Supplementary Information

An ion-exchange route for the synthesis of hierarchical In$_2$S$_3$/ZnIn$_2$S$_4$ bulk composite and its photocatalytic activity under visible-light irradiation

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Experimental Section

The reagents were purchased from Wako Pure Chemical Industries, Ltd. (Japan), including sodium sulfide nonahydrate (Na$_2$S·9H$_2$O), indium chloride tetrahydrate (InCl$_3$·4H$_2$O), zinc chloride (ZnCl$_2$), magnesium chloride hexahydrate (MgCl$_2$·6H$_2$O), ethylene glycol dehydrated (HOCH$_2$CH$_3$OH; EG), ethanol dehydrated (CH$_3$CH$_2$OH), and dihydrogen hexachloroplatinate (IV) hexahydrate (H$_2$PtCl$_6$·(H$_2$O)$_6$). They were of analytical grade and used without further treatment.

Synthesis of hierarchical NaInS$_2$ microflowers

In a typical process, 50 ml of EG and 50 ml of absolute ethanol were magnetically stirred for 10 min in a beaker firstly, then 2 mmol of InCl$_3$·4H$_2$O was added into the mixed organic solution and continuously stirred for 15 min, and then 12 mmol of Na$_2$S·9H$_2$O was added into the solution and stirred for another 30 min. Subsequently, the mixture was transferred into a Teflon liner with 120-ml capacity, which was then sealed in a stainless steel autoclave and heated at 180 °C for 12 h. Finally, the autoclave was cooled to room temperature naturally and the products were washed by distilled water and absolute ethanol for several times, respectively. After drying at 70 °C in an oven, the products were collected for further characterizations and treatments.

Synthesis of In$_2$S$_3$/ZnIn$_2$S$_4$ bulk composite

For the synthesis of an In$_2$S$_3$/ZnIn$_2$S$_4$ bulk composite, x mmol of ZnCl$_2$, (2-x) mmol of MgCl$_2$·6H$_2$O, and 1 mmol of the as-synthesized NaInS$_2$ were added into the mixture of absolute ethanol (97 ml) and pure water (3 ml). The mixture was filled in a Teflon liner with 120-ml capacity. Then the liner was sealed in a stainless steel autoclave when ZnCl$_2$ and MgCl$_2$·6H$_2$O were totally dissolved. Subsequently, the whole system was heated at 200 °C for 24 h in an oven. After the heat treatment, it was cooled to room temperature
naturally. The products were washed with distilled water and ethanol for several times, respectively. Finally, the products were dried at 70 °C for further characterization. As a reference, In$_2$S$_3$ and ZnIn$_2$S$_4$ were fabricated by the similar procedure. The products were In$_2$S$_3$ when the starting reagents were 2 mmol of MgCl$_2$·6H$_2$O and 1 mmol of NaInS$_2$; while the products became ZnIn$_2$S$_4$ when the starting reagents were 2 mmol of ZnCl$_2$ and 1 mmol of NaInS$_2$.

**Characterization**

Powder X-ray diffraction (XRD) characterization was performed by using an X’Pert PRO X-ray diffraction system (PANalytical B.V., Netherlands) operating at 45 kV and 40 mA for Cu Kα radiation (λ = 1.5406 Å). The UV-visible diffuse reflection spectra were recorded on a UV-2500PC recording spectrophotometer (Shimadzu Co., Japan). The reflectance spectra were converted into absorption spectra using the Kubelka-Munk equation. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM), scanning transmission electron microscopy and elemental mapping (STEM elemental mapping) were performed on a 300 kV JEM-3100 FEF (JEOL, Japan) microscope. The photocatalytic evolved H$_2$ was analyzed by an on-line gas chromatography (GC-8A, Shimadzu Co., Japan) equipped with a thermal conductivity detector (TCD).

Apparent quantum efficiency (AQE) was calculated by the following equation:

$$AQE(\%) = \frac{\text{The number of reacted electrons}}{\text{The number of incident photons}} \times 100\%$$

$$= \frac{\text{The number of evolved H}_2 \text{ molecules} \times 2}{\text{The number of incident photons}} \times 100\%$$
**Fig. S1**

XRD pattern of as-synthesized NaInS$_2$.

**Fig. S2**

SEM images of as-synthesized NaInS$_2$ at different magnifications.
Fig. S3 XRD patterns of as-synthesized (A) NaInS$_2$, (B) In$_2$S$_3$, and (C) ZnIn$_2$S$_4$. 
**Fig. S4**

Fig. S4 SEM images of as-synthesized (a), (b) In$_2$S$_3$, and (c), (d) ZnIn$_2$S$_4$ at different magnifications.

**Fig. S5**

Fig. S5 TEM images of (a) In$_2$S$_3$ and (c) ZnIn$_2$S$_4$; and HRTEM images of (b) In$_2$S$_3$ and (d) ZnIn$_2$S$_4$. 
**Fig. S6**

Fig. S6 SEM images at different magnifications of In$_2$S$_3$/ZnIn$_2$S$_4$ bulk composites synthesized from different amount of ZnCl$_2$ (presented as Zn$^{2+}$) and MgCl$_2$·6H$_2$O (not shown): (a), (b) 0.1 mmol; (c),(d) 0.2 mmol; (e), (f) 0.3 mmol; (g), (h) 0.4 mmol; (i), (j) 0.8 mmol.
Fig. S7

(a) TEM image and (b) HRTEM image (inset: SAED patterns) of an In$_2$S$_3$/ZnIn$_2$S$_4$ bulk composite synthesized by using 0.3 mmol of ZnCl$_2$, 1.7 mmol of MgCl$_2$·6H$_2$O, and 1 mmol of NaInS$_2$ as the reagents at 200 °C for 24 h.

Results and discussion

Fig. S3 shows the XRD patterns of the as-synthesized NaInS$_2$, In$_2$S$_3$, and ZnIn$_2$S$_4$ materials. According to the patterns, NaInS$_2$ was totally transformed into pure tetragonal In$_2$S$_3$ (JCPDS 73-1366) and cubic ZnIn$_2$S$_4$ (JCPDS 72-0305) after the ion-exchange reaction, respectively. Fig. S4 shows the SEM images of the synthesized In$_2$S$_3$ and ZnIn$_2$S$_4$, the morphologies don’t show obvious transformation in comparison with that of the NaInS$_2$ precursor. The TEM and HRTEM images of In$_2$S$_3$ and ZnIn$_2$S$_4$ are depicted in Fig. S5. The separated nanoplates of the microflower structures are seen on TEM images in Fig. S5 (a) and (c). Fig. S5 (b) and (d) exhibit the interplanar spacings of 3.11 Å and 3.06 Å, which belong to the (206) of In$_2$S$_3$ and (222) of ZnIn$_2$S$_4$, respectively. Fig. S6 shows the SEM images of the In$_2$S$_3$/ZnIn$_2$S$_4$ bulk composites mentioned in the text. They were synthesized from different amount of ZnCl$_2$ and MgCl$_2$·6H$_2$O. The bulk composites are all microflowers with similar morphologies. Fig. S7 shows the TEM, HRTEM images, and SAED patterns of one nanoplate of the In$_2$S$_3$/ZnIn$_2$S$_4$ bulk composite. It was synthesized by using 0.3 mmol of ZnCl$_2$, 1.7 mmol of MgCl$_2$·6H$_2$O, and 1 mmol of NaInS$_2$ as the reagents at 200 °C for 24 h. The HRTEM and SAED results were the characterizations of red-rectangle-marked region in Fig. S7 (a). The calculated
intersection angles of $\alpha$ (between (117) and (1 0 10)) and $\beta$ (between (1 0 10) and (0 1 3)) are 28.5° and 57.9°, respectively. These results reveal that the planes (117), (1 0 10), and (0 1 3) belong to the tetragonal In$_2$S$_3$ and are consistent with the HRTEM result in Fig. S7 (b). The lattice spacing of 6.23 Å is the value of {103} of the tetragonal In$_2$S$_3$.

Fig. S8

(a) UV-vis absorption spectra of an In$_2$S$_3$/ZnIn$_2$S$_4$ bulk composite synthesized by using different amount of ZnCl$_2$ and MgCl$_2$·6H$_2$O at 200 °C for 24 h, and (b) Plots of $(ahv)^2$ against photon energy ($hv$).
Fig. S9

**Fig. S9** Time course of photocatalytic H\textsubscript{2} evolution of individual In\textsubscript{2}S\textsubscript{3}, and ZnIn\textsubscript{2}S\textsubscript{4} phases and an In\textsubscript{2}S\textsubscript{3}/ZnIn\textsubscript{2}S\textsubscript{4} bulk composite synthesized from different amounts of ZnCl\textsubscript{2} (presented in the picture; mmol) and MgCl\textsubscript{2}·6H\textsubscript{2}O (not shown) as reagents at 200 °C for 24 h. Photocatalyst: 0.1 g; Cocatalyst: 1 wt% of Pt; Light source: 300 W of Xe lamp with a L42 cut filter. Sacrificial reagents: 280 ml of Na\textsubscript{2}S (0.35 mol/L)/K\textsubscript{2}SO\textsubscript{3} (0.25 mol/L) aqueous solution.