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Supplementary Information

Ultrathin-Nanosheet-based 3D Hierarchical Porous In_2S_3 Microspheres: Chemical Transformation Synthesis, Characterization, and Enhanced Photocatalytic and Photoelectrochemical Property

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1. Materials

All reagents were used without further purification.

2. Experimental Section

2.1 Synthesis of InS-TETA

In a typical synthesis, tartaric acid (2 mmol, 0.3 g), $InCl_3$ (1 mmol, 0.2212 g) and L-cysteine (6 mmol, 0.7269 g) were added into a mixture solvent of deionized water (DIW) and TETA with a total volume of 18 mL (V_{DIW}/V_{TETA}=2:1) in a 50 mL Teflon-lined stainless-steel autoclave. After stirring to form a homogeneous solution, the system was treated at 160℃ for 24 h and cooled down naturally. The white floccule formed after reaction was washed by DIW and absolute ethanol, respectively, and dried in a vacuum oven.

2.2 Synthesis of 3HPM In_2S_3

10 mg as-prepared InS-TETA was put into a solvent of 12 mL DIW in a 20 Teflon-lined stainless-steel autoclave under stirring to form a homogeneous solution. After kept at 180℃ for 10 h, the yellow floccule formed after reaction was washed by DIW and absolute ethanol, respectively, and dried in a vacuum oven.

2.3 Synthesis of 3SM In_2S_3

3SM In_2S_3 was prepared using a modified procedure according to the synthesis of InS-TETA. In short, tartaric acid (2 mmol, 0.3 g), $InCl_3$ (1 mmol, 0.2212 g) and L-

cysteine (6 mmol, 0.7269 g) were added into a single solvent of 18 mL DIW. The followed procedure was as mentioned before.

2.4 Characterizations

The scanning electron microscopy (SEM) images and Energy-dispersive X-ray spectroscopic (EDX) analysis were taken with a Hitachi S-4800 scanning electron microscope (SEM, 5 kV) equipped with the Thermo Scientific energy-dispersion X-ray fluorescence analyzer. Transmission electron microscopy (TEM) and higher-magnification transmission electron microscopy (HRTEM) were obtained with FEI Tecnai G^2F20 system equipped with GIF 863 Tridiem (Gatan). Specimens for TEM and HRTEM measurements were prepared via dropcasting a droplet of ethanol suspension onto a copper grid, coated with a thin layer of amorphous porous carbon film, and allowed to dry in air. The X-ray diffraction patterns (XRD) of the products were recorded with Bruker D8 Focus Diffraction System using a Cu Kα source (λ= 0.154178 nm). The pore size distributions of the synthesized materials were determined by nitrogen physisorption using Quadrasorb SII Quantachrome Instrument. Pore size distributions were calculated using the Barrett-Joyner-Halenda method from the desorption branch. FTIR spectra were recorded on a MAGNA-IR 750 (Nicolet Instrument Co) FTIR spectrometer. UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded on a Lambda 750 UV-vis-NIR spectrometer (Perkin-Elmer) equipped with an integrating sphere. The UV-vis DRS of solid samples were collected in 200-800 nm against $BaSO_4$ reflectance standard.

2.5 Photocatalytic Measurement

For both 3HPM In_2S_3 and comparison group, 15 mg sample was first immersed in the MO solution (15 mg/L) with a total volume of 100 mL and kept for a whole night to get absorption equilibrium. The system was irradiated directly under a 300W Xe lamp (Perfectlight) for 90 min at ambient atmosphere under UV-visible irradiation. After each 30 min intervals, 5 mL of MO solution was removed from the system for analysis. The degradation of MO was investigated by measuring its absorption spectra using UV-vis spectrophotometer.

2.5 Photoelectrochemical (PEC) Measurement

PEC measurements were carried out in a standard three-compartment cell consisting of a working electrode, a Pt gauze counter electrode, and a saturated calomel reference electrode (SCE) performed using an electrochemical workstation (CHI 660D, CH Instruments, Austin, TX) under UV-visible irradiation (the same with

that in photocatalytic measurement) in the presence of H_2SO_4 (0.5 M) as electrolyte and scarifying agent. An indium-tin oxide glass (ITO) decorated with catalyst samples were used as the working electrode. For a typical procedure for fabricating the working electrode, 4 mg of 3HPM In_2S_3 catalysts were dispersed in 4.384 mL of water containing Nafion solution (40 μL, 5 wt%), then the mixture was ultrasonicated to generate a homogeneous ink. Then 160 μL of the catalyst ink (containing 0.145 mg of catalyst) was spreaded on an ITO glass (loading amount: ~ 0.12 mg/cm^2).

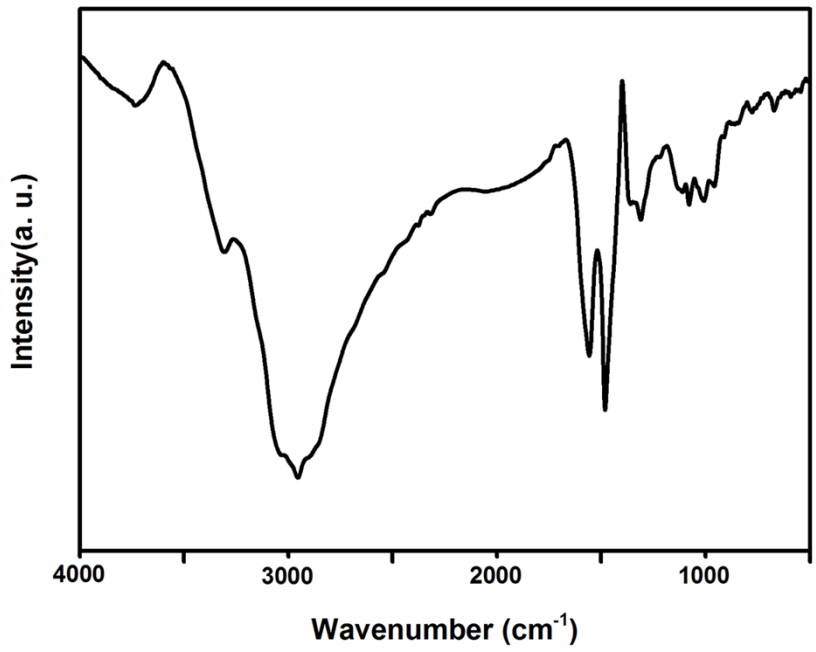

Figure S1. FTIR spectra of InS-TETA hybrid precursor, suggesting the existence of TETA in this hybrid.

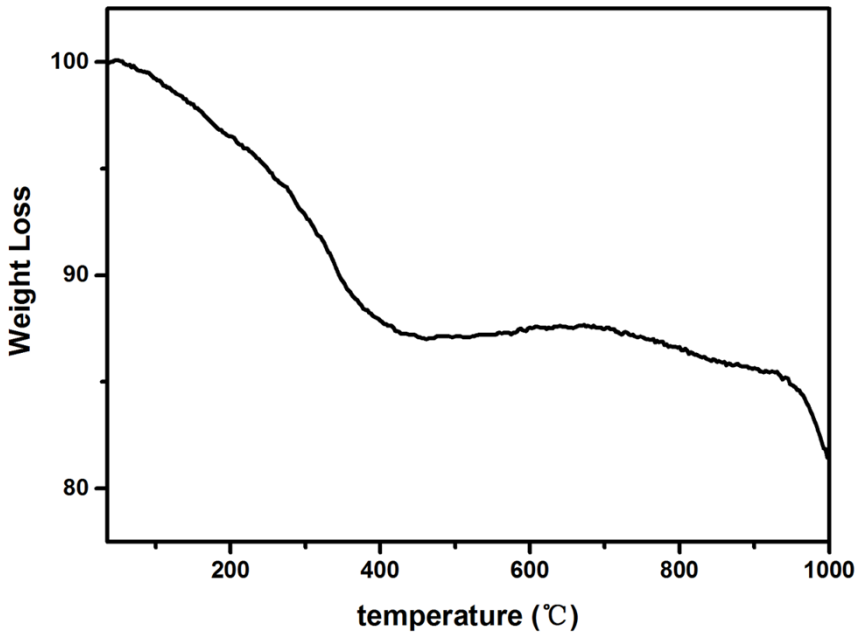

Figure S2. Thermogravimetric analysis curve of In_2S_3 prepared at 120℃, showing that as-prepared products still contain organic components.

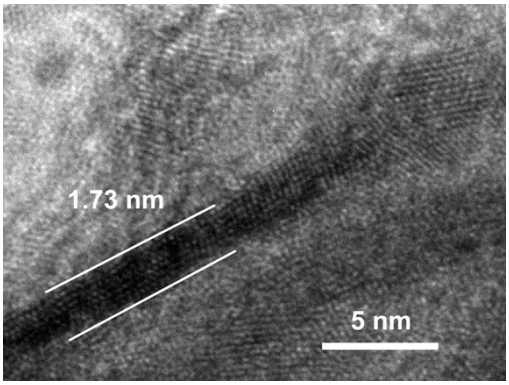

Figure S3. Magnified TEM image of a vertical nanosheet in 3HPM In_2S_3, suggesting the thickness of a typical nanosheets to be 1.73 nm.

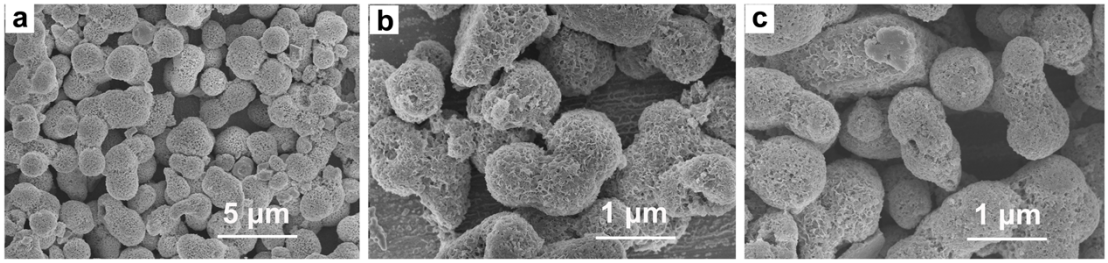

Figure S4. SEM images of In_2S_3 prepared at different temperatures: (a) 120 ℃, (b) 150 ℃ and (c) 200 ℃. It demonstrates that under different temperatures, nanosheet-like building block will not change, but the macro-morphology cannot be maintained.

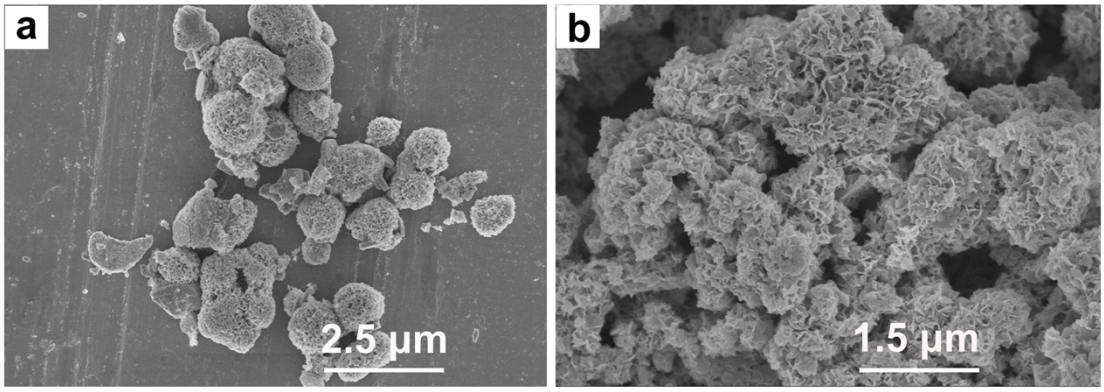

Figure S5. SEM images of In_2S_3 prepared using different amount of InS-TETA hybrid precursors: (a) 2 mg; (b) 30 mg, revealing that different concentrations of

starting materials will result in irregular macro-morphology with nanosheet-like building blocks unchanged.

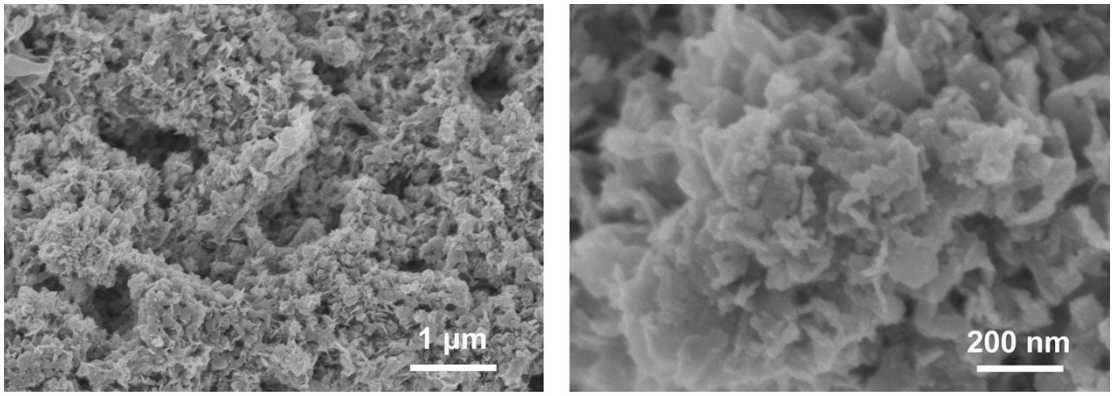

Figure S6. SEM images of In_2S_3 prepared using TETA and DIW as solvent (V_{TETA}/V_{DIW} = 1/3 with total volume of 12 mL), confirming the importance of using single DIW as solvent for the maintaining of macro-sized morphology.

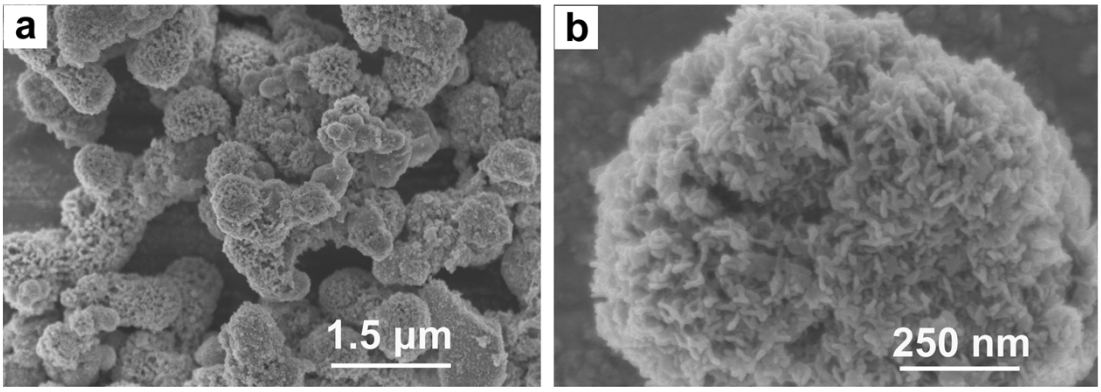

Figure S7. SEM images of In_2S_3 prepared using EG as solvent: (a) a general overview; (b) one typical microsphere, demonstrating that with EG as solvent, the building blocks change into nanorods.

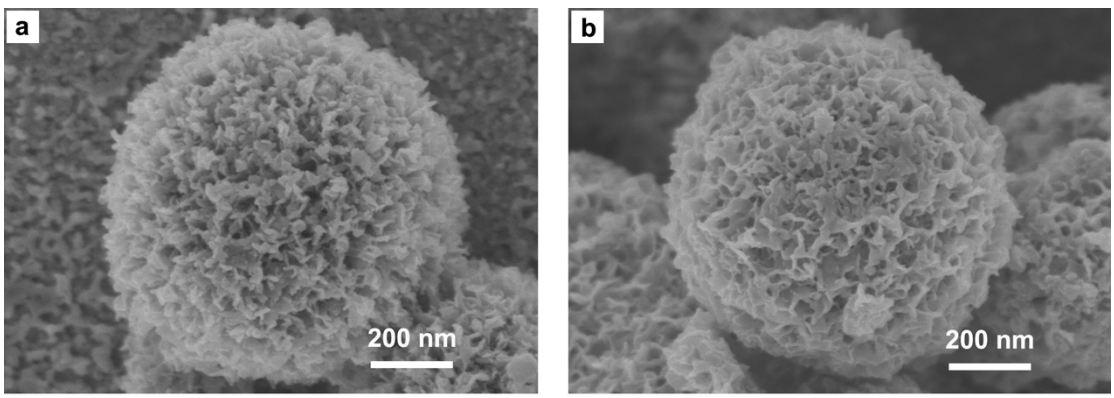

Figure S8. SEM images of time-dependent intermedias: (a) at 1 h; (b) at 3 h.

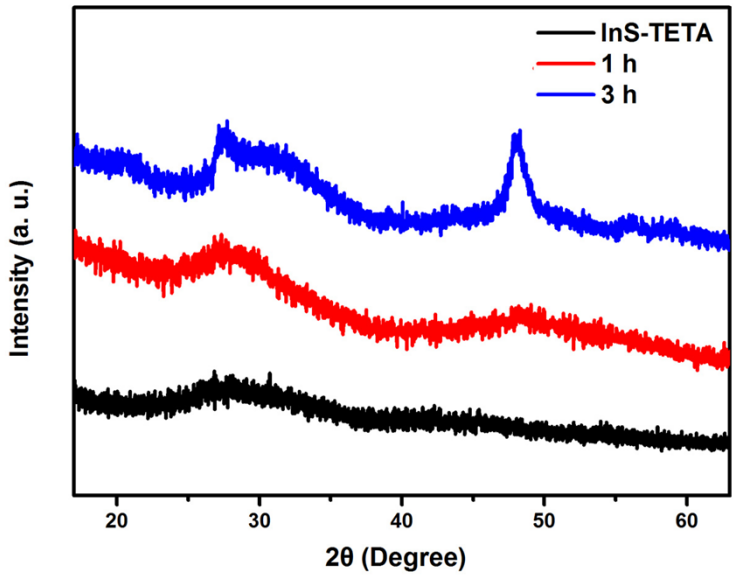

Figure S9. XRD patterns of inorganic-organic InS-TETA hybrid precursors and time-dependent intermediates at 1 h and 3 h. It's demonstrated that InS-TETA precursors are not well-crystalline, and with further reaction, peaks for inorganic In_2S_3 (PDF no. 00-32-0456) are becoming more and more obvious, suggesting the gradual formation of inorganic In_2S_3. Thus, the successful transformation from inorganic-organic InS-TETA precursors into inorganic In_2S_3 has been confirmed.

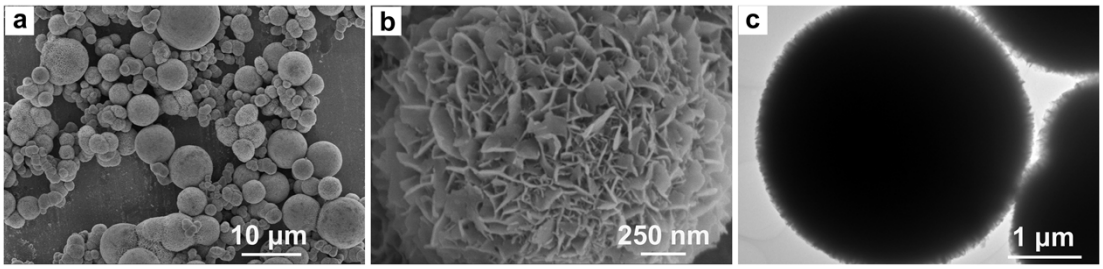

Figure S10. SEM images (a, b) and TEM image (c) of 3SM In_2S_3, revealing the 3D solid structure for comparison group.

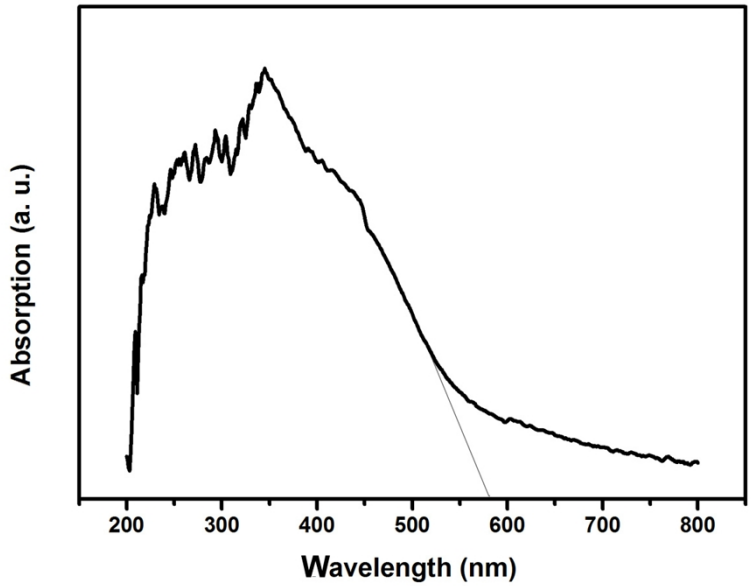

Figure S11. UV/Vis diffuse reflectance spetra of In_2S_3 microspheres, showing the band gap of 3HPM In_2S_3 to be about 2.14 eV as well as a strong absorption in ranging from visible to UV region.

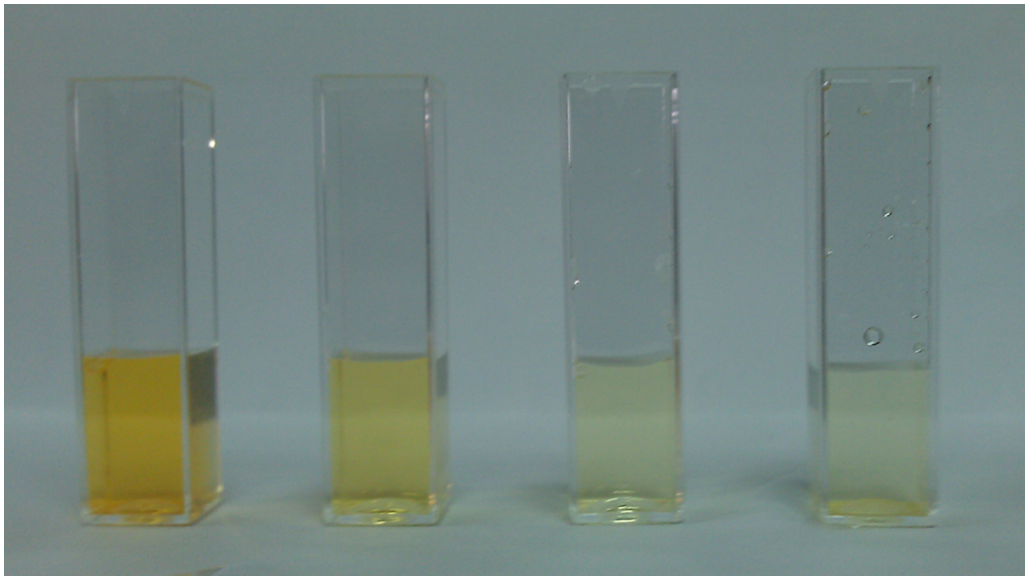

Figure S12. Color change of degradation of MO using 3HPM In_2S_3 as catalyst. The color change during photodegradation of MO is evident.