Synthesis and characterization of ternary $AgInS_2$ nanocrystals by dual- and multiple-source methods†

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The precursors [In(bipy)(SC{O}Ph)$_3$] and [Ag(SC{O}Ph)] have been used to prepare monodispersed polyhedral shaped $AgInS_2$ 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 $AgInS_2$ 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$_3$P)$_2$AgIn(SC{O}Ph)$_4$] has been proposed to have formed which decompose subsequently to $AgInS_2$ NCs.

Introduction

Ternary compounds possess a wide variety of physical properties, including electroluminescent displays,[1] superconductivity,[2,3] and magnetic properties,[4,5] 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.[6,7] Nowadays scientists have been exploiting this challenging field to synthesize ternary compounds at low temperatures and control their size in the nano-range.[8] Beside the gas-phase deposition methods (*e.g.*, sputtering,[9] MBE,[10] MOCVD[11]), some solution routes, such as solvothermal method,[12] photochemical decomposition[13] or wet chemical process[14] 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.[15,16]

I–III–VI$_2$ ternary compounds are attractive materials as active semiconductors in photovoltaic and optoelectronic applications.[17,18] Ternary $AgInS_2$ 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.[19,20] In this work, our interest in this system prompted us to explore diverse ways to synthesize $AgInS_2$ NCs. Recently we have reported one-pot colloidal synthesis of high-quality NCs of $AgInS_2$ by direct thermal decomposition of the single-source precursor [(Ph$_3$P)$_2$AgIn(SC{O}Ph)$_4$], **1** in bisurfactant system.[21] In order to expand the synthetic methodology of $AgInS_2$, 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$_3$P)$_2$AgIn(SC{O}Ph)$_4$], **1**, [Ag(SC{O}Ph)], **2**, [Et$_3$NH][In(SC{O}Ph)$_4$], **3**, and (PPh$_3$)$_2$AgCl were synthesized according to reported methods.[22–24]

[In(bipy)(SC{O}Ph)$_3$], **4**, was synthesized as follows: sodium thiobenzoate, PhC{O}S$^-$Na$^+$, 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 $InCl_3$ (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)$_3$], **4**, was separated by filtration and the product was rinsed with EtOH, H_2O and dried *in vacuo*. Yield: 0.28 g (83%). Anal (%). Calc. for [In(bipy)(SC{O}Ph)$_3$] (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. ^{1}H NMR (δ, $CDCl_3$): 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). ^{13}C{^{1}H} NMR (δ, $CDCl_3$): for thiobenzoate anion: 128.0 ($C_{2/6}$ or $C_{3/5}$), 128.9 ($C_{2/6}$ or $C_{3/5}$), 139.9 (C_4), 143.5 (C_1); 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)$_3$], **4**, (35 mg, 0.051 mmol) were added to

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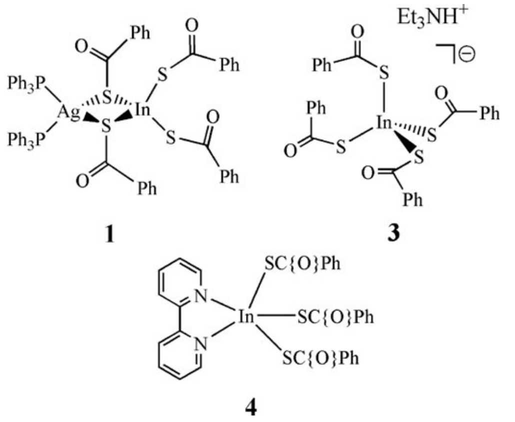

Scheme 1 Molecular structure diagrams of **1**, **3** and **4**.

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 ~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.[25]

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-Kα radiation. An accelerating voltage and current of 40 kV and 40 mA, respectively, and scan speed of 0.012° 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.[21] The mean diameter of the individual NCs is measured to be 10.9 ± 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.[25] The morphology and quality of NCs are very similar to that obtained from **1**.[21]

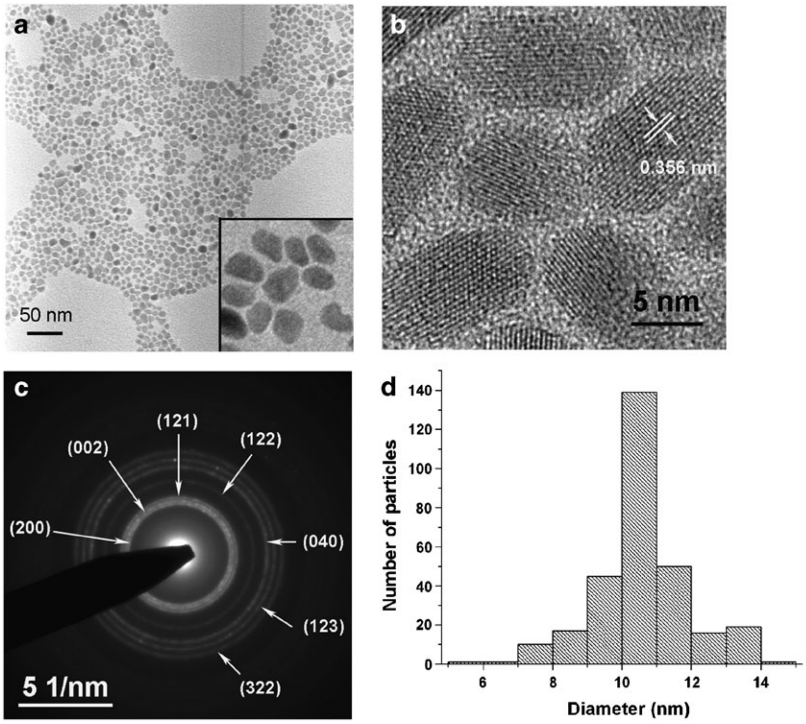

Fig. 1 (a) Typical TEM images of $AgInS_2$ NCs produced from **2** and **4** in DT and OA at 200 °C for 2 h (molar ratio of precursor : DT = 1 : 50; volume ratio of DT : OA = 1 : 3), (b) HRTEM images, (c) SAED pattern and (d) histogram of the $AgInS_2$ NCs.

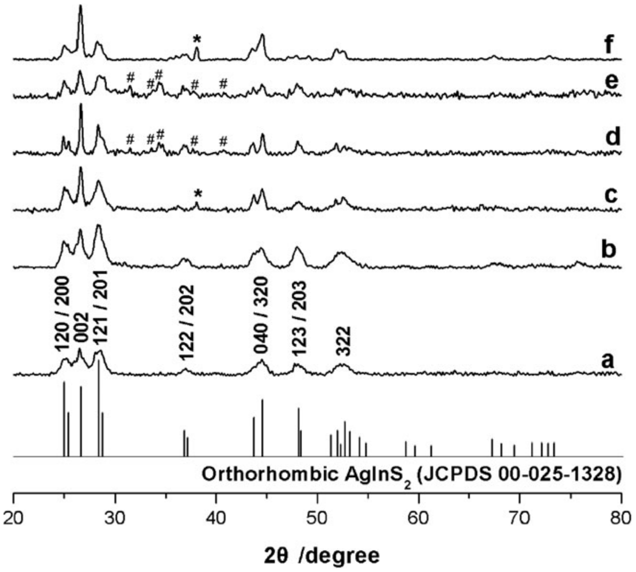

Fig. 2 Typical XRPD patterns of AgInS$_2$ prepared from (a) **2** and **4** in DT and OA at 200 °C for 2 h (molar ratio of precursor : DT = 1 : 50; volume ratio of DT : OA = 1 : 3); (b) **2** and **3**; (c) (PPh$_3$)$_2$AgCl, InCl$_3$, PhCOSH and NaOH; (d) (PPh$_3$)$_2$AgCl, InCl$_3$ and PhCOSH; (e)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

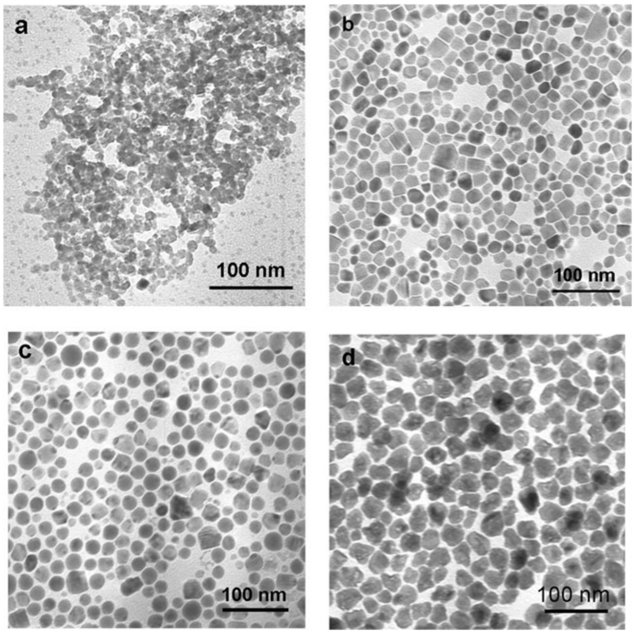

Fig. 3 Typical TEM images of AgInS$_2$ NCs prepared in DT and OA at 200 °C for 2 h (molar ratio of precursor : DT = 1 : 50; volume ratio of DT : OA = 1 : 3) from (a) **2** and **3**; (b) (PPh$_3$)$_2$AgCl, InCl$_3$, PhCOSH and NaOH; (c) AgCl, InCl$_3$ and S in oleylamine; (d) AgCl, InCl$_3$ and thiourea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

XRPD patterns of AgInS$_2$ NCs prepared by dual and multiple sources are shown in Fig. 2. Fig. 2(a) shows the XRPD patterns of AgInS$_2$ NCs prepared from **2** and **4** in DT and OA at 200 °C for 2 h. All the observed peaks can be indexed to the orthorhombic phase of AgInS$_2$ (JCPDS 00-025-1328). Peaks are slightly broadened with decreasing nanocrystal size. Fig. 2(b) shows the XRPD patterns of AgInS$_2$ NCs prepared from **2** and **3** revealing pure orthorhombic phase 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 AgInS$_2$ NCs. However Qian and co-workers[26] have proposed that nucleophilic attack by ethylenediamine at the thione carbon atoms of metal diethyldithiocarbamates generates compounds with inorganic cores [InS$_{1.5}$] and [Cu$_2$S$_2$], and then they combine stoichiometrically with each other producing 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 (PPh$_3$)$_2$AgCl, InCl$_3$, PhCOSH and NaOH were heated with bisurfactants, AgInS$_2$ NCs were obtained as major product; Ag was an impurity according to the XRPD pattern as shown in Fig. 2(c). A small amount of Ag may come from direct decomposition of (PPh$_3$)$_2$AgCl. Fig. 3(b) shows that the obtained NCs have a diameter of 18.0 ± 2.7 nm. On the contrary, mixtures of (PPh$_3$)$_2$AgCl, InCl$_3$ and PhCOSH without NaOH can only produce bulk AgInS$_2$ with Ag$_2$S impurity (XRPD pattern in Fig. 2(d)). It is presumed that in the absence of NaOH, both Cl$^-$ and PhCOS$^-$ may compete to bridge Ag to form [(Ph$_3$P)$_2$Ag(μ-Cl$_x$)(μ-SCOPh)$_{2-x}$In(SC{O}Ph)$_2$] which can easily dissociate to form [(Ph$_3$P)$_2$Ag(SC{O}Ph)] and further decompose to Ag$_2$S, thus accounting for Ag$_2$S as impurity. On the other hand facile formation of a heterobimetallic thiobenzoate intermediate similar to **1** can occur from the precursors [In(bipy)(SC{O}Ph)$_3$] or [Et$_3$NH][In(SC{O}Ph)$_4$ and [Ag(SC{O}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 In(S$_2$CNEt$_2$)$_3$ and Cu(S$_2$CNEt$_2$)$_2$ or Ag(S$_2$CNEt$_2$) have been used for CuInS$_2$ and AgInS$_2$ nanorods in solvothermal processes.[26] This group has also developed the solvothermal synthesis of AgGaS$_2$ and AgInS$_2$ using AgCl, Ga (or In) and S as the reactants[27] and hydrothermal synthesis of AgInS$_2$ by using AgCl, InCl$_3$ and thiourea as starting materials.[28] while our results show that under normal atmospheric pressure, a mixture of AgCl, InCl$_3$ and S upon heating with oleylamine produced AgInS$_2$ NCs as well as Ag$_2$S impurity (Fig. 2(e)). Fig. 3(c) shows that the obtained NCs are more spherical with diameter of 22.0 ± 2.9 nm. When AgCl, InCl$_3$ and thiourea were mixed under similar experimental conditions, the major product is AgInS$_2$ NCs with Ag impurity (Fig. 2(f)). Fig. 3(d) shows that the obtained NCs have diameter of 32.1 ± 3.5 nm. On the contrary, when bisurfactants (DT and OA) were employed for this multi-source synthesis, there is no formation of AgInS$_2$.[25] Obviously oleylamine plays a key role in this synthesis. It was found that amine could lower reaction temperature and facilitate the formation of nanoparticles.[29] In conclusion, among all the

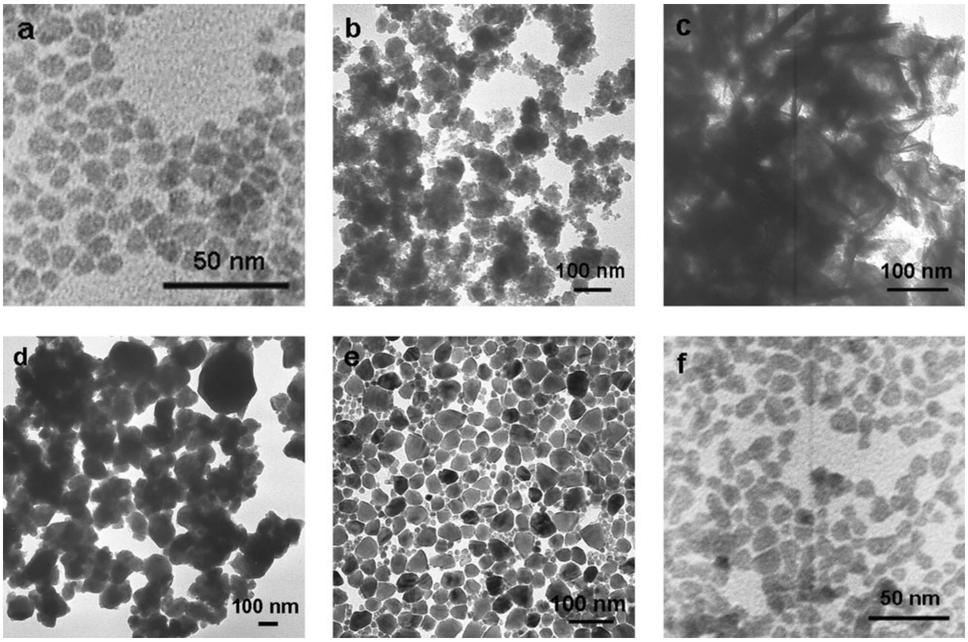

Fig. 4 Typical TEM images of $AgInS_2$ NCs prepared from (a) **2** and **4** in DT at 200 °C for 2 h (molar ratio of precursor : DT = 1 : 50); (b) **1** in DT at 200 °C for 2 h; (c) **2** and **4** in OA at 200 °C for 2 h (molar ratio of precursor : OA = 1 : 50); (d) **1** in OA at 200 °C for 2 h; (e) **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 $AgInS_2$ NCs.

Guided by these results, [In(bipy)(SC{O}Ph)$_3$] and [Ag(SC{O}Ph)] have been chosen to prepare $AgInS_2$ 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 $AgInS_2$ NCs.

$AgInS_2$ NCs

When DT alone was used as the capping agent, $AgInS_2$ NCs with diameter 8.4 ± 1.2 nm were formed, which are different

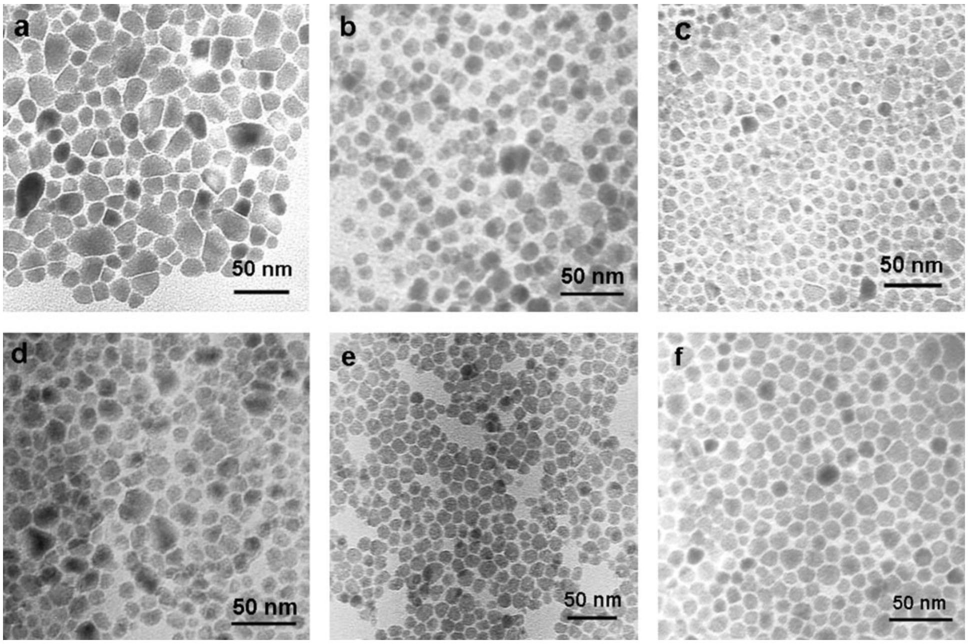

Fig. 5 Typical TEM images of $AgInS_2$ NCs prepared from **2** and **4** at 200 °C for 2 h (molar ratio of precursor : surfactant = 1 : 50 : 50) in (a) DT + TOPO (20.5 ± 5.6 nm); (b) oleylamine + TOPO (13.7 ± 3.0 nm); (c) oleylamine + DT (8.3 ± 0.9 nm); (d) oleylamine + OA (16.5 ± 4.8 nm); (e) oleylamine (14.1 ± 1.2 nm); (f) HDA + TOPO (12.0 ± 1.7 nm).

from agglomerated product obtained from **1**.[21] The $AgInS_2$ 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 $AgInS_2$ particles (Fig. 4(c) and (d)). A reaction temperature range from 125–250 °C was found to be suitable for the production of uniform $AgInS_2$ NCs in both cases. The $AgInS_2$ 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 $AgInS_2$ NCs from the dual-source precursor system. For all the samples discussed above, the XRPD patterns show orthorhombic phase $AgInS_2$ (JCPDS 00-025-1328).[25]

When the time duration of the reaction varies from 2 to 16 h, there is no change in the size or shape of the $AgInS_2$ 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 $AgInS_2$ (JCPDS 00-025-1328).[25]

Conclusions

We have successfully synthesized high-quality NCs of $AgInS_2$ from dual-source precursors [In(bipy)(SC{O}Ph)$_3$] or [Et$_3$NH][In(SC{O}Ph)$_4$], and [Ag(SC{O}Ph)]. The synthetic routes to the ternary system have been extended and the quality of $AgInS_2$ NCs obtained from dual- or multiple-source methods has been compared. In other words, low-temperature synthetic routes for $AgInS_2$ 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 $AgInS_2$ NCs.

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