

## **Synthesis and characterization of ternary AgInS<sub>2</sub> nanocrystals by dual and multiple source methods**

Lu Tian and Jagadese J. Vittal\*

Department of chemistry, National University of Singapore, 3 Science Drive 3, SINGAPORE

117543. E-mail: [chmjiv@nus.edu.sg](mailto:chmjiv@nus.edu.sg)

### **Supporting information**

For fig. 2b sample:

The precursors [Ag(SC{O}Ph)], **2** (13 mg, 0.051 mmol) and [Et<sub>3</sub>NH][In(SC{O}Ph)<sub>4</sub>], **3** (39 mg, 0.051 mmol) were added to dodecanethiol (DT, C<sub>12</sub>H<sub>25</sub>SH, Aldrich, 2.55 mmol, 0.61 ml) and oleic acid (OA, C<sub>17</sub>H<sub>33</sub>COOH, Aldrich, 1.83 ml) at room temperature (the molar ratio of precursor : DT =1:50; the volume ratio of DT : OA =1:3) and the contents were heated at 200 °C for 2 h with gentle stirring under nitrogen atmosphere. The solution was cooled to ~ 70°C and then an excess of EtOH was added, and a flocculent precipitate was formed. The black solid was separated by centrifugation, washed with EtOH and dried by vacuum.

For fig. 2c sample:

(PPh<sub>3</sub>)<sub>2</sub>AgCl, (34 mg, 0.051 mmol), InCl<sub>3</sub>, (11 mg, 0.051 mmol), PhCOSH (24 µl, 0.204 mmol) and NaOH (8 mg, 0.204 mmol) were mixed for 30 mins and then added to DT (2.55 mmol, 0.61 ml) and OA (1.83 ml) at room temperature (the molar ratio of precursor : DT =1:50; the volume ratio of DT : OA =1:3) and the contents were heated at 200 °C for 2 h with gentle stirring under nitrogen atmosphere. And final product was isolated as described above.

For fig. 2d sample:

(PPh<sub>3</sub>)<sub>2</sub>AgCl, (34 mg, 0.051 mmol), InCl<sub>3</sub>, (11 mg, 0.051 mmol) and PhCOSH (24  $\mu$ l, 0.204 mmol) were mixed for 30 mins and then added to DT (2.55 mmol, 0.61 ml) and OA (1.83 ml) at room temperature (the molar ratio of precursor : DT =1:50; the volume ratio of DT : OA =1:3) and the contents were heated at 200 °C for 2 h with gentle stirring under nitrogen atmosphere. And final product was isolated as described above.

For fig. 2e sample:

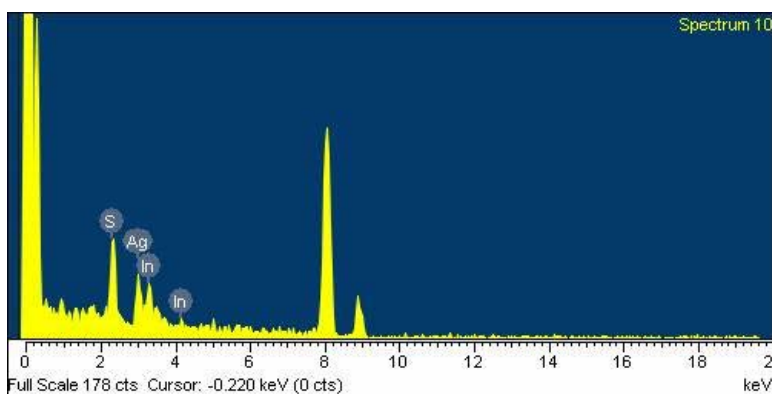
AgCl, (7 mg, 0.051 mmol), InCl<sub>3</sub>, (11 mg, 0.051 mmol) and S (3.3 mg, 0.102 mmol) were added to Oleyamine (2.55 mmol, 0.61 ml) at room temperature (the molar ratio of precursor : oleyamine =1:50) and the contents were heated at 200 °C for 2 h with gentle stirring under nitrogen atmosphere. And final product was isolated as described above.

For fig. 2f sample:

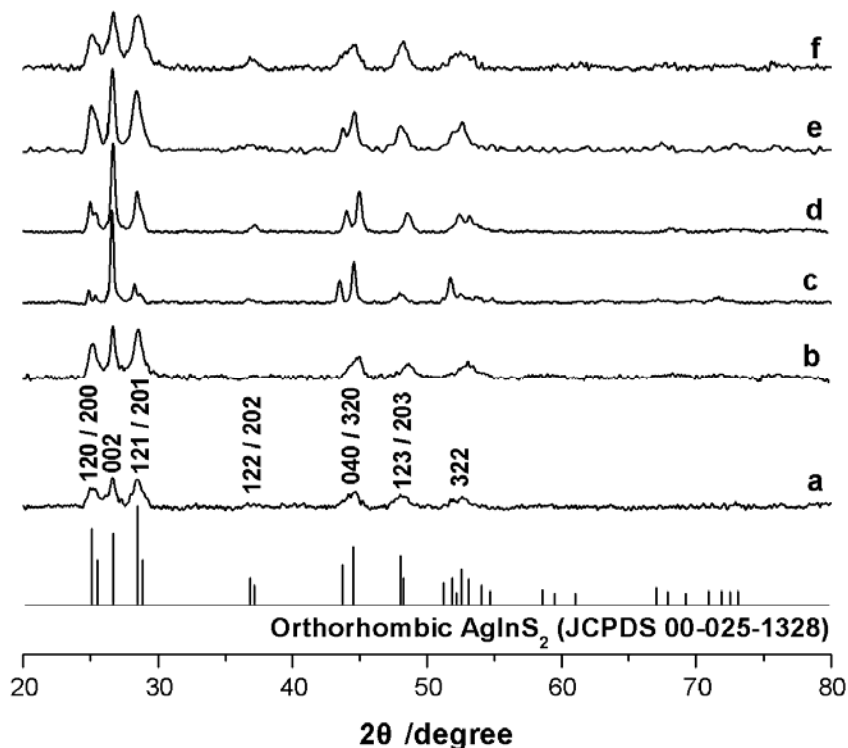
AgCl, (7 mg, 0.051 mmol), InCl<sub>3</sub>, (11 mg, 0.051 mmol) and thiourea (39 mg, 0.151 mmol) were added to Oleyamine (2.55 mmol, 0.61 ml) at room temperature (the molar ratio of precursor : oleyamine =1:50) and the contents were heated at 200 °C for 2 h with gentle stirring under nitrogen atmosphere. And final product was isolated as described above.

AgCl, (7 mg, 0.051 mmol), InCl<sub>3</sub>, (11 mg, 0.051 mmol) and S (3.3 mg, 0.102 mmol) were added to DT (2.55 mmol, 0.61 ml) and OA (1.83 ml) at room temperature (the molar ratio of precursor : DT =1:50; the volume ratio of DT : OA =1:3) and the contents were heated at 200 °C for 2 h with gentle stirring under nitrogen atmosphere. Finally deep yellow suspension with black precipitate was obtained. XRPD shows it unknown mixture including silver sulfide and S etc. There is no AgInS<sub>2</sub> formed in this reaction.

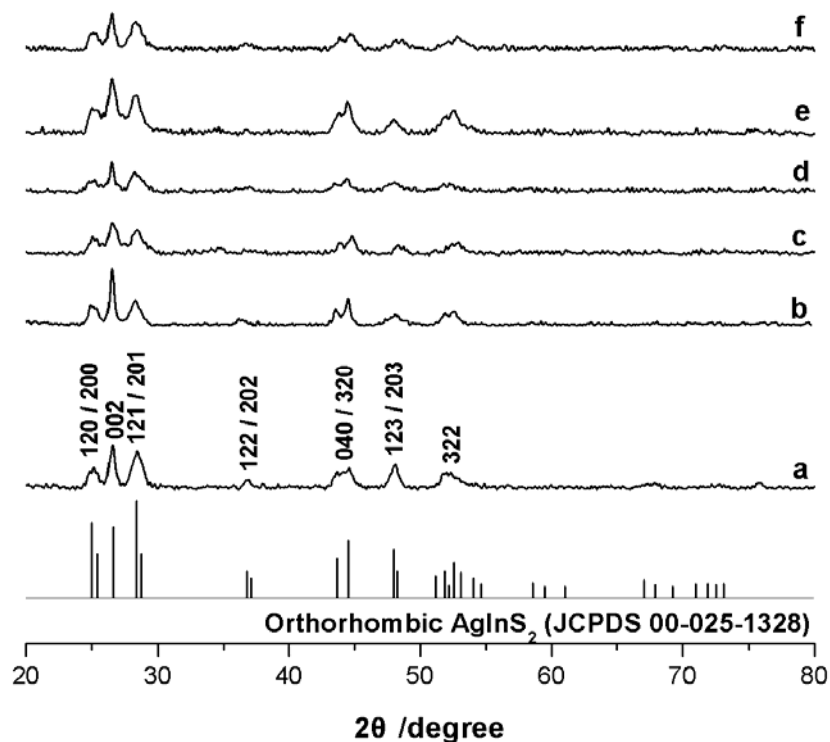
AgCl, (34 mg, 0.051 mmol), InCl<sub>3</sub>, (11 mg, 0.051 mmol) and thiourea (38.8 mg, 0.51 mmol) were added to DT (2.55 mmol, 0.61 ml) and OA (1.83 ml) at room temperature (the molar ratio of precursor : DT =1:50; the volume ratio of DT : OA =1:3) and the contents were heated at 200 °C for 2 h with gentle stirring under nitrogen atmosphere. Finally colorless clear solution was obtained. It can be concluded that there is no AgInS<sub>2</sub> formed in this reaction.



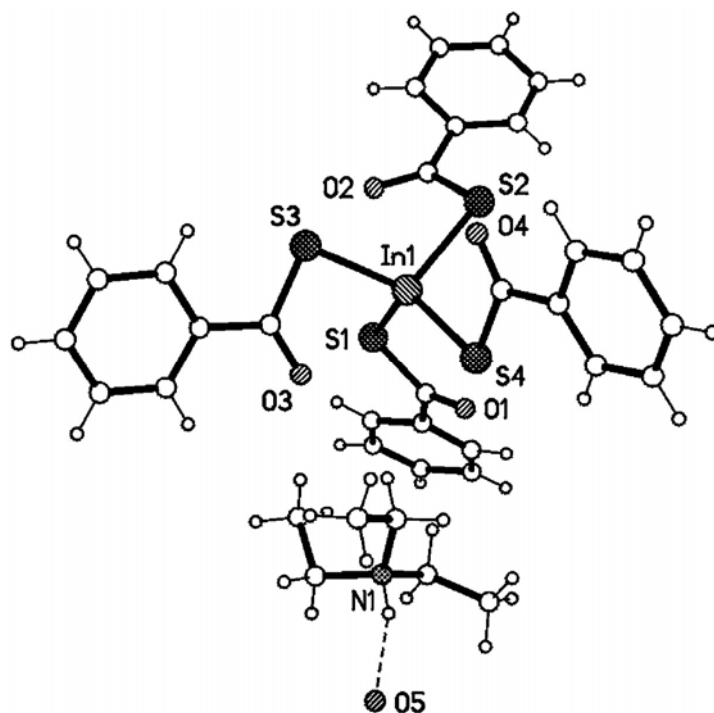
**Figure S1.** EDAX spectrum of AgInS<sub>2</sub> nanoparticles



**Fig. S2** (for fig. 4 samples) Typical XRPD patterns of  $\text{AgInS}_2$  prepared from (a) **2** and **4** in DT at 200 °C for 2 h (the molar ratio of precursor : DT =1:50); (b) **1** in DT at 200 °C for 2 h; (c) **2** and **4** in OA at 200 °C for 2 h (the molar ratio of precursor : OA =1:50); (d) **1** in OA at 200 °C for 2 h; (e) **1** in DT and OA at 250 °C for 2 h (the molar ratio of precursor : DT =1:50; the volume ratio of DT : OA =1:3); (f) **2** and **4** in DT and OA at 250 °C for 2 h.



**Fig. S3** (for fig. 5 samples) Typical XRPD patterns of  $\text{AgInS}_2$  NCs prepared from **2** and **4** at 200 °C for 2 h (the molar ratio of precursor : surfactant =1:50:50) in (a) DT + TOPO; (b) oleyamine + TOPO; (c) oleyamine+ DT; (d) oleyamine + OA; (e) oleyamine; (f) HDA + TOPO.



**Fig. S4** Structure of precursor **3**·H<sub>2</sub>O (Lin, M.; Loh, K. P.; Deivaraj, T. C.; Vittal, J. J. *Chem. Commun.s* **2002**, 1400-1401)