

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

Lu Tian and Jagadese J. Vittal\*

Received (in Durham, UK) 25th May 2007, Accepted 19th July 2007

First published as an Advance Article on the web 8th August 2007

DOI: 10.1039/b707960e

The precursors [In(bipy)(SC(O)Ph)<sub>3</sub>] and [Ag(SC(O)Ph)] have been used to prepare monodispersed polyhedral shaped AgInS<sub>2</sub> nanocrystals (NCs). The NCs were fully characterized by X-ray powder diffraction, transmission electron microscopy, selected area electron diffraction and energy dispersive X-ray analysis. The synthesis of AgInS<sub>2</sub> NCs was further investigated by varying the dual- and multiple-source precursors and other parameters such as surfactants, surfactant ratio, temperature and time duration, to optimize the conditions to get better quality NCs. In all these reactions, a heterobimetallic thiobenzoate intermediate similar to the single-source precursor [(Ph<sub>3</sub>P)<sub>2</sub>AgIn(SC(O)Ph)<sub>4</sub>] has been proposed to have formed which decompose subsequently to AgInS<sub>2</sub> NCs.

## Introduction

Ternary compounds possess a wide variety of physical properties, including electroluminescent displays,<sup>1</sup> superconductivity,<sup>2,3</sup> and magnetic properties,<sup>4,5</sup> that are important for many scientific advances and technological applications. Traditionally, high-temperature arc melting or powder metallurgy techniques have been used to produce ternary compounds. They generally yield thermodynamically stable structures and offer little control over nanostructure and morphology.<sup>6,7</sup> Nowadays scientists have been exploiting this challenging field to synthesize ternary compounds at low temperatures and control their size in the nano-range.<sup>8</sup> Beside the gas-phase deposition methods (*e.g.*, sputtering,<sup>9</sup> MBE,<sup>10</sup> MOCVD<sup>11</sup>), some solution routes, such as solvothermal method,<sup>12</sup> photochemical decomposition<sup>13</sup> or wet chemical process<sup>14</sup> have also been developed. Low-temperature solution synthesis may be more attractive because the solvent and the surface stabilizing agents can play a key role in kinetically trapping metastable phases with more complex structures and compositions.<sup>15,16</sup>

I–III–VI<sub>2</sub> ternary compounds are attractive materials as active semiconductors in photovoltaic and optoelectronic applications.<sup>17,18</sup> Ternary AgInS<sub>2</sub> has a distinctive absorption in the visible and near-infrared region because of its large absorption coefficient and its band gap energy between 1.87 and 2.03 eV.<sup>19,20</sup> In this work, our interest in this system prompted us to explore diverse ways to synthesize AgInS<sub>2</sub> NCs. Recently we have reported one-pot colloidal synthesis of high-quality NCs of AgInS<sub>2</sub> by direct thermal decomposition of the single-source precursor [(Ph<sub>3</sub>P)<sub>2</sub>AgIn(SC(O)Ph)<sub>4</sub>], **1** in bisurfactant system.<sup>21</sup> In order to expand the synthetic methodology of AgInS<sub>2</sub>, we have now investigated dual- and

multiple-source methods using a number of simple inorganic compounds. The details are discussed below.

## Experimental

### Synthesis of precursors

All the solvents and chemicals, unless stated otherwise, were commercially available and used as received. [(Ph<sub>3</sub>P)<sub>2</sub>AgIn(SC(O)Ph)<sub>4</sub>], **1**, [Ag(SC(O)Ph)], **2**, [Et<sub>3</sub>NH][In(SC(O)Ph)<sub>4</sub>], **3**, and (PPh<sub>3</sub>)<sub>2</sub>AgCl were synthesized according to reported methods.<sup>22–24</sup>

[In(bipy)(SC(O)Ph)<sub>3</sub>], **4**, was synthesized as follows: sodium thiobenzoate, PhC(O)S<sup>−</sup>Na<sup>+</sup>, was obtained by reacting NaOH (0.06 g, 1.5 mmol) with 176 μL of PhC(O)SH in 15 mL of EtOH. To this clear yellow solution, 2,2′-bipyridyl (bipy, 0.08 g, 0.5 mmol) and then InCl<sub>3</sub> (0.11 g, 0.5 mmol) in 10 mL of EtOH were added. A creamy yellow precipitate was formed and the contents were stirred for 30 min. Light yellow [In(bipy)(SC(O)Ph)<sub>3</sub>], **4**, was separated by filtration and the product was rinsed with EtOH, H<sub>2</sub>O and dried *in vacuo*. Yield: 0.28 g (83%). Anal (%). Calc. for [In(bipy)(SC(O)Ph)<sub>3</sub>] (Mol wt. 682.55): C, 54.55; H, 3.40; N, 4.10; S, 14.09. Found: C, 54.04; H, 3.51; N, 4.01; S, 14.19. <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): for 2,2′-bipyridyl: 7.62–7.66 (2H, 4,4′), 8.25–8.28 (2H, 6,6′), 9.48–9.50 (2H, 3,3′); for thiobenzoate anion: 7.26–7.32 (6H, *m*), 7.40–7.44 (3H, *p*), 8.04–8.11 (8H, overlapped with 6H from *o* of thiobenzoic ligand and 2H from 5,5′ of bipyridyl). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, CDCl<sub>3</sub>): for thiobenzoate anion: 128.0 (C<sub>2/6</sub> or C<sub>3/5</sub>), 128.9 (C<sub>2/6</sub> or C<sub>3/5</sub>), 139.9 (C<sub>4</sub>), 143.5 (C<sub>1</sub>); for 2,2′-bipyridyl: 121.4 (6,6′), 126.6 (4,4′), 132.3 (5,5′), 149.1 (3,3′), 156.5 (1,1′).

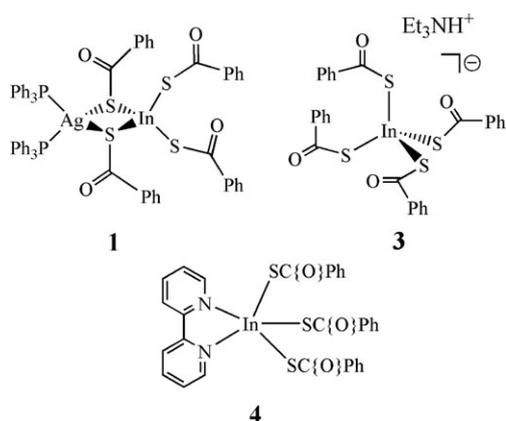
Molecular structure diagrams of **1**, **3** and **4** are shown in Scheme 1.

### Synthesis of nanocrystals

The precursors [Ag(SC(O)Ph)], **2**, (13 mg, 0.051 mmol) and [In(bipy)(SC(O)Ph)<sub>3</sub>], **4**, (35 mg, 0.051 mmol) were added to

Department of Chemistry, National University of Singapore, Singapore 117543. E-mail: chmjv@nus.edu.sg

† Electronic supplementary information (ESI) available: Experimental details, EDX analysis spectrum and XRPD patterns. See DOI: 10.1039/b707960e



**Scheme 1** Molecular structure diagrams of **1**, **3** and **4**.

dodecanethiol (DT,  $C_{12}H_{25}SH$ , Aldrich, 2.55 mmol, 0.61 mL) and oleic acid (OA,  $C_{17}H_{33}COOH$ , Aldrich, 1.83 mL) at room temperature (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  $\sim 70$  °C and then an excess of EtOH was added, and a dark red flocculent precipitate was formed which was separated by centrifugation, washed with EtOH and dried *in vacuo*. This can be easily redispersed in solvents such as toluene, chloroform and hexane. For multiple-source methods, a similar synthetic strategy was applied.<sup>25</sup>

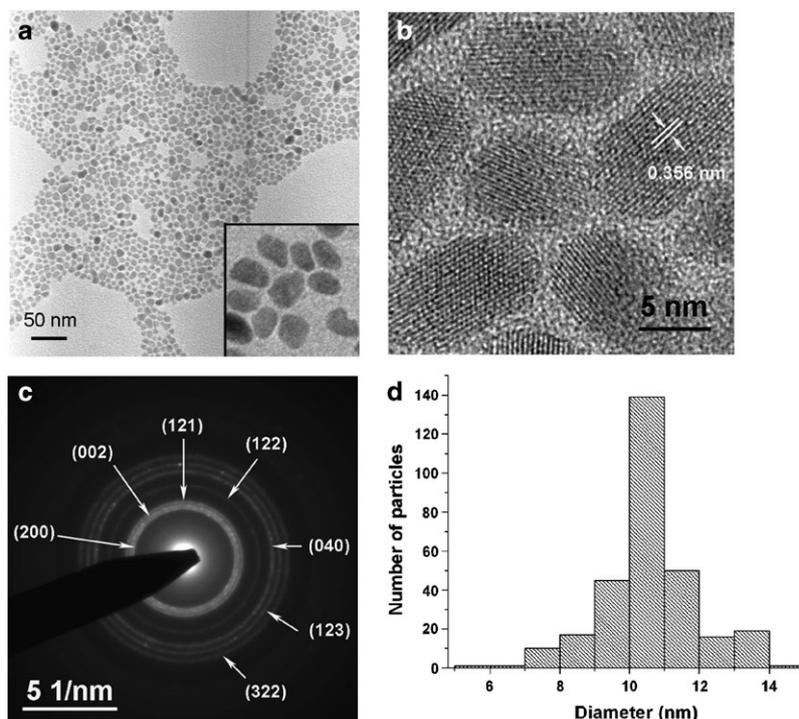
#### Measurements

The microanalytical laboratory at the Department of Chemistry, National University of Singapore performed the microanalysis. The yields were calculated with respect to the indium

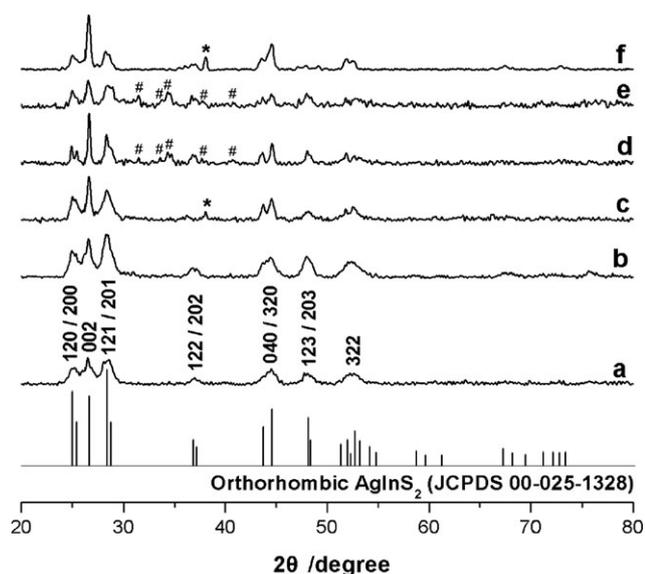
salt.  $^1H$  and  $^{13}C\{^1H\}$  NMR were recorded on a Bruker ACF 300 MHz instrument with TMS as internal reference at 25 °C. X-Ray powder diffraction (XRPD) patterns were obtained using a D5005 Bruker X-ray diffractometer equipped with Cu-K $\alpha$  radiation. An accelerating voltage and current of 40 kV and 40 mA, respectively, and scan speed of  $0.012^\circ s^{-1}$  were employed. Transmission electron microscopy (TEM) was performed on a Philips CM 10 microscope operating at 100 kV. High resolution transmission electron microscopy (HRTEM) images and electron diffraction patterns were obtained from a JEOL JSM-3010 instrument.

## Results and discussion

As-synthesized  $AgInS_2$  NCs from precursors, **2** and **4**, were characterized by TEM, as shown in Fig. 1. Fig. 1(a) reveals that NCs have polyhedral shapes and narrow size distribution (see histogram in Fig. 1(d)), which are comparable with  $AgInS_2$  NCs by single-source method.<sup>21</sup> The mean diameter of the individual NCs is measured to be  $10.9 \pm 1.3$  nm (based on 300 particles from the TEM image). The clear lattice fringes of NCs in Fig. 1(b) show that individual NCs are single crystals. The width of 0.356 nm from neighboring lattice fringes corresponds to plane (120) of  $AgInS_2$ . The strong ring patterns from selected area electron diffraction (SAED) given in Fig. 1(c) can be well indexed to the orthorhombic phase  $AgInS_2$  (JCPDS 00-025-1328). The XRPD data is given in the spectrum of Fig. 2(a). Energy dispersive X-ray (EDX) analysis of NCs in the electron microscope showed the ratio of Ag, In and S is 1 : 1.05 : 2.18.<sup>25</sup> The morphology and quality of NCs are very similar to that obtained from **1**.<sup>21</sup>

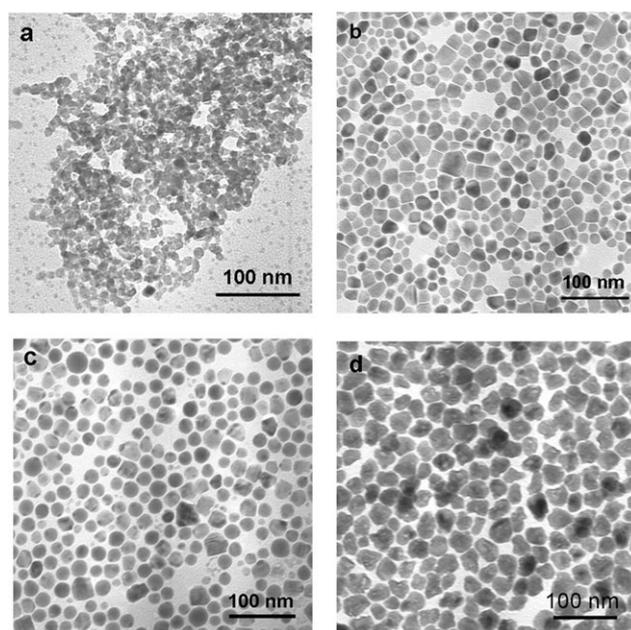


**Fig. 1** (a) Typical TEM images of  $AgInS_2$  NCs produced from **2** and **4** in DT and OA at 200 °C for 2 h (molar ratio of precursor : DT = 1 : 50; volume ratio of DT : OA = 1 : 3), (b) HRTEM images, (c) SAED pattern and (d) histogram of the  $AgInS_2$  NCs.



**Fig. 2** Typical XRPD patterns of  $\text{AgInS}_2$  prepared from (a) **2** and **4** in DT and OA at  $200^\circ\text{C}$  for 2 h (molar ratio of precursor : DT = 1 : 50; volume ratio of DT : OA = 1 : 3); (b) **2** and **3**; (c)  $(\text{PPh}_3)_2\text{AgCl}$ ,  $\text{InCl}_3$ ,  $\text{PhCOS}^-\text{H}$  and  $\text{NaOH}$ ; (d)  $(\text{PPh}_3)_2\text{AgCl}$ ,  $\text{InCl}_3$  and  $\text{PhCOS}^-\text{H}$ ; (e)  $\text{AgCl}$ ,  $\text{InCl}_3$  and  $\text{S}$  in oleylamine; (f)  $\text{AgCl}$ ,  $\text{InCl}_3$  and thiourea in oleylamine. The experimental conditions for (b)–(f) are otherwise similar to that for (a). \* Corresponds to peak of  $\text{Ag}$  (JCPDS 00-001-1167) and # corresponds the peak of  $\text{Ag}_2\text{S}$  (JCPDS 00-009-0422).

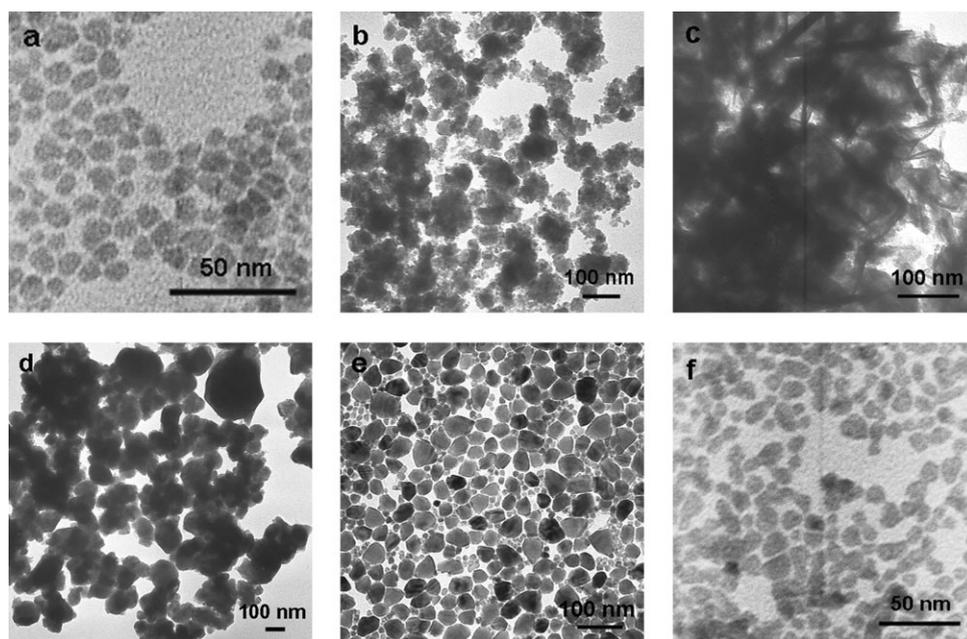
XRPD patterns of  $\text{AgInS}_2$  NCs prepared by dual and multiple sources are shown in Fig. 2. Fig. 2(a) shows the XRPD patterns of  $\text{AgInS}_2$  NCs prepared from **2** and **4** in DT and OA at  $200^\circ\text{C}$  for 2 h. All the observed peaks can be indexed to the orthorhombic phase of  $\text{AgInS}_2$  (JCPDS 00-025-1328). Peaks are slightly broadened with decreasing nanocrystal size. Fig. 2(b) shows the XRPD patterns of  $\text{AgInS}_2$  NCs prepared from **2** and **3** revealing pure orthorhombic phase  $\text{AgInS}_2$  NCs. The TEM image of these NCs as shown in Fig. 3(a) reveals that the nanosize particles are agglomerated. The ionic precursor **3** may have affected the capping by the surfactants on the formed NCs. We propose that the dual- or multiple-source precursors react to form an intermediate similar to the single molecular precursor **1** and then decomposed to the corresponding  $\text{AgInS}_2$  NCs. However Qian and co-workers<sup>26</sup> have proposed that nucleophilic attack by ethylenediamine at the thione carbon atoms of metal diethyldithiocarbamates generates compounds with inorganic cores  $[\text{InS}_{1.5}]$  and  $[\text{Cu}_2\text{S}_2]$ , and then they combine stoichiometrically with each other producing  $\text{CuInS}_2$  grains. The dual-source method has prompted us to widen the synthetic route to multiple-source methods. Experimental results have shown that when mixtures of  $(\text{PPh}_3)_2\text{AgCl}$ ,  $\text{InCl}_3$ ,  $\text{PhCOS}^-\text{H}$  and  $\text{NaOH}$  were heated with bisurfactants,  $\text{AgInS}_2$  NCs were obtained as major product;  $\text{Ag}$  was an impurity according to the XRPD pattern as shown in Fig. 2(c). A small amount of  $\text{Ag}$  may come from direct decomposition of  $(\text{PPh}_3)_2\text{AgCl}$ . Fig. 3(b) shows that the obtained NCs have a diameter of  $18.0 \pm 2.7$  nm. On the contrary, mixtures of  $(\text{PPh}_3)_2\text{AgCl}$ ,  $\text{InCl}_3$  and  $\text{PhCOS}^-\text{H}$  without  $\text{NaOH}$  can only produce bulk  $\text{AgInS}_2$  with  $\text{Ag}_2\text{S}$  impurity (XRPD pattern in Fig. 2(d)). It is presumed



**Fig. 3** Typical TEM images of  $\text{AgInS}_2$  NCs prepared in DT and OA at  $200^\circ\text{C}$  for 2 h (molar ratio of precursor : DT = 1 : 50; volume ratio of DT : OA = 1 : 3) from (a) **2** and **3**; (b)  $(\text{PPh}_3)_2\text{AgCl}$ ,  $\text{InCl}_3$ ,  $\text{PhCOS}^-\text{H}$  and  $\text{NaOH}$ ; (c)  $\text{AgCl}$ ,  $\text{InCl}_3$  and  $\text{S}$  in oleylamine; (d)  $\text{AgCl}$ ,  $\text{InCl}_3$  and thiourea in oleylamine.

that in the absence of  $\text{NaOH}$ , both  $\text{Cl}^-$  and  $\text{PhCOS}^-$  may compete to bridge  $\text{Ag}$  to form  $[(\text{Ph}_3\text{P})_2\text{Ag}(\mu\text{-Cl}_x)(\mu\text{-SCOPh})_{2-x}\text{In}(\text{SC}\{\text{O}\}\text{Ph})_2]$  which can easily dissociate to form  $[(\text{Ph}_3\text{P})_2\text{Ag}(\text{SC}\{\text{O}\}\text{Ph})]$  and further decompose to  $\text{Ag}_2\text{S}$ , thus accounting for  $\text{Ag}_2\text{S}$  as impurity. On the other hand facile formation of a heterobimetallic thiobenzoate intermediate similar to **1** can occur from the precursors  $[\text{In}(\text{bipy})(\text{SC}\{\text{O}\}\text{Ph})_3]$  or  $[\text{Et}_3\text{NH}][\text{In}(\text{SC}\{\text{O}\}\text{Ph})_4]$  and  $[\text{Ag}(\text{SC}\{\text{O}\}\text{Ph})]$  at the first stage of reaction, compared to the multiple-source methods.

According to the papers published by Qian and co-workers, mixtures of  $\text{In}(\text{S}_2\text{CNET}_2)_3$  and  $\text{Cu}(\text{S}_2\text{CNET}_2)_2$  or  $\text{Ag}(\text{S}_2\text{CNET}_2)$  have been used for  $\text{CuInS}_2$  and  $\text{AgInS}_2$  nanorods in solvothermal processes.<sup>26</sup> This group has also developed the solvothermal synthesis of  $\text{AgGaS}_2$  and  $\text{AgInS}_2$  using  $\text{AgCl}$ ,  $\text{Ga}$  (or  $\text{In}$ ) and  $\text{S}$  as the reactants<sup>27</sup> and hydrothermal synthesis of  $\text{AgInS}_2$  by using  $\text{AgCl}$ ,  $\text{InCl}_3$  and thiourea as starting materials.<sup>28</sup> while our results show that under normal atmospheric pressure, a mixture of  $\text{AgCl}$ ,  $\text{InCl}_3$  and  $\text{S}$  upon heating with oleylamine produced  $\text{AgInS}_2$  NCs as well as  $\text{Ag}_2\text{S}$  impurity (Fig. 2(e)). Fig. 3(c) shows that the obtained NCs are more spherical with diameter of  $22.0 \pm 2.9$  nm. When  $\text{AgCl}$ ,  $\text{InCl}_3$  and thiourea were mixed under similar experimental conditions, the major product is  $\text{AgInS}_2$  NCs with  $\text{Ag}$  impurity (Fig. 2(f)). Fig. 3(d) shows that the obtained NCs have diameter of  $32.1 \pm 3.5$  nm. On the contrary, when bisurfactants (DT and OA) were employed for this multiple-source synthesis, there is no formation of  $\text{AgInS}_2$ .<sup>25</sup> Obviously oleylamine plays a key role in this synthesis. It was found that amine could lower reaction temperature and facilitate the formation of nanoparticles.<sup>29</sup> In conclusion, among all the



**Fig. 4** Typical TEM images of AgInS<sub>2</sub> NCs prepared from (a) **2** and **4** in DT at 200 °C for 2 h (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 (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 (molar ratio of precursor : DT = 1 : 50; volume ratio of DT : OA = 1 : 3); (f) **2** and **4** in DT and OA at 250 °C for 2 h.

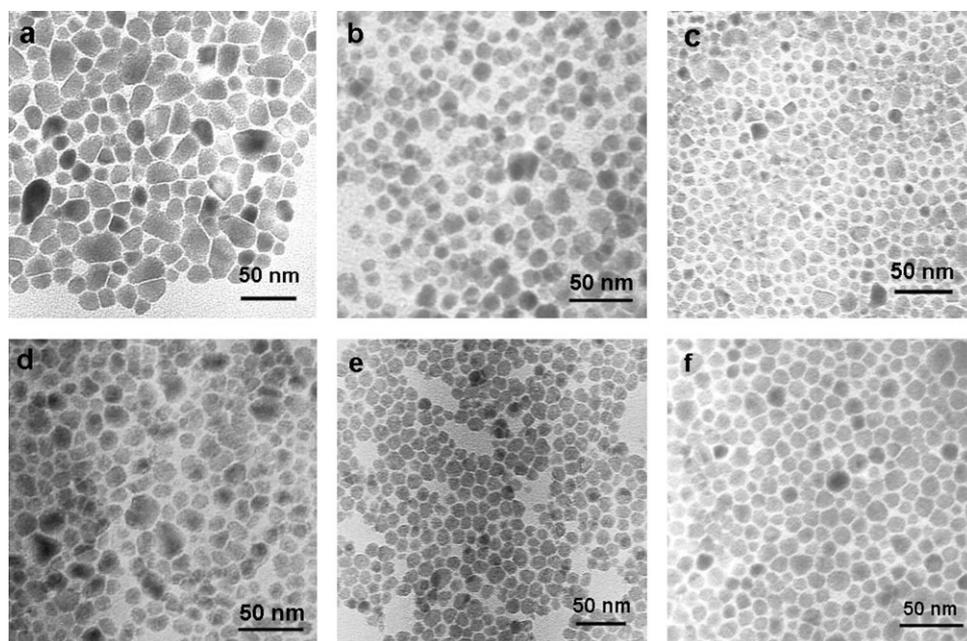
above dual- or multiple-source methods, **2** and **4** are the best combination to synthesize AgInS<sub>2</sub> NCs.

Guided by these results, [In(bipy)(SC(O)Ph)<sub>3</sub>] and [Ag(SC(O)Ph)] have been chosen to prepare AgInS<sub>2</sub> NCs and the effect of the reaction conditions on the size and morphology of NCs have been investigated. When the ratio of DT to OA was varied from 2 : 1 to 1 : 1, 1 : 3 and 1 : 6, there

is no obvious effect on the size and morphology of the obtained AgInS<sub>2</sub> NCs.

#### AgInS<sub>2</sub> NCs

When DT alone was used as the capping agent, AgInS<sub>2</sub> NCs with diameter  $8.4 \pm 1.2$  nm were formed, which are different



**Fig. 5** Typical TEM images of AgInS<sub>2</sub> NCs prepared from **2** and **4** at 200 °C for 2 h (molar ratio of precursor : surfactant = 1 : 50 : 50) in (a) DT + TOPO ( $20.5 \pm 5.6$  nm); (b) oleylamine + TOPO ( $13.7 \pm 3.0$  nm); (c) oleylamine + DT ( $8.3 \pm 0.9$  nm); (d) oleylamine + OA ( $16.5 \pm 4.8$  nm); (e) oleylamine ( $14.1 \pm 1.2$  nm); (f) HDA + TOPO ( $12.0 \pm 1.7$  nm).

from agglomerated product obtained from **1**.<sup>21</sup> The AgInS<sub>2</sub> NCs prepared by the above two different methods are shown in Fig. 4(a) and (b), respectively. They indicate that dual-source method does not rely on the bisurfactant system so much as compared to the single-source precursor method. The use of OA alone in both cases, however, resulted in micrometer sized AgInS<sub>2</sub> particles (Fig. 4(c) and (d)). A reaction temperature range from 125–250 °C was found to be suitable for the production of uniform AgInS<sub>2</sub> NCs in both cases. The AgInS<sub>2</sub> NCs prepared from **1** at 250 °C were of polyhedral shape with wider size distribution (Fig. 4(e)) while the NCs prepared from **2** and **4** at 250 °C were of irregular shape with size of 11.4 ± 3.7 nm (Fig. 4(f)). These results infer that the NCs prepared from **1** at 250 °C may have undergone Ostwald ripening. Larger nanocrystals (44.4 ± 8.4 nm) were formed when many small nanocrystals (12.0 ± 2.6 nm) dissolved back and slowly disappeared, while the NCs prepared from **2** and **4** at 250 °C seem to be a kinetically trapped product. This may be due to the two-step formation of AgInS<sub>2</sub> NCs from the dual-source precursor system. For all the samples discussed above, the XRPD patterns show orthorhombic phase AgInS<sub>2</sub> (JCPDS 00-025-1328).<sup>25</sup>

When the time duration of the reaction varies from 2 to 16 h, there is no change in the size or shape of the AgInS<sub>2</sub> NCs formed. In the presence of other surfactant systems such as DT + trioctylphosphine oxide (TOPO), oleylamine + TOPO, oleylamine + DT, oleylamine + OA, oleylamine, and hexadecylamine (HDA) + TOPO, the final particles have similar polyhedral shape, as observed in separate experiments. It was found that when long-chain amine was used as capping agent, smaller size particles were obtained. The TEM images are displayed in Fig. 5. The XRPD patterns show all the products are orthorhombic phase AgInS<sub>2</sub> (JCPDS 00-025-1328).<sup>25</sup>

## Conclusions

We have successfully synthesized high-quality NCs of AgInS<sub>2</sub> from dual-source precursors [In(bipy)(SC(O)Ph)<sub>3</sub>] or [Et<sub>3</sub>NH][In(SC(O)Ph)<sub>4</sub>], and [Ag(SC(O)Ph)]. The synthetic routes to the ternary system have been extended and the quality of AgInS<sub>2</sub> NCs obtained from dual- or multiple-source methods has been compared. In other words, low-temperature synthetic routes for AgInS<sub>2</sub> NCs have been successfully employed and size control has been accomplished by using dual- and multi-source molecular precursors. All these NCs can be dispersed freely in toluene, chloroform or hexane, which enable investigation of physical properties in solution. In all the dual- and multiple-source methods, a heterobimetallic thiobenzoate intermediate similar to single molecular precursor **1** is proposed to have formed and decompose to AgInS<sub>2</sub> NCs.

## Acknowledgements

We would like to thank NUS (Grant No. R-143-000-283-112) for their generous financial support. We thank Mr Liu Binghui for the HRTEM images.

## References

- N. Miura, H. Matsumoto and R. Nakano, *Oyo Butsuri*, 2005, **74**, 617.
- N. L. Zeng and W. H. Lee, *Phys. Rev. B*, 2002, **66**, 092503.
- T. He, Q. Huang, A. P. Ramirez, Y. Wang, K. A. Regan, N. Rogado, M. A. Hayward, M. K. Haas, J. S. Slusky, K. Inumara, H. W. Zandbergen, N. P. Ong and R. J. Cava, *Nature*, 2001, **411**, 54.
- W. Bensch, B. Sander, C. Nather, R. K. Kremer and C. Ritter, *Solid State Sci.*, 2001, **3**, 559.
- N. Tateiwa, N. Kimura, H. Aoki and T. Komatsubara, *J. Phys. Soc. Jpn.*, 2000, **69**, 1517.
- L. I. Berger and V. D. Prochukhan, *Ternary Diamond-like Semiconductors*, New York, Consultants Bureau, New York, 1969.
- T. J. Coutts, *Current Topics in Photovoltaics*, ed. J. D. Meakin, Academic Press, London, 1985.
- H. Nakamura, W. Kato, M. Uehara, K. Nose, T. Omata, S. Otsuka-Yao-Matsuo, M. Miyazaki and H. Maeda, *Chem. Mater.*, 2006, **18**, 3330.
- L. C. Yang, *J. Cryst. Growth*, 2006, **294**, 202.
- K. Sato, T. Ishibashi, K. Minami, H. Yuasa, J. Jogo, T. Nagatsuka, A. Mizusawa, Y. Kangawa and A. Koukitu, *J. Phys. Chem. Solids*, 2005, **66**, 2030.
- J. H. Park, M. Afzaal, M. Kemmler, P. O'Brien, D. J. Otway, J. Raftery and J. Waters, *J. Mater. Chem.*, 2003, **13**, 1942.
- X. Gou, F. Cheng, Y. Shi, L. Zhang, S. Peng, J. Chen and P. Shen, *J. Am. Chem. Soc.*, 2006, **128**, 7222.
- J. J. Nairn, P. J. Shapiro, B. Twamley, T. Pounds, R. von Wandruszka, T. R. Fletcher, M. Williams, C. M. Wang and M. G. Norton, *Nano Lett.*, 2006, **6**, 1218.
- Q. L. Wei and J. Mu, *J. Dispersion Sci. Technol.*, 2005, **26**, 555.
- B. M. Leonard and R. E. Schaak, *J. Am. Chem. Soc.*, 2006, **128**, 11475.
- B. M. Leonard, N. S. P. Bhuvanesh and R. E. Schaak, *J. Am. Chem. Soc.*, 2005, **127**, 7326.
- J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications*, Pergamon Press, New York, 1975.
- R. W. Birkmire, in *26th IEEE Photovoltaic Specialists Conference*, Anaheim, CA, 1997, pp. 295–300.
- K. J. Hong, J. W. Jeong, T. S. Jeong, C. J. Youn, W. S. Lee, J. S. Park and D. C. Shin, *J. Phys. Chem. Solids*, 2003, **64**, 1119.
- M. Ortega-Lopez, O. Vigil-Galan, F. C. Gandarilla and O. Solorza-Feria, *Mater. Res. Bull.*, 2003, **38**, 55.
- L. Tian, H. I. Elim, W. Ji and J. J. Vittal, *Chem. Commun.*, 2006, 4276.
- V. V. Savant, J. Gopalakrishnan and C. C. Patel, *Inorg. Chem.*, 1970, **9**, 748.
- T. C. Deivaraj, M. Lin, K. P. Loh, M. Yeadon and J. J. Vittal, *J. Mater. Chem.*, 2003, **13**, 1149.
- G. A. Bowmaker, Effendy, J. V. Hanna, P. C. Healy, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1993, 1387.
- See ESI† for details.
- Y. Cui, J. Ren, G. Chen, Y. T. Qian and Y. Xie, *Chem. Lett.*, 2001, 236.
- J. Hu, Q. Lu, K. Tang, Y. Qian, G. Zhou and X. Liu, *Chem. Commun.*, 1999, 1093.
- J. Q. Hu, B. Deng, K. B. Tang, C. R. Wang and Y. T. Qian, *J. Mater. Res.*, 2001, **16**, 3411.
- M. T. Ng, C. Boothroyd and J. J. Vittal, *Chem. Commun.*, 2005, 3820.