Supplementary Information for:

Quantum Confinement in Silver Selenide Semiconductor Nanocrystals

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Chemicals:

Carbon tetrachloride (reagent grade, 99.9%), tetrachloroethylene (TCE, spectrophotometric grade, ≥99%), selenium pellets (Se, 99.999%), tri-*n*-octylphosphine oxide (TOPO, technical grade, 90%), oleyl amine (OM, technical grade, 70%), octane (reagent grade, 98%) and tri-*n*-octylphosphine (TOP, technical grade, 90%) were purchased from Sigma-Aldrich. Hexanes (ACS grade) was purchased from VWR International. Reagent alcohol (histological grade, 90% ethyl alcohol, 5% methyl alcohol, 5% butyl alcohol) and butyl alcohol were obtained from Fisher Scientific. Silver nitrate ($AgNO_3$, 99.9995%) and silver chloride (AgCl, 99.9%) were purchased from Strem Chemicals. All chemicals were used as delivered without further purification.

Experimental:

FEI Tecnai T12 and G^2 F30 transmission electron microscopes (TEM) were used to image the nanocrystals with an acceleration voltage of 120 kV and 300 kV, respectively. Films were prepared for X-ray diffraction (XRD) by drop-casting a dispersion of nanocrystals in an 8:1 hexane:octane mixture on heavily doped Si wafers covered with a thermally grown 300-nm-thick SiO_2 layer and the patterns (Cu-K_α) were collected using a Bruker-AXS microdiffractometer. Optical absorption data for the smallest nanocrystals (dispersed in carbon tetrachloride or TCE) were measured with a Cary 5 (Varian) ultraviolet-visible-near-infrared (UV-VIS-NIR) spectrometer. A JEOL 8900R electron probe micro analyzer was used for electron probe micro analyses (EPMA) with an acceleration voltage of 10 kV and a beam current of 50 nA with a 75 micron beam diameter. Pure metals or binary compounds were used as standards for Ag and Se. Both elements were analyzed in their respective wavelength-dispersive spectrometers. For subsequent quantitative elemental analyses, we used a JEOL thin-film correction algorithm. Films of Ag_2Se nanocrystals were spin-coated from dispersions in octane on a heavily doped Si wafer covered with a thermally grown 300-nm-thick SiO_2 layer. Data for EPMA was collected from 10 different points on the film and analyzed. Films were prepared for attenuated total internal reflection Fourier transform infrared (ATR-FTIR) spectroscopy by drop-casting a dispersion of nanocrystals in hexanes onto a trapezoidal-shaped Germanium (Ge) ATR crystal ($5 \times 1 \times 0.1$ cm^3) and allowing the deposit to dry for nearly 20 minutes. FTIR absorption spectra were collected using a Nicolet Magna 550 series II FTIR spectrophotometer with an ATR accessory (Harrick Scientific) and a Glowbar source. The infrared beam was focused normal onto the 45° beveled edge of the trapezoidal Ge ATR crystal. All spectra were obtained by averaging 100 interferograms at 4 cm^{-1} resolution. Peak assignments were made with the assistance of Ref. S1.

Synthesis of 2.8-nm Ag_2Se Nanocrystals:

For the synthesis of the smallest sized Ag_2Se nanocrystals, an approach similar to the one described in the main text was followed. 4 ml of TOP-Se was added to the mixture of OM and TOPO and the temperature raised to 150 °C. The heating mantle was then removed and the reaction flask was cooled down using a water bath. As the temperature dropped, 4 ml of Ag-TOP was rapidly injected at 130 °C and the reaction was quenched within 15 seconds by addition of 24 mL butanol.

Synthesis of Ag_2Se Nanocrystals with Sizes Greater than 7.5 nm:

Following the recipe mentioned in the main text, we were able to obtain fairly monodisperse (σ~10%) nanocrystals with sizes less than 7.5 nm by varying the growth times between 1 to 6 minutes. Growing the particles longer did result in an increase of the average size. However, the size distribution also broadened, presumably due to Ostwald ripening. To obtain bigger nanocrystals, we therefore modified the synthesis by using a different precursor to introduce silver. Instead of a TOP complex with $AgNO_3$, we used an AgCl-TOP complex instead. In a N_2-filled glovebox, 14.32 g of AgCl was dissolved in 100 mL TOP to obtain 1M AgCl-TOP. 2 mL of TOP-Se was added to the mixture of OM and TOPO after degassing and the temperature was raised to 180 °C. 2 mL of AgCl-TOP was injected to this rapidly stirring mixture and the reaction was allowed to proceed for nearly 20 minutes at 170 °C to yield 10.4-nm Ag_2Se nanocrystals. The reaction was quenched using a water bath and 10 mL of butanol was injected to prevent the unreacted TOPO from solidifying. Around 8 mL of ethanol was added to precipitate the nanocrystals. Care was taken while purifying these particles. Owing to their large size, they tend to crash out of solution and are unrecoverable if excess alcohol is added during the cleaning procedure.

Electron Probe Micro Analysis (EPMA):

Table S1 summarizes the atomic ratios calculated from various points on a film of 6.8-nm-diameter Ag_2Se nanocrystals. The standard deviation (σ) in the ratios obtained was ~ 2.4 %.

No.	Se	Ag	Comment	Atomic Ratio	
1	34.25	65.09	Ag_2Se pnt 1	1.900	
2	33.76	65.27	Ag_2Se pnt 2	1.933	
3	33.70	65.53	Ag_2Se pnt 3	1.945	
4	33.30	65.67	Ag_2Se pnt 4	1.972	
5	33.04	67.19	Ag_2Se pnt 5	2.033	
6	34.45	64.78	Ag_2Se pnt 6	1.881	
7	34.04	65.31	Ag_2Se pnt 7	1.919	
8	34.87	65.90	Ag_2Se pnt 8	1.890	
9	34.46	65.35	Ag_2Se pnt 9	1.896	
10	34.05	66.45	Ag_2Se pnt 10	1.951	
Average	**33.99**	**65.65**		**1.932**	**Ag/Se**
Stdev	**0.53**	**0.67**		**0.046**	**1.932**
% Stdev	**1.56**	**1.02**		**2.4**	

Table S1 EPMA data for films of 6.8-nm-diameter Ag_2Se nanocrystals.

Photoluminescence Spectroscopy:

The fluorescence spectrum was measured in a Bruker Vertex 80 Fourier-transform infrared (FTIR) spectrometer. The excitation source was an OSRAM OSTAR® model SFH 4751 infrared light source emitting at a wavelength of 940 nm. The photoluminescence was detected by a liquid nitrogen-cooled InSb photodiode from Bruker.

Supplementary Figures:

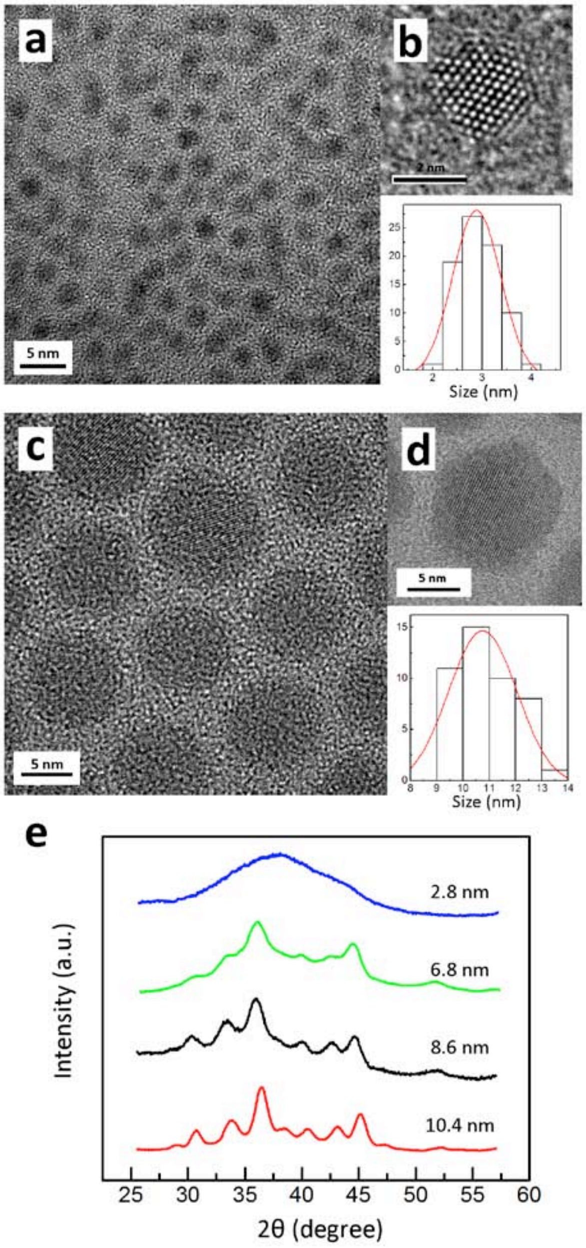

Fig. S1 (a, c) Low-magnification transmission electron microscope (TEM) images and size histograms showing the size distribution of an ensemble of Ag_2Se nanocrystals with average sizes of 2.8 and 10.4 nm, respectively. (b, d) Lattice-resolved high-resolution TEM micrographs of 2.3- and 10.3-nm single-crystalline Ag_2Se nanocrystals, respectively. (e) X-ray diffraction patterns of different-sized Ag_2Se nanocrystals. The average diameter obtained from TEM is indicated next to each pattern. The observed peak broadening with decreasing diameter is expected due to size effects.

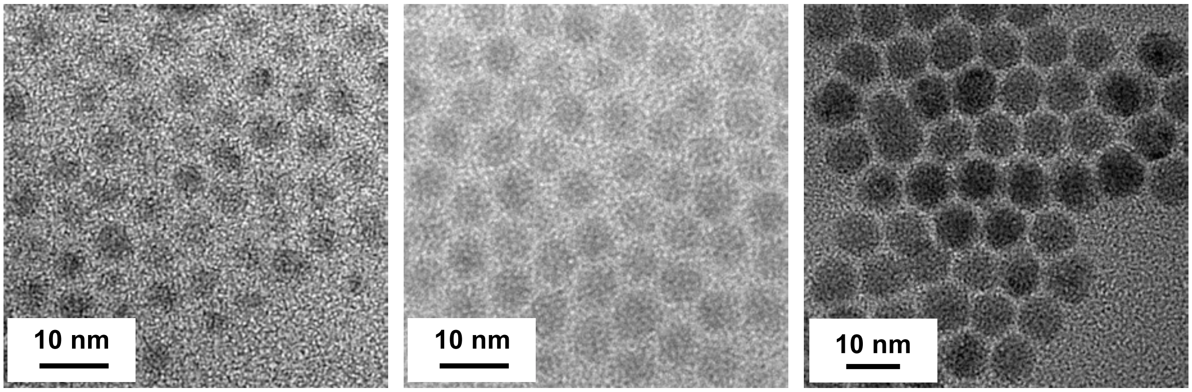

Fig. S2 Transmission electron microscope (TEM) images for 4.2-nm, 5.9-nm and 8.6-nm Ag_2Se nanocrystals.

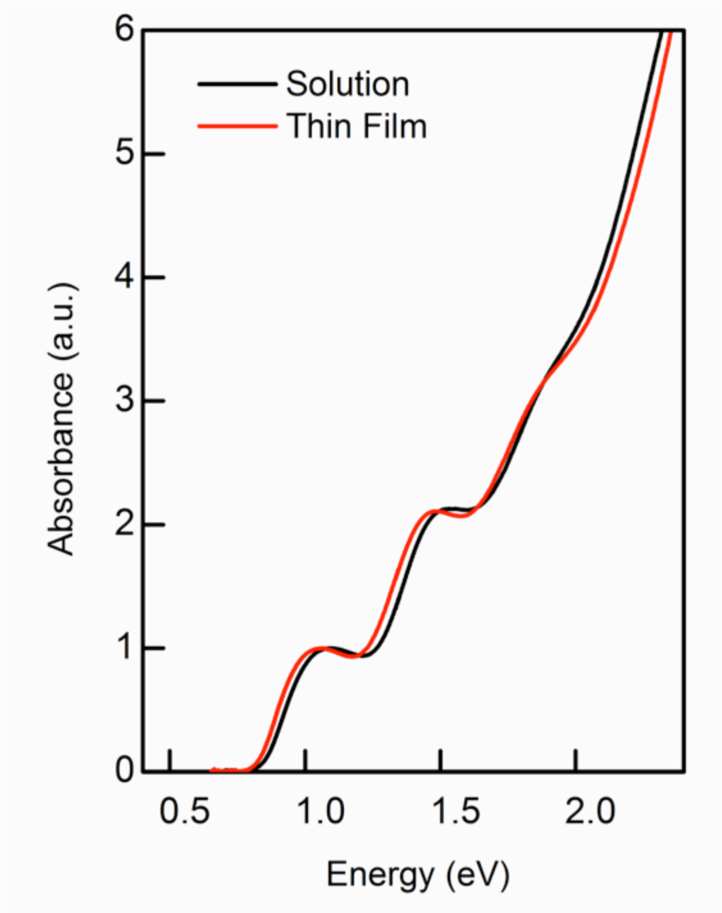

Fig. S3 Room-temperature near-IR absorbance spectra of 2.7-nm Ag_2Se nanocrystals dispersed in carbon tetrachloride (black) and as a thin solid film on a sapphire disk (red). The energy of the lowest optical transition undergoes a red shift of nearly 26 meV when cast as a thin film due to a combination of changes in the dielectric function of the film and increased electronic coupling between the quantum dots (Ref. S2).

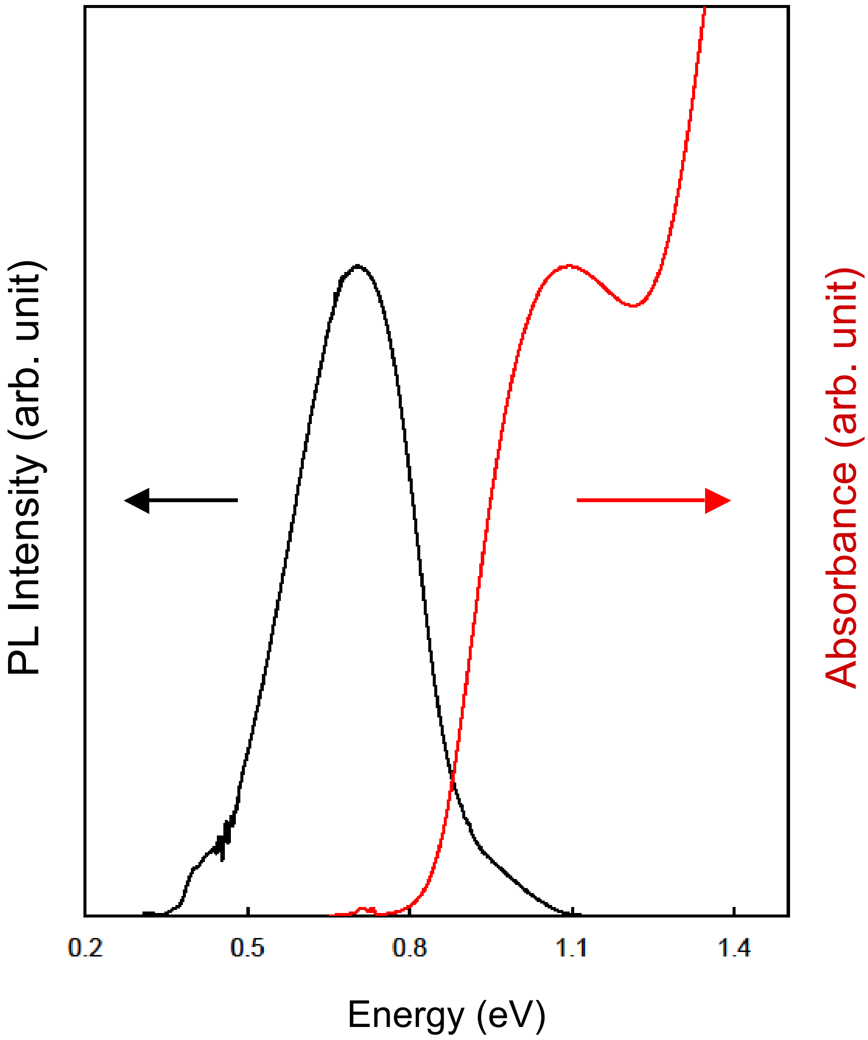

Fig. S4 Absorbance (red) and emission (black) spectra of 2.7-nm Ag_2Se nanocrystals dispersed in carbon tetrachloride. The absorption and photoluminescence maxima are at 1.093 and 0.703 eV, respectively, indicating a large Stokes shift of ~390 meV.

References:

(S1) Silverstein, R. M. *Spectrometric Identification of Organic Compounds,* 4th ed.; Wiley: New York, 1981.

(S2) C. A. Leatherdale and M. G. Bawendi, *Phys. Rev. B*, 2001, **63**, 165315.