**Supporting Information** 

## Preparation of Single-Crystalline AgIn<sub>5</sub>S<sub>8</sub> Octahedrons with Exposed {111} Facets and Its Visible-Light-Responsive Photocatalytic H<sub>2</sub> Production Activity

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**Figure S1.** Typical XPS spectra of the obtained  $AgIn_5S_8$  octahedrons. The survey spectrum (a), the regional spectra of Ag 3d (b), In 3d (c), and S 2p (d).



**Figure S2.** Typical FESEM images of the products derived from the hydrothermal treatment of the reaction solution (pH10.60) at 180 °C for 10 min (a), 20 min (b), 30 min (c), 50 min (d), 90 min (e), and 120 min (f).



**Figure S3.** Typical XRD patterns of the products derived from the hydrothermal treatment of the reaction solution (pH10.60) at 180 °C for different times.



**Figure S4.** Typical FESEM images of the products derived from hydrothermal treatment of the reaction solution (pH  $\sim$ 10.60) at 180 °C for 5 h (a), 10 h (b), 15h (c) and 20 h (d).



**Figure S5.** Typical XRD patterns of the products derived from the hydrothermal treatment of the reaction solution (pH  $\sim$ 10.60) at 180 °C for different times.



**Figure S6.** Typical FESEM image (a) and XRD pattern (b) of product derived from the hydrothermal treatment of the brown amorphous matter (pH  $\sim$ 10.60) at 180 °C for 20 h.



**Figure S7.** The possible nucleation mechanisms of  $Ag_2S$  (charcoal grey) and  $In_2S_3$  nanocrystals (brown), and the accurately released  $S^{2^-}$  ions from the decomposition of TAA with enhancing the pH value, as well as the growth mechanism of the  $AgIn_5S_8$  octahedrons (AIS-10.6).



**Figure S8.** Typical FESEM image (a) and the XRD pattern (b) of the product (AIS-10.6K) derived from the hydrothermal treatment of the reaction solution (pH  $\sim$ 10.60) at 180 °C for 20 h by using KOH instead of NaOH as pH modifier.



**Figure S9.** Top-view SEM images and elemental mappings (a, c, e, g, i) as well as the corresponding elemental composition total spectra (b, d, f, h, j) of the  $Ag_xIn_yS_{(x+3y/2)}$  products. AIS-3.0 (a, b), AIS-5.0 (c, d), AIS-7.0 (e, f), AIS-10.6 (g, h), AIS-12.0 (i, j). The scale bar is 10 µm.



Figure S10. UV-vis diffuse reflectance absorption spectra (DRS) of the obtained Ag<sub>x</sub>In<sub>y</sub>S<sub>(x+3y/2)</sub> products.



**Figure S11.** Transient photocurrent response curves of the AIS-x products derived from the hydrothermal treatment (at 180 °C for 20 h) of the reaction solutions with different pH values.



**Figure S12.** (a) Typical FESEM image of the product (AIS-ir) derived from the water bath process without NaOH solution as pH modifier; (b) XRD patterns of AIS-10.6, AIS-ir, and AIS-ir/an derived from the annealing process of AIS-ir.



**Figure S13.** Liquid nitrogen adsorption–desorption isotherms and the corresponding BJH pore size distribution n curves (inset) of the obtained AIS-10.6 AIS-ir, and AIS-ir/an.



Figure S14. Comparison of the XRD patterns of the  $AgIn_5S_8$  octahedrons (AIS-10.6) before and after the photocatalytic reaction for 20 h.