

Electronic Supplementary Information

A General Route to Template-Free Synthesis Diverse Ternary Sulfides Submicrospheres as Visible Light Responded Photocatalyst

Jianhui Huang, Wahkit Cheuk, Yifan Wu, Frank S. C. Lee, Wingkei Ho*

Characterization of Metal Ternary Sulfides Submicrospheres

The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) at a scan rate of $0.05^\circ 2\theta/\text{s}$. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. SEM images of the samples were performed on a JEOL JSM-6300F microscope operated at an accelerating voltage of 25 kV. Transmission electron microscopy (TEM) study was carried out on a Philips CM-120 electron microscopy instrument. The samples for TEM were prepared by dispersing the final powders in methanol; the dispersion was then dropped on carbon copper grids. A Varian Cary 100 Scan UV-Visible system equipped with a Labsphere diffuse reflectance accessory was used to obtain the reflectance spectra of the catalysts over a range of 200 - 800 nm. Labsphere USRS-99-010 was employed as a reflectance standard. The spectra were converted from reflection to absorbance by Kubelka-Munk method. The Brunauer-Emmett-Teller (BET) surface areas were determined by nitrogen adsorption-desorption isotherm measurements at 77 K by using Micromeritics ASAP 2020 equipment. The samples were degassed under vacuum at 140 °C until a pressure lower than 10^{-6} Torr was reached and kept for 5 h before data acquisition.

Preparation of Ternary Sulfides Submicrospheres

Ternary sulfides submicrospheres were prepared by ultrasonic pyrolysis method. The dissolvable metal salts and excess thiourea was added into water under magnetic stirring to form a transparent colourless solution. Typical weights of added precursor are presented in Table S1. The solution was nebulized at $1.7 \text{ MHz} \pm 10\%$ (YUYUE402AI, Shanghai) and then carried by air with different flow rate 10 L/min through a quartz tube surrounded by a furnace thermostated at 500 or 700 °C. The quartz reaction tube with the diameter of 3.5 cm was 1 m long. The products were collected in a percolator with distilled water, then separated by centrifugation, and then washed thoroughly with ethanol and distilled water. The product was finally dried in an oven at 100 °C for 2 h.

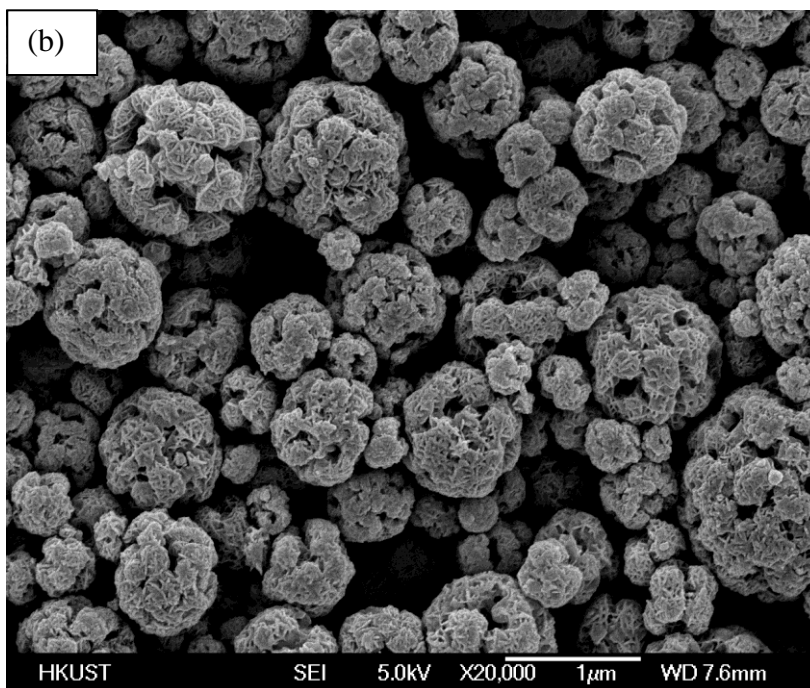
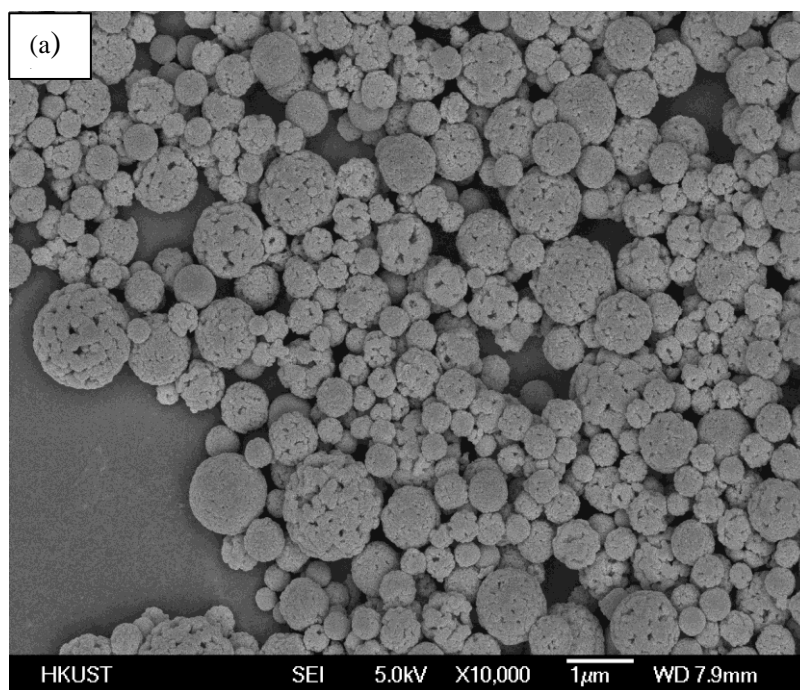
Table S1: Precursor Weight Summary for Different Catalyst Preparation

| Sample | Cd(AC) ₂ ·2(H ₂ O) | AgNO ₃ | ZnCl ₂ | InN ₃ O ₉ ·xH ₂ O | H ₂ O | CH ₄ N ₂ S |
|----------------------------------|--|-------------------|-------------------|--|------------------|----------------------------------|
| CdIn ₂ S ₄ | 0.532 g | — | — | 1.20 g | 150 g | 0.76 g |
| ZnIn ₂ S ₄ | — | — | 0.272 g | 1.20 g | 150 g | 0.76 g |
| AgIn ₃ S ₈ | — | 0.34 | — | 3.01 g | 150 g | 1.60 g |

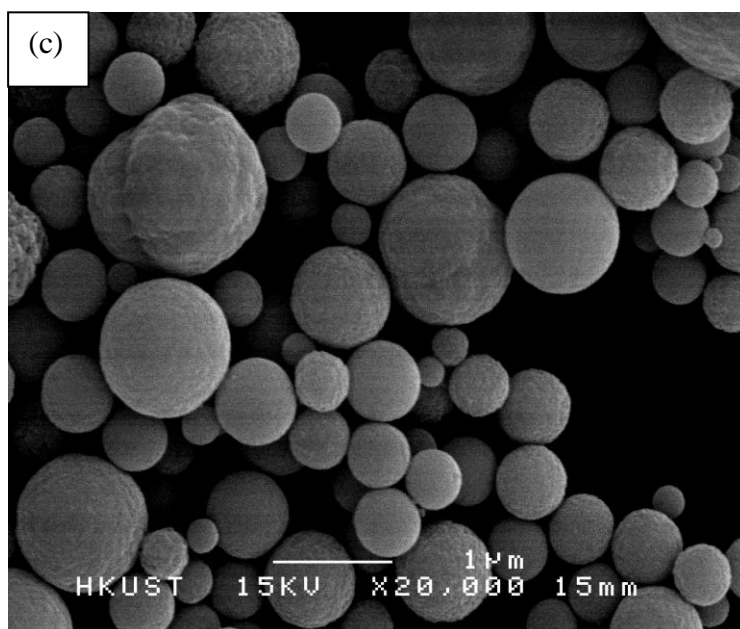
45 Photocatalytic degradation of nitric oxide

The nitric oxide removal test with the resulting samples was performed at ambient condition in a continuous flow reactor. The volume of the rectangular reactor which was made of stainless steel and covered with Saint-Glass was 4.5 L (10 cm × 30 cm × 15 cm (H × L × W)). The sample was prepared by coating an aqueous suspension of the photocatalyst onto a petri-dish with a diameter of 5.0 cm. The weight of the photocatalysts used for each experiment was kept at 0.2 g. The dish containing the photocatalyst was pretreated at 70 °C for several hours until a complete removal of water in the suspension and then cooled to room temperature before use. The visible light lamp was vertically placed outside the reactor above the sample dish, and a glass filter was placed to remove the light below 400 nm. Four mini fans were fixed around the lamp to avoid the temperature rise of the flow system. Furthermore, adequate distance was also kept from the lamp to the reactor for the same purpose to avoid the temperature rise. The NO gas was acquired from compressed gas cylinder at a concentration of 30 ppm NO (N₂ balance, BOC gas) with traceable National Institute of Standards and Technology (NIST) standard. The initial concentration of NO was diluted to about 500 ± 10 ppb by the air stream supplied by a zero air generator (Thermo Environmental Inc. Model 111). The desired humidity level of the NO flow was controlled at 70% (2100 ppmv) by passing the zero air streams through a humidification chamber. The gas streams were pre-mixed completely by a gas blender and the flow rate was controlled at 3 Lmin⁻¹ by a mass flow controller. After the adsorption–desorption equilibrium among water vapor, gases and photocatalysts was achieved, the lamp was turned on. The concentration of NO was continuously measured by a chemiluminescence NO analyzer (Thermo Environmental Instruments Inc. Model 42c), which monitors NO, NO₂, and NO_x (NO_x represents NO + NO₂) with a sampling rate of 0.7 L min⁻¹. The reaction of NO with air was ignorable when performing a control experiment with or without light in the absence of photocatalyst.

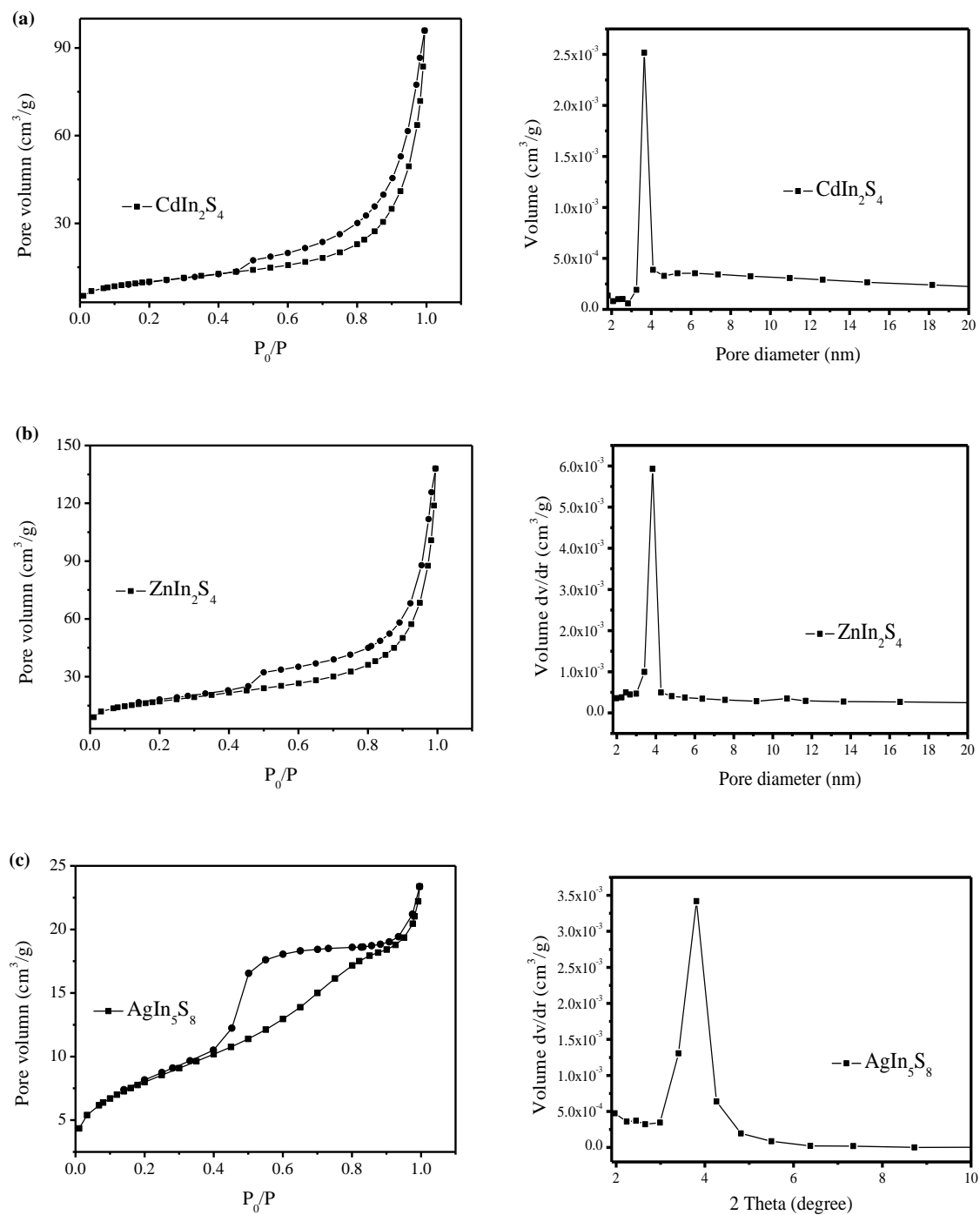
70 **Figure S1** The FSEM images of (a) CdIn_2S_4 , (b) ZnIn_2S_4 and (c) AgIn_5S_8 prepared at 500°C .



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80 **Figure S2** N_2 adsorption-desorption isothermal curves and pore-size distribution plots of $CdIn_2S_4$ (a), $ZnIn_2S_4$ (b) and $AgIn_3S_8$ (c) prepared at $500^\circ C$. The pore size distribution was determined from the desorption branch of the isothermal.



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Fig. S3 Plots of the $(\alpha h\nu)^{1/2}$ vs the energy of absorbed and UV-vis diffuse reflectance spectra (inset) of CdIn_2S_4 , ZnIn_2S_4 and AgIn_5S_8 prepared at 500°C

