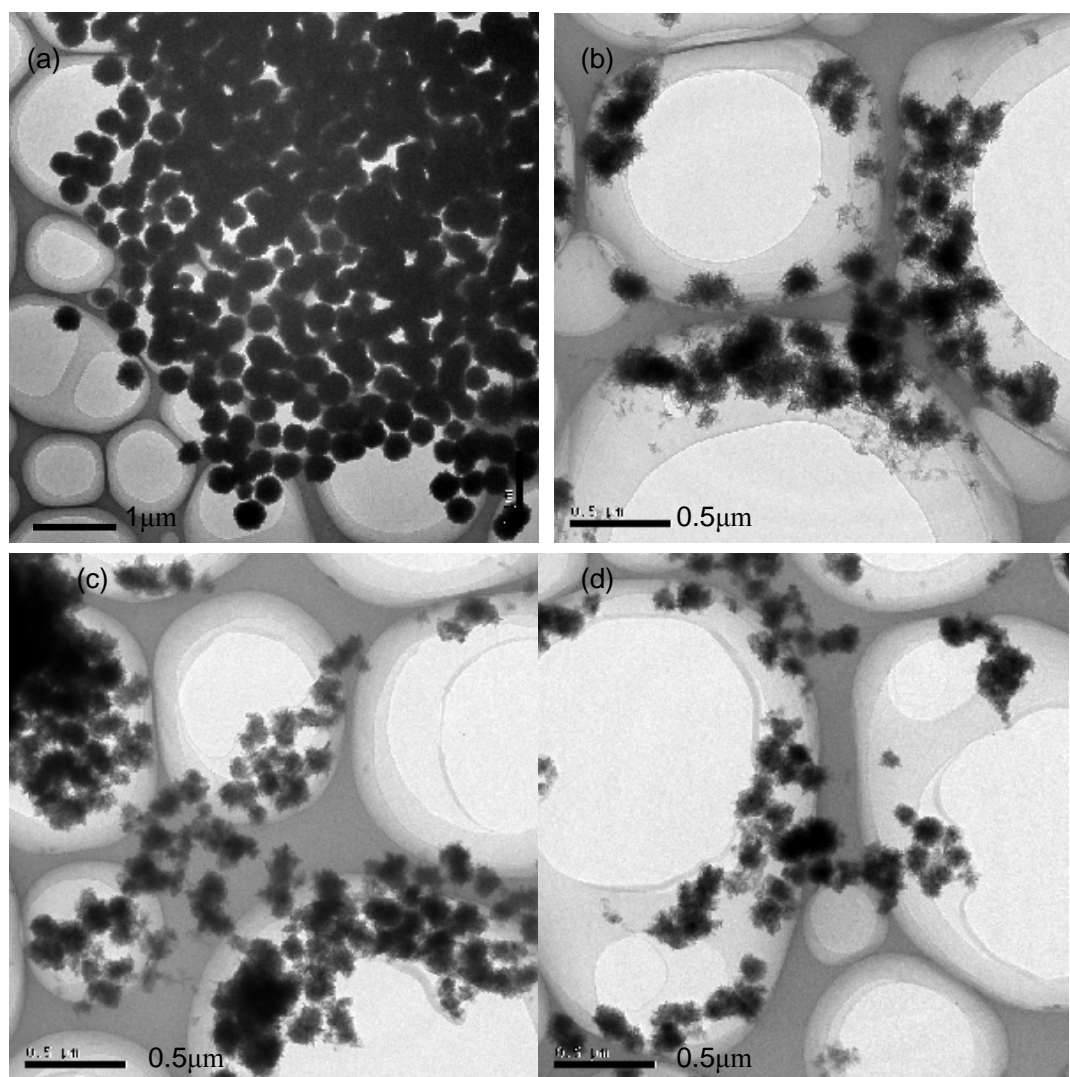
Fig. S1. TEM images of $ZnIn_{0.23}Ag_{2x}S_{1.345+x}$ (x = 0-0.045): (a) $ZnIn_{0.23}S_{1.345}$; (b) $ZnIn_{0.23}Ag_{0.04}S_{1.37}$; (c) $ZnIn_{0.23}Ag_{0.07}S_{1.38}$; (d) $ZnIn_{0.23}Ag_{0.09}S_{1.39}$.

Table S1. Dependence of photocatalytic activities for H_2 evolution from an aqueous 0.6 M Na_2SO_3–0.1 M Na_2S solution under visible light irradiation over $ZnIn_{0.23}Ag_{2x}S_{1.345+x}$ solid solutions upon the composition (Value of x). The samples were illuminated continuously with light from a 300 W Xe lamp for 4 h. The average crystallite sizes calculated from the line broadening of the XRD peaks using the Scherer formula.

Composition x	Band gap (eV)	Rate of H_2 evolution (mmol/h/0.015g cat)	A.Q.Y. (%)	Average crystallite sizes (nm)
0	3.26	0.7	0	12.2
0.02	2.88	3.3	19.8	11.8.
0.035	2.76	2.8	19.6	12.0
0.045	2.58	2.3	14.8	11.6
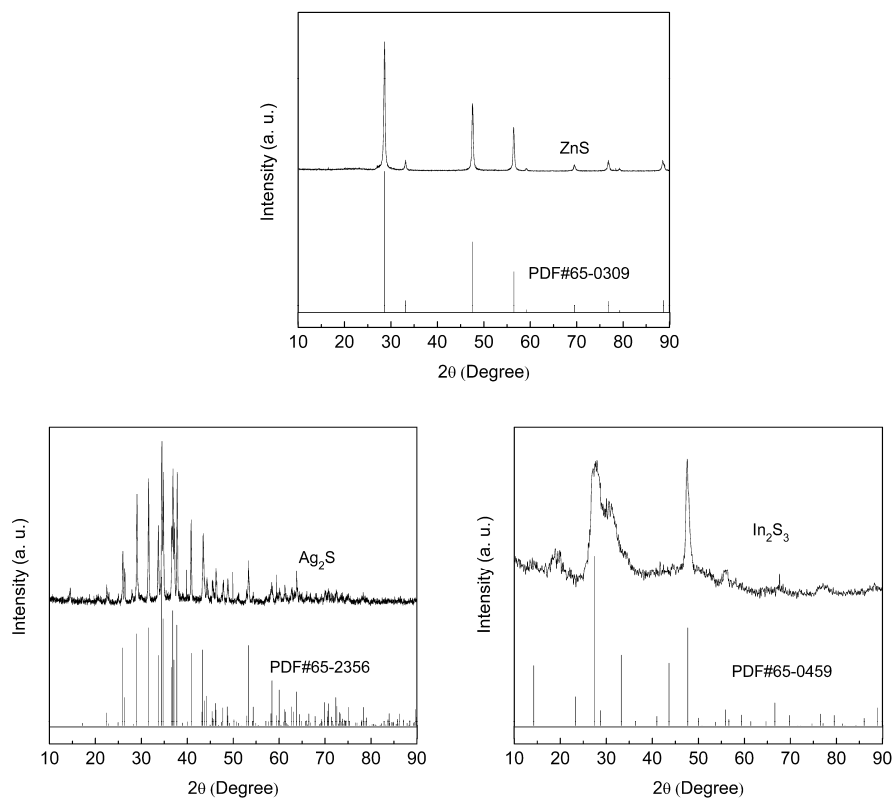
Fig. S2. Powder XRD patterns of ZnS, Ag$_2$S and In$_2$S$_3$

Table S2. Photocatalytic activities of ZnS, In$_2$S$_3$ and Ag$_2$S

Samples	Rate of H$_2$ evolution (mmol/h/0.015g cat)
ZnS	0.021
In$_2$S$_3$	0.022
Ag$_2$S	0