

Shape and size control of Ag₂Se nanocrystals from a single precursor [(Ph₃P)₃Ag₂(SeC{O}Ph)₂][†]

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Monodispersed Ag₂Se nanocubes and faceted nanocrystals have been synthesized by hexadecylamine (HDA) induced thermolysis of [(PPh₃)₃Ag₂(SeC{O}Ph)₂] in a mixture of TOP (tri-*n*-octyl phosphine) and HDA in the temperature range 95–180 °C.

Nanoparticles with different morphologies are of great interest and importance, as different particle shapes can introduce electronic, optical and magnetic properties that are different from those observed in their spherical counterparts.¹ For this reason morphology control of nanoparticles has been the subject of much interest for modifying the properties of materials. To date, semiconductor nanoparticles of various shapes (triangles, rods, cubes, arrows and tetrapods)² have been successfully synthesized by solution methods employing appropriate capping agents.

The low phase transition temperature makes silver selenide an interesting metal selenide with many useful properties.³ Its high-temperature phase (β-Ag₂Se, >133 °C) is a superionic conductor that is useful as a solid electrolyte in photochargeable secondary batteries. The low-temperature phase (α-Ag₂Se) is a narrow band-gap semiconductor, and has been widely used as a photosensitizer in photographic films or thermochromic materials. α-Ag₂Se is also a promising candidate for thermoelectric applications because of its relatively high Seebeck coefficient (−150 μV K^{−1} at 300 K), low lattice thermal conductivity, and high electrical conductivity.⁴ A large magnetoresistance has also been reported for a non-stoichiometric derivative of this solid.⁵ Recently, Jeong and Xia have shown that the reversible phase transition associated with Ag₂Se provides a new platform for the fabrication of photonic crystals with thermally switchable stop bands.⁶ Despite the usefulness of Ag₂Se, to date there are only a few reports on the preparation of Ag₂Se nanoparticles,^{7a–c} nanowires^{7d} and nanoscale dendrites.^{7e,f} In this report, we demonstrate the one pot synthesis of structurally well defined Ag₂Se nanocubes and faceted nanocrystals under mild conditions *via* an amine mediated synthetic approach. Further, in this study, we elucidate the formation of Ag₂Se faceted nanocrystals and nanocubes based on an unprecedented intermediate product isolated from the growth

of Ag₂Se nanocubes and examine the roles of parameters critical to the formation of Ag₂Se nanoparticles.

Recently, our group have demonstrated that Cu_{2–x}Se nanoparticles can be synthesized by thermolysis of copper selenocarboxylate in trioctylphosphine oxide (TOPO)/trioctylphosphine (TOP).⁸ Here we further extend our work by using silver(I) selenocarboxylate [(PPh₃)₃Ag₂(SeC{O}Ph)₂][†] as the precursor to synthesize Ag₂Se nanoparticles. This precursor can be easily prepared (see ESI[†]) and is found to be a good source for the preparation of Ag₂Se nanoparticles. In addition, we found that this precursor decomposes rapidly in amine at room temperature and this could be due to the β-elimination reaction as suggested for the thiocarboxylate compounds by Chin *et al.*⁹ From the latter observation, it was suggested that the amine could serve as a “nucleation initiator”¹⁰ which helps to separate the nucleation and growth stages, and this is the most important criterion in obtaining monodispersed nanoparticles.¹¹ In our study, cube shaped and faceted Ag₂Se nanocrystals have been synthesized by the thermal decomposition of [(PPh₃)₃Ag₂(SeC{O}Ph)₂] in a hot solution containing capping ligands (TOP and probably HDA^{2d}) under anaerobic conditions by varying the HDA to precursor ratio, heating time and solution temperature. The influence of these conditions on the size and morphology of the prepared Ag₂Se nanocrystals is summarized in Table 1.

Table 1 Summary of the size and morphology of Ag₂Se obtained under different reaction conditions

[HDA] : [Precursor] Molar ratio	Reaction temperature/ °C	Reaction time/min	Average particle size/nm	Morphology ^{b,c}	
25 : 1	95	15 ^a	25.1 ± 3.3	CU	
		125	15 ^a	19.9 ± 2.5	Small CU
	145	60		47.6 ± 3.0	Big CU
				73.6 ± 4.6	CU
		5 ^a		22.5 ± 2.0	Small CU
				49.6 ± 2.8	CU
50 : 1	95	15	53.6 ± 4.0	CU	
		15	44.0 ± 3.7	FC & CU	
	145	5	48.5 ± 5.8	FC	
		15 ^d	11.2 ± 0.8	FC	
	125	15 ^a		17.4 ± 1.4	Small CU
				48.0 ± 2.9	Big CU
60			64.6 ± 4.3	CU	
		15	49.8 ± 3.6	CU	
165	15		36.6 ± 3.8	FC & CU	
		5	37.4 ± 4.2	FC	

^a Prolonged heating of these reactions only increased the size of the Ag₂Se nanoparticles. ^b From TEM studies. ^c FC: Faceted crystals; CU: Cubes. ^d The faceted crystals will transform into cube shaped nanocrystals after 2 h of heating.

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[†] Electronic supplementary information (ESI) available: Synthesis and structure of [(PPh₃)₃Ag₂(SeC{O}Ph)₂], TEM images of silver selenide nanoparticles prepared at 95 °C, 125 °C, 145 °C and 165 °C, XRPD spectrum of the Ag₂Se synthesized at different temperatures, DSC spectrum of the prepared Ag₂Se nanoparticles, energy-dispersive X-ray spectrum of Ag₂Se. See <http://dx.doi.org/10.1039/b506203a>

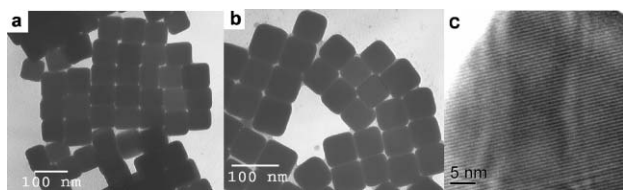


Fig. 1 TEM images of Ag_2Se nanocubes produced at $125\text{ }^\circ\text{C}$ after 60 min with $[\text{HDA}] : [\text{precursor}]$ ratios of (a) 25 and (b) 50 respectively; (c) high resolution TEM image showing the lattice fringes from a single nanocube.

TEM images of the Ag_2Se nanocubes formed at $125\text{ }^\circ\text{C}$ after 60 min of heating reveal a self-assembled close-packed monolayer array (Fig. 1a & b). Clear lattice planes visible in a high resolution TEM image (Fig. 1c) indicate good crystallinity of the particles. There was no drastic change in the morphology and only a slight change in the size of the particles when we increased the amount of HDA under the same conditions. When we raised the reaction temperature to $145\text{ }^\circ\text{C}$, a shorter reaction time (15 min) was required for Ag_2Se particles to fully evolve into nanocubes, since nuclei grow at a faster rate at higher temperature. The Ag_2Se nanocubes obtained at $145\text{ }^\circ\text{C}$ (15 min) are smaller (53.6 nm^{12a} & 49.8 nm^{12b}) than those grown at $125\text{ }^\circ\text{C}$ (60 min) due to the high nuclei concentration, as will be discussed later.

To study the growth of these nanocubes, we isolated the Ag_2Se nanocrystals before they grew into perfect cubes and two different sizes of Ag_2Se nanocubes were observed, as shown in Fig. 2. An overlap of the nucleation and growth stages is evident from this observation but it is highly unusual for aging of these poly-dispersed particles to lead to monodispersed particles. In addition, the size of the big cubes (average size distribution = 6.0%) is almost double the size of the small cubes (average size distribution = 9.8%) and both of these cubes are monodispersed with respect to their own kind. Thus, we believe this is due to the extremely slow nucleation process as compared to the growth process. For example, when we injected the precursor into the hot solution, Ag_2Se nuclei formed and instantly grew into nanocubes (big cubes as seen in Fig. 2a & b). During the growth of these nuclei, a new batch of nuclei (small cubes as seen in Fig. 2a & b) formed and grew in the same way as the first batch. As the concentration of the precursor fell below the critical threshold, the nucleation process stopped.¹¹ In our experiments, we have added TOP (a solvent to dissolve the precursor) to the reaction solution. In addition, free PPh_3 ligands will be released into the solution as the precursor decomposes. Thus, at low temperature, these phosphine ligands stabilize the precursor and hinder the degradation process, resulting in a much slower nucleation process. This ligand effect is well known in the synthesis of CdSe nanoparticles.¹³

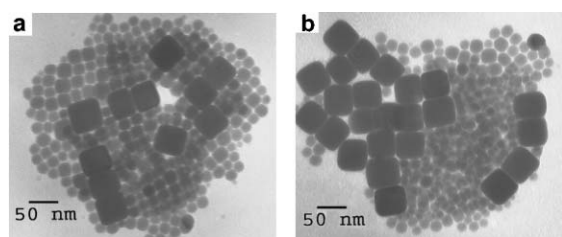


Fig. 2 TEM image of silver selenide nanocubes synthesized under same conditions as in Fig. 1a and 1b, except the growth time was shortened from 60 min to 15 min.

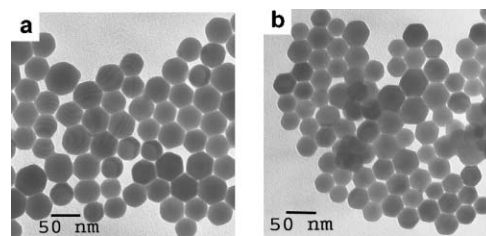


Fig. 3 TEM images of faceted Ag_2Se nanocrystals prepared at $180\text{ }^\circ\text{C}$ for 5 min with (a) $[\text{HDA}] : [\text{precursor}] = 25$; (b) $[\text{HDA}] : [\text{precursor}] = 50$.

By increasing the injection temperature to $165\text{ }^\circ\text{C}$, a mixture of faceted crystals and nanocubes is obtained (see ESI†). As we further increased the temperature to $180\text{ }^\circ\text{C}$, exclusively faceted Ag_2Se nanocrystals were observed (Fig. 3a & b). These faceted crystals self-assemble into a hexagonal closed-packed lattice on the TEM grid. Prolonged heating of these reaction mixtures did not change the particle shape and particle sizes were only slightly affected indicating that the reaction was complete within 15 min.

It is well known that amine disrupts the growth of particular crystal planes which leads to the formation of various shapes of nanoparticle.^{2b,d,e,i} However, in our case, varying the concentration of HDA doesn't change the morphology of Ag_2Se . This suggests the Ag_2Se particles have a strong tendency to form the preferred cube shaped nanoparticles and a similar phenomenon has been reported for MnS nanoparticles by Cheon and co-workers recently.^{2d} This intrinsic property of Ag_2Se is believed to be responsible for the formation of various nanoparticle shapes (see below).

In this study, we noticed that the degradation of the precursor is affected mainly by the reaction temperature and the amount of amine added. A rapid degradation occurred readily at either high temperature or high amine concentration, which would result in a high concentration of nuclei. In general, for a spherical single-phase crystal whose size is smaller than 10–20 nm, its surface must be a polyhedron containing high-index crystallographic planes.^{2g} Thus, we found that the nanoparticles obtained with high amine concentration at high temperature are mainly small faceted crystals, since more nuclei were generated under these conditions as shown in Fig. 4. In order to understand the mechanism of the shape transformation of Ag_2Se nanoparticles, we further examined a series of Ag_2Se nanocrystals isolated at $95\text{ }^\circ\text{C}$, $125\text{ }^\circ\text{C}$ and $145\text{ }^\circ\text{C}$ (see ESI†) and found that the shape of the Ag_2Se nanoparticles evolved from small faceted crystals to nanocubes. This shape transformation process further supports our suggestion that the Ag_2Se nanoparticles intrinsically grow into cube shaped crystals as discussed earlier. Overall, when there is insufficient precursor (high nuclei concentration) in the solution, the nuclei have no choice but to grow into small faceted crystals. However, when the precursor concentration is high enough (low nuclei concentration), the nuclei grew into cubes. To demonstrate the effect of nuclei concentration on the morphology of Ag_2Se , we isolated the nanoparticles at higher temperatures ($165\text{ }^\circ\text{C}$ & $180\text{ }^\circ\text{C}$) and Fig. 4 illustrates that faceted crystals are formed under these conditions.

Ag_2Se is known to exist in two phases, a cubic phase above $133\text{ }^\circ\text{C}$ and an orthorhombic phase below $133\text{ }^\circ\text{C}$.¹⁴ However, we found no difference in the room temperature XRPD patterns of the nanoparticles synthesized above and below $133\text{ }^\circ\text{C}$ (see ESI†). This indicates the phase transition of these nanoparticles is

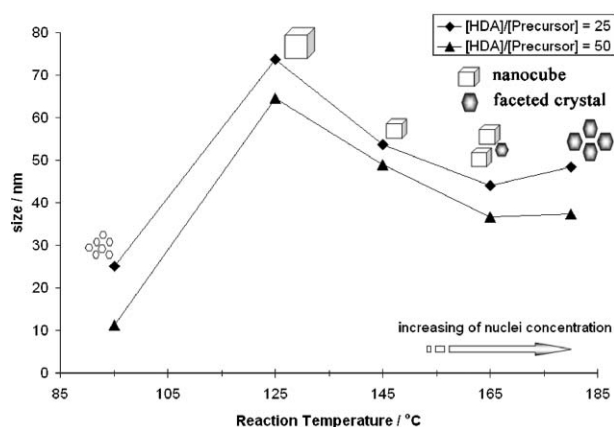


Fig. 4 Shapes and sizes of Ag_2Se nanoparticles produced under different conditions after 15 min of heating.

reversible. High-resolution TEM images of the Ag_2Se nanoparticles taken at room temperature show they are almost all single crystals, while energy-dispersive X-ray spectra (see ESI†) indicated the presence of Ag and Se atoms in all the prepared nanoparticles. The lack of any significant difference in the crystal shape and structure between particles prepared above and below the transition temperature is interesting and suggests that single-crystal cubic phase nanoparticles transform on cooling to single-crystal orthorhombic nanoparticles. It has been reported that in the bulk the transformation between these two phases is reversible.^{7b} Thus, we used DSC to investigate the transformation of the faceted and cube shaped Ag_2Se particles and our results (see ESI†) agreed with those reported for bulk Ag_2Se , where the orthorhombic phase transforms to the cubic phase upon heating and back to the orthorhombic phase while cooling.^{7b} The ease of transformation suggests that above 133 °C the particles have the cubic structure and transform to the orthorhombic structure on cooling.

In conclusion, nearly monodispersed silver selenide nanocubes and faceted crystals were prepared under mild conditions by chemical activation of a single precursor with amine. A possible growth mechanism for the observed Ag_2Se nanoparticle shapes has been elucidated based on our experimental results. We have shown that these Ag_2Se nanoparticles have a tendency to grow into cube shaped crystals. Varying the nuclei concentration by changing the reaction temperature enables us to tune the shapes of these Ag_2Se nanoparticles. Further, the size of these Ag_2Se nanoparticles can be tuned by changing the temperature and the HDA concentration. Our TEM study of Ag_2Se particles has revealed that the phase transformation has no effect on the shape or the crystallinity of the nanoparticles, which further proves that the shapes and sizes of the Ag_2Se nanoparticles are determined by well-controlled experimental conditions. The morphology of the Ag_2Se particles prepared causes them to self-assemble on TEM grids which may imply that these nanoparticles are good candidates for synthesizing photonic crystals.

Notes and references

† X-Ray crystallography: Intensity data for $[(\text{PPh}_3)_3\text{Ag}_2(\text{SeC}\{\text{O}\}\text{Ph})_2]$ were collected on a Bruker APEX diffractometer attached with a CCD detector

and graphite-monochromated $\text{MoK}\alpha$ radiation using a sealed tube (2.4 kW) at 223(2) K.¹⁵ Absorption corrections were made with the program SADABS¹⁶ and the crystallographic package SHELXTL¹⁷ was used for all calculations. Cell Data: Triclinic space group $\text{P}\bar{1}$, $a = 12.8425(5)$ Å, $b = 22.6356(9)$ Å, $c = 23.9270(9)$ Å, $\alpha = 109.383(1)^\circ$, $\beta = 96.183(1)^\circ$, $\gamma = 104.859(1)^\circ$, $V = 6198.5(4)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.495$ Mg m⁻³, $\mu = 1.928$ mm⁻¹. Final R indices [$I > 2\sigma(I)$], $R1 = 0.0533$, $wR2 = 0.1201$, R indices (all data), $R1 = 0.1067$, $wR2 = 0.1388$ GooF on F^2 , 0.985. CCDC 265722. See <http://dx.doi.org/10.1039/b506203a> for crystallographic data in CIF or other electronic format.

§ A degassed solution of $[(\text{PPh}_3)_3\text{Ag}_2(\text{SeC}\{\text{O}\}\text{Ph})_2]$ (see ESI†) (50 mg) in TOP (0.5 mL) was injected into a hot solution (95 °C/125 °C/145 °C/165 °C/180 °C) of HDA. After these components had been mixed, the pale yellow solution rapidly changed to brown. After 15 min, the reaction solution was cooled to room temperature, ca. 1 mL of toluene was added and the product was precipitated by further adding 20 mL of ethanol. The precipitate was centrifuged, washed thoroughly with 20 mL of ethanol, and dried in a vacuum overnight.

- (a) B. M. I. Van Der Zande, M. R. Bohmer, L. G. Fokkink and J. C. Schonenberger, *J. Phys. Chem. B*, 1997, **101**, 852; (b) Y.-Y. Yu, S.-S. Chang, C.-L. Lee and C. R. C. Wang, *J. Phys. Chem. B*, 1997, **101**, 6661; (c) C. Sonnichsen, T. Franzl, T. Wilk, G. Plessen, V. J. Feldmann, O. Wilson and P. Mulvaney, *Phys. Rev. Lett.*, 2002, **88**, 77402.
- (a) X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich and A. P. Alivisatos, *Nature*, 2000, **404**, 59; (b) Y.-W. Jun, S.-M. Lee, N.-J. Kang and J. Cheon, *J. Am. Chem. Soc.*, 2001, **123**, 5150; (c) L. Manna, D. J. Milliron, A. Meisel, E. C. Scher and A. P. Alivisatos, *Nat. Mater.*, 2003, **2**, 382; (d) Y.-W. Jun, Y.-Y. Jung and J. Cheon, *J. Am. Chem. Soc.*, 2002, **124**, 615; (e) S.-M. Lee, Y.-W. Jun, S.-N. Cho and J. Cheon, *J. Am. Chem. Soc.*, 2002, **124**, 11244; (f) T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein and M. A. El-Sayed, *Science*, 1996, **272**, 1924; (g) Z. L. Wang, *J. Phys. Chem. B*, 2000, **104**, 1153; (h) N. Pinna, K. Weiss, H.-S. Kongehl, W. Vogel, J. Urban and M. P. Pileni, *Langmuir*, 2001, **17**, 7982; (i) J. Cheon, N.-J. Kang, S.-M. Lee, J.-H. Lee, J.-H. Yoon and S. J. Oh, *J. Am. Chem. Soc.*, 2004, **126**, 1950.
- (a) M. Kobayashi, *Solid State Ionics*, 1990, **39**, 121; (b) F. Shimojo and H. Okazaki, *J. Phys. Soc. Jpn.*, 1993, **62**, 179; (c) K. L. Lewis, A. M. Pitt, T. Wyatt-Davies and J. R. Milward, *Mater. Res. Soc. Symp. Proc.*, 1994, **374**, 105; (d) S. S. P. Parkin, *Annu. Rev. Mater. Sci.*, 1995, **25**, 88.
- M. Ferhat and J. Nagao, *J. Appl. Phys.*, 2000, **88**, 813.
- R. Xu, A. Husmann, T. F. Rosenbaum, M. L. Saboungi, J. E. Enderby and P. B. Littlewood, *Nature*, 1997, **390**, 57.
- U. Jeong and Y. Xia, *Angew. Chem., Int. Ed.*, 2005, **44**, 2.
- (a) W. Wang, Y. Geng, Y. Qian, M. Ji and Y. Xie, *Mater. Res. Bull.*, 1999, **34**, 877; (b) R. Harpeness, O. Palchik, A. Gedanken, V. Palchik, S. Amiel, M. A. Slifkin and A. M. Weiss, *Chem. Mater.*, 2002, **14**, 2094; (c) Y. Cui, G. Chen, J. Ren, M. Shao, Y. Xie and Y. Qian, *J. Solid State Chem.*, 2003, **172**, 17; (d) B. Gates, Y. Wu, Y. Yin, P. Yang and Y. Xia, *J. Am. Chem. Soc.*, 2001, **123**, 11500; (e) J. Xiao, Y. Xie, R. Tang and W. Luo, *J. Mater. Chem.*, 2002, **12**, 1148; (f) S. K. Batabyal, C. Basu, A. R. Das and G. S. Sanyal, *Cryst. Growth Des.*, 2004, **4**, 509.
- Z. Lu, W. Huang and J. J. Vittal, *New J. Chem.*, 2002, **26**, 1122.
- W. P. Lim, Z. H. Zhang, H. Y. Low and W. S. Chin, *Angew. Chem., Int. Ed.*, 2004, **43**, 5685.
- (a) S. L. Li, N. Pradhan, Y. Wang and X. Peng, *Nano Lett.*, 2004, **4**, 2261; (b) Y. C. Cao and J. Wang, *J. Am. Chem. Soc.*, 2004, **126**, 14336.
- Y. Waseda, *Morphology Control of Materials and Nanoparticles*, ed. A. Muramatsu, Springer, Germany, 2004, p. 25.
- (a) [HDA] / [precursor] = 25; (b) [HDA] / [precursor] = 50.
- (a) C. R. Bullen and P. Mulvaney, *Nano Lett.*, 2004, **4**, 2303; (b) Z. A. Peng and X. Peng, *J. Am. Chem. Soc.*, 2002, **124**, 3343; (c) Z. A. Peng and X. Peng, *J. Am. Chem. Soc.*, 2001, **123**, 1389; (d) W. W. Yu, Y. A. Wang and X. Peng, *Chem. Mater.*, 2003, **15**, 4300.
- (a) T. Okabe and K. Ura, *J. Appl. Crystallogr.*, 1994, **27**, 140; (b) G. Sáfran, L. Malicskó, O. Geszti and G. Radnóczy, *J. Cryst. Growth*, 1999, **205**, 153.
- SMART & SAINT Software Reference Manuals, Version 6.22*, Bruker AXS Analytical X-Ray Systems, Inc., Madison, WI, USA, 2000.
- G. M. Sheldrick, *SADABS, Software for Empirical Absorption Correction*, University of Gottingen, Germany, 2000.
- SHELXTL Reference Manual, Version 5.1*, Bruker AXS Analytical X-Ray Systems, Inc., Madison, WI, USA, 1997.