Electronic Supporting Information

Shape and size control of Ag_2Se nanocrystals from single precursor $[(Ph_3P)_3Ag_2(SeC\{O\}Ph)_2]$

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Synthesis of $[(PPh_3)_3Ag_2(SeC\{O\}Ph)_2]$: $[(PPh_3)_2Ag(NO_3)]$[1] and sodium monoseleno-carboxylate,[2] $Na^+PhC\{O\}Se^-$ were prepared using methods reported in the literature. To the $Na^+PhC\{O\}Se^-$ (3.02 mmole) solution in 15 mL of MeCN was cooled to 0 ºC, an ice-cold solution of $(PPh_3)_2Ag(NO_3)$ (2.09 g, 3.02 mmole) in 5 mL CH_2Cl_2 was added very close to the surface using a syringe, to produce a yellow solution. This solution was stirred for 1 h and the insoluble NaCl was filtered off. The solvent from the filtrate was removed and then the yellow solid was dissolved in 10 mL of acetone, layered with ca. 20 mL of hexane and left at 5 ºC overnight to obtain a yellow microcrystalline product. The crystals were filtered and washed with MeOH and a small amount of Et_2O, and dried under nitrogen. Yield: 1.68 g (40 %). Elemental Anal: Calcd. for $Ag_2P_3Se_2C_{68}H_{55}O_2$ (mol wt 1370.76): C, 59.58; H, 4.04 %. Found C, 60.76; H, 4.03 %. ^{1}H NMR (d_6-Acetone) δ_H: 7.72 – 7.74 (4H, d, J = 6 Hz, *ortho*-proton), 7.08 – 7.13 (4H, t, J = 15 Hz, *meta*-proton), 7.24 – 7.42 (47H, m, *para*-proton and PPh_3). δ_c (d_6-Acetone): For selenobenzoate ligand: 127.12 ($C_{2/6}$ or $C_{3/5}$), 128.61 ($C_{2/6}$ or $C_{3/5}$), 131.05 (C_4), 142.94 (C_1), 201.50 (COSe). For PPh_3: 128.15 (C_3), 129.30 (C_4), 133.14 (C_1), 133.95 (C_2). δ_p (d_6-Acetone): 5.49.

References:

1. Bowmaker, G. A.; A. Effendy, H. J.; Healy, P. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc. Dalton Trans.* 1993, 1387.

2. Kato, S.; Kageyama, H.; Takagi, K.; Mizoguchi, K.; Murai, T. *J. Prakt. Chem.*1990, 332, 898.

X-Ray Crystallography: Intensity data for $[(PPh_3)_3Ag_2(SeC\{O\}Ph)_2]$ were collected on a Bruker APEX diffractometer attached with a CCD detector and graphite-monochromated MoKα radiation using a sealed tube (2.4 kW) at 223(2) K.[1] Absorption corrections were made with the program SADABS[2] and the crystallographic package SHELXTL[3] was used for all calculations. ***Cell Data***: Triclinic space group Pī, a = 12.8425(5) Å, b = 22.6356(9) Å, c = 23.9270(9) Å a= 109.3830(10)°, b= 96.1830(10)°, g = 104.8590(10)°, Volume, 6198.5(4) $Å^3$, Z, 4, D_{calc}, 1.495 Mg/m^3, μ, 1.928 mm^{-1}. Final R indices [I>2sigma(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 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

References:

1. SMART & SAINT Software Reference Manuals, Version 6.22, Bruker AXS Analytic X-ray Systems, Inc., Madison, WI, 2000.
2. G. M. Sheldrick, SADABS, Software for Empirical Absorption Correction, University of Gottingen, Germany, 2000.
3. SHELXTL Reference Manual, Version 5.1, Bruker AXS, Analytic X-Ray Systems, Inc., Madison, WI, 1997.

Figures

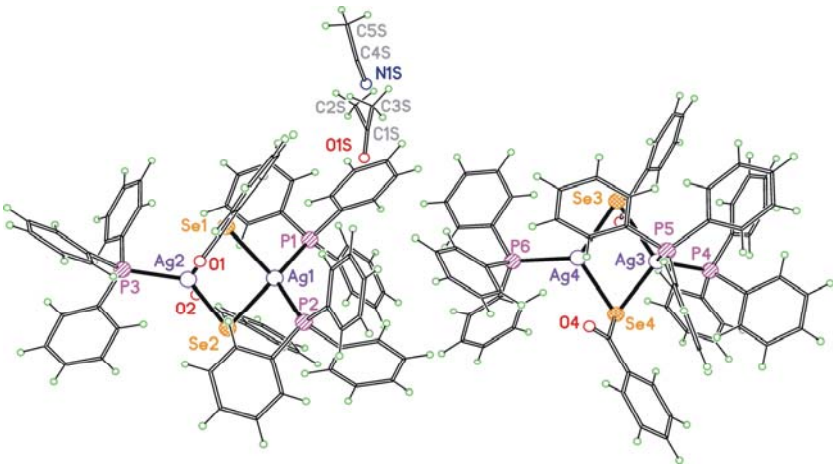

Figure S1. Crystal structure of $[(PPh_3)_3Ag_2(SeC\{O\}Ph)_2]$

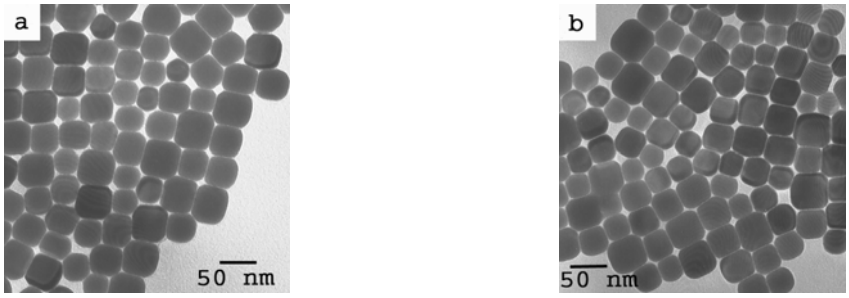

Figure S2. TEM images of Ag_2Se nanocrystals prepared at 165 °C for 15 min with a) [HDA] / [precursor] = 25; b) [HDA] / [precursor] = 50.

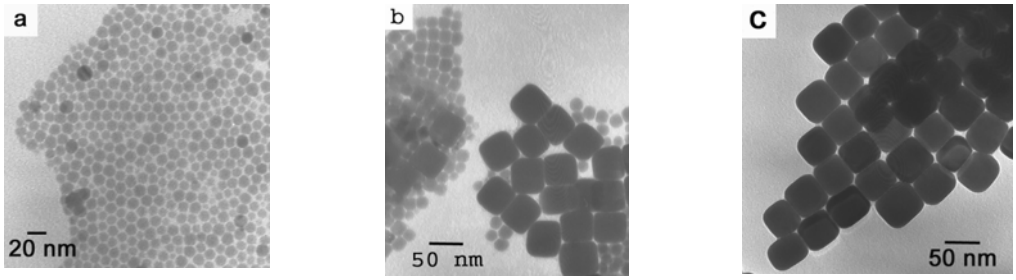

Figure S3. TEM images of silver selenide nanoparticles synthesized using an amine-to-precursor ratio of 50 after 15 min of heating at (a) 95 °C, (b) 125 °C and (c) 145 °C.

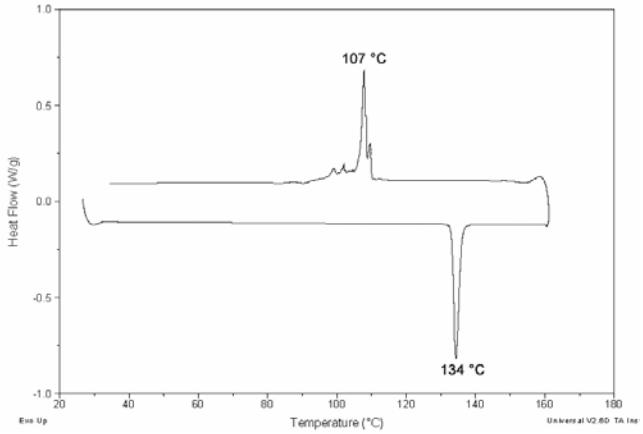

Figure S4. DSC curve of the prepared Ag_2Se nanoparticles.

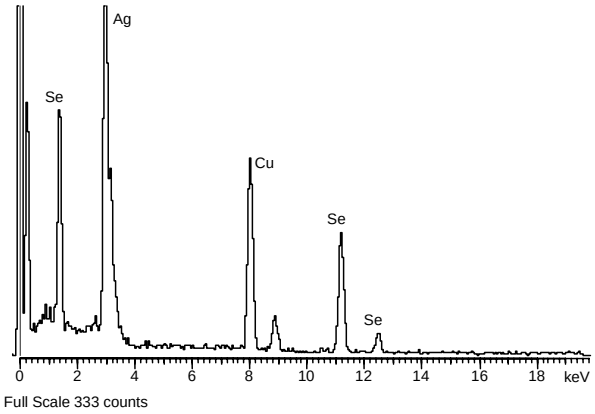

Figure S5. Energy-dispersive X-ray spectrum of Silver Selenide nanocubes prepared at 145 °C (amine-to-precursor ratio = 25). The Cu peak is from the Cu support grid.

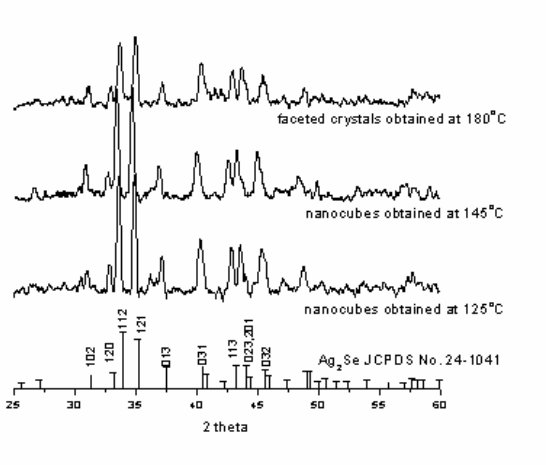

Figure S6. X-ray powder diffraction patterns obtained at room temperature from Ag_2Se nanoparticles synthesized at different temperatures.