Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Sub-10 nm Monodisperse PbS Cubes by Post-Synthesis Shape Engineering

Haitao Zhang,[a] Jun Yang,[a] Tobias Hanrath,[b] and Frank W. Wise [a]

[a] School of Applied and Engineering Physics, [b] School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853.

General Procedures

All of the manipulations were carried out in a N_2 atmosphere by employing standard Schlenk line and glove box techniques unless otherwise noted. Hexanes (≥98.5%), ethanol (≥99.5%), acetone (99%), 1-octadecene (90%), oleic acid (90%), ammonium sulfide (40-48 wt% solution in water), oleylamine (80-90%), octylamine (99%), and lead (II) oxide (≥99.0%) were purchased from Aldrich; molecular sieves (UOP type 3 Å) were purchased from Aldrich and activated at 300 ^oC under dynamic vacuum for 3 hours before use. Anhydrous $(NH_4)_2S$ oleylamine solution was prepared by dissolving ammonium sulfide 40-48 wt% aqueous solution in oleylamine. H_2O was then removed by freshly activated 3 Å molecular sieves.

The conventional transmission electron microscopy (TEM) images were recorded on an FEI Tecnai T12 transmission electron microscope operating at 120 kV. Samples for TEM analysis were prepared by putting a drop of solution containing nanoparticles on the surface of a copper grid coated with an amorphous carbon film. X-ray diffraction data were collected on a Scintag Theta-Theta X-ray diffractometer (Cu Kα radiation). UV-vis absorption data were collected on a Shimadzu UV-3101PC spectrometer. The photoluminescence spectra of PbS NCs were taken by a home built setup, with an Acton spectrometer (SP2300), a Femtowatt IR detector and a lock in amplifier (SR830). NCs were excited by either a 632nm diode laser (CW,20mW/cm^2) or a 976nm diode laser (CW,70mW/cm^2).

Photoluminescence (PL) Quantum Yield Measurement

PL Quantum yield was measured using an integrating sphere (Labsphere) following previous method.[1] Briefly, three measurements were done (a) without the sample in the sphere, (b) with sample in the sphere out of the direct laser beam, and (c) with sample in the sphere in the direct laser beam. The light was collected from a small port of the integrating sphere, coupled into a glass fiber and guided into the spectrometer. The sensitivity of the setup was independently calibrated with a quartz tungsten halogen lamp. Both the spectrum of the laser $L_{a,b,c}$ and spectrum of photoluminescence $P_{b,c}$ were collected, and quantum yield was calculated as

$$\eta_{PL} = \frac{P_c - (1 - A)P_b}{L_a A}$$

where $A = 1 - \frac{L_c}{L_b}$.

PbS Cube Bandgap Calculation

The bandgap of PbS cubes is calculated using the 4-band model previously used for PbS/PbSe spherical nanoparticles.[2] The coupling between the highest valence band and the conduction bands as well as coupling between the lowest conduction band and the valence bands are included in a second-order perturbation approximation. Spin-orbit interaction is also accounted for in the model. The boundary condition is assumed to be an infinite well. The inter-valley coupling, band anisotropy, and coulomb interaction and exchange interaction are neglected. The 4-band Hamiltonian is:

$$H_0(k) = \begin{bmatrix} \left(\frac{E_g}{2} + \frac{\hbar^2 k^2}{2m^-}\right)I & \frac{\hbar P}{m} k \cdot \sigma \\ \frac{\hbar P}{m} k \cdot \sigma & -\left(\frac{E_g}{2} + \frac{\hbar^2 k^2}{2m^+}\right)I \end{bmatrix} \tag{1}$$

which is a 4×4 matrix, where P is the Kane momentum-matrix element between the conduction and balance band-edge Bloch functions, and in the isotropic approximation, $3P = 2P_t^2 + P_l^2$; m^- and m^+ are the band-edge effective masses for the conduction band and valence band respectively, and in the isotropic approximation, $3/m^\pm = 2/m_t^\pm + 1/m_l^\pm$; m is the free electron mass; σ is the Pauli matrix. All parameters in the calculation uses the values in ref2, which are listed in Table S1

Material	$E_g(T = 300K)00Ki$	m/m^-	m/m^+	$2P^2/m$
PbS	0.41 eV	2.5	3.0	2.5 eV

Table S1: Parameters used in the calculations

The quantum confined levels are obtained by solving the envelope function equation with imposed boundary condition

$$H_0(-i\nabla)F(r) = EF(r) \tag{2}$$

$$F(r_i = 0,L) = 0\,, \qquad for\ i = x,y,z \tag{3}$$

Here the envelope wavefunction $F(r)$ is a four component vector $[F_j(r)]$, $j = 1\ldots4$. It is not clear whether an analytic solution exists at all. However, it can always be expanded in a set of basic functions that satisfy the boundary conditions

$$F_j(r) = \sum_{\alpha,\beta,\gamma > 0} A_{j,\alpha,\beta,\gamma} \sin\left(\frac{\alpha\pi x}{L}\right) \sin\left(\frac{\beta\pi y}{L}\right) \sin\left(\frac{\gamma\pi z}{L}\right) \tag{4}$$

where, α, β, γ are all natural numbers. Plug this into the Schrödinger Equation (2), and use the orthogonal relations:

$$\int_0^{\pi} \sin \alpha x \sin \beta x dx = \frac{\pi}{2}\delta_{\alpha\beta} \tag{5a}$$

$$\int_0^{\pi} \sin \alpha x \cos \beta x dx = \frac{2\alpha}{\alpha^2 - \beta^2}\delta_{\alpha,\beta\ not\ all\ odd\ or\ even} \tag{5b}$$

we obtain a coupled equations for the coefficients $A_{j,\alpha,\beta,\gamma}$:

$$\frac{4\hbar P}{mL}\left[-i\sum_{\gamma}^{'} A_{3,\alpha0,\beta0,\gamma}\frac{\gamma\gamma_0}{\gamma_0^2 - \gamma^2} - i\sum_{\alpha}^{'} A_{4,\alpha,\beta0,\gamma0}\frac{\alpha\alpha_0}{\alpha_0^2 - \alpha^2} - \sum_{\beta}^{'} A_{4,\alpha0,\beta,\gamma0}\frac{\beta\beta_0}{\beta_0^2 - \beta^2}\right] = \Bigl[E - \frac{E_g}{2} - \frac{\hbar^2\pi^2}{2m^{-}L^2}\bigl(\alpha_0^2 \tag{6a}$$

$$\frac{4\hbar P}{mL}\left[-i\sum_{\alpha}^{'} A_{3,\alpha,\beta0,\gamma0}\frac{\alpha\alpha_0}{\alpha_0^2 - \alpha^2} + \sum_{\beta}^{'} A_{3,\alpha0,\beta,\gamma0}\frac{\beta\beta_0}{\beta_0^2 - \beta^2} + i\sum_{\gamma}^{'} A_{4,\alpha0,\beta0,\gamma}\frac{\gamma\gamma_0}{\gamma_0^2 - \gamma^2}\right] = \Bigl[E - \frac{E_g}{2} - \frac{\hbar^2\pi^2}{2m^{-}L^2}\bigl(\alpha_0^2 \tag{6b}$$

$$\frac{4\hbar P}{mL}\left[-i\sum_{\gamma}^{'} A_{1,\alpha0,\beta0,\gamma}\frac{\gamma\gamma_0}{\gamma_0^2 - \gamma^2} - i\sum_{\alpha}^{'} A_{2,\alpha,\beta0,\gamma0}\frac{\alpha\alpha_0}{\alpha_0^2 - \alpha^2} - \sum_{\beta}^{'} A_{2,\alpha0,\beta,\gamma0}\frac{\beta\beta_0}{\beta_0^2 - \beta^2}\right] = \Bigl[E + \frac{E_g}{2} + \frac{\hbar^2\pi^2}{2m^{+}L^2}\bigl(\alpha \tag{6c}$$

$$\frac{4\hbar P}{mL}\left[-i\sum_{\alpha}^{'} A_{1,\alpha,\beta0,\gamma0}\frac{\alpha\alpha_0}{\alpha_0^2 - \alpha^2} + \sum_{\beta}^{'} A_{1,\alpha0,\beta,\gamma0}\frac{\beta\beta_0}{\beta_0^2 - \beta^2} + i\sum_{\gamma}^{'} A_{2,\alpha0,\beta0,\gamma}\frac{\gamma\gamma_0}{\gamma_0^2 - \gamma^2}\right] = \Bigl[E + \frac{E_g}{2} + \frac{\hbar^2\pi^2}{2m^{+}L^2}\bigl(\tag{6d}$$

Here, the summation $\sum_{\alpha}^{'} A\frac{\alpha\alpha_0}{\alpha_0^2 - \alpha^2}$ sums over all the natural numbers α that have a different parity with α_0 in the denominator. These coupled equations give an eigenvalue problem that by solving it one can obtain the energies and wavefunctions for different states.

It is expected that for low energy states, there will be very small contributions from bases that have large momentum (high energy). Therefore, in order to calculate energy of states close to the band edge, one only needs to account for a limited number of basic functions to give a satisfactory solution. Here we use a simple cutoff number N, and count only basic function with $1 \leq \alpha,\beta,\gamma \leq N$. This corresponds to the total of $4 \times N^3$ basic functions.

Figure S1 shows the convergence on the cutoff number of basic functions used in the calculation for 4.2 nm length cube. One can see that the result converges quickly. One interesting thing is that the error depends critically on the parity of the number of basis. Calculations with odd number of bases systematically underestimate the bandgap, and have larger error than the ones with even number of bases. For the rest of the calculation, $N = 8$ is used.

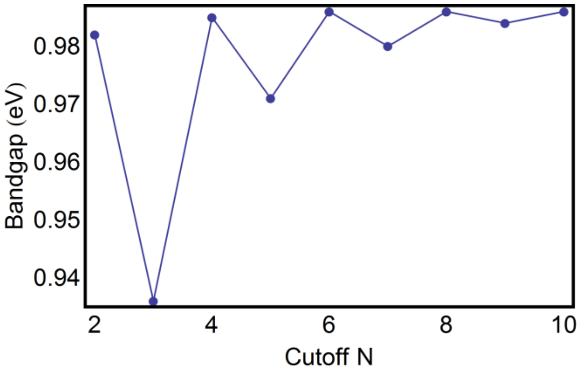


Figure S1: Convergence of bandgap energy calculated for PbS cube 4.2nm in length, with different cutoff order for the basic functions.

Figure S2 shows the energy of states calculated for 4.2 nm length PbS cubes for the first 30 states. It is clear that the degeneracy of states is very similar to what one would expect from a 1-band model. The first two states in the conduction band are labeled $(n_x n_y n_z)_e = (111)_e$ states with spin degeneracy; the next six states are $(211)_e$, $(121)_e$, and $(112)_e$; next group corresponds to $(122)_e$, $(212)_e$, and $(221)_e$. To look more closely, the group that contains $(112)_e$ state has a slight splitting of degeneracy, into four states with slightly smaller energy, and two states with higher energy. This is very similar to PbS spheres (ref2), where $j = 3/2, \pi = 1$ has four fold degeneracy and $j = 1/2, \pi = 1$ state has two fold degeneracy, but has slightly higher energy. Both states can be assigned to p orbital (orbital angular momentum $l = 1$) but with different total angular momentum ($j = 1/2$ or $j = 3/2$). The splitting is due to spin-orbit interaction. This should be the case for PbS cubes as well. The hole states are more or less mirror image of electron states due to the nearly symmetric conduction band and valence band in lead sulfide crystal.

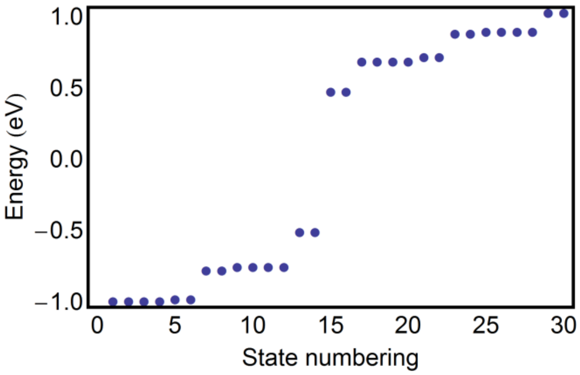


Figure S2: Energies of the first 30 states for PbS cube 4.2nm in length

Figure S3 summarizes energy level changes as a function of length of the cubes. The first 14 states for electron and hole are all plotted.

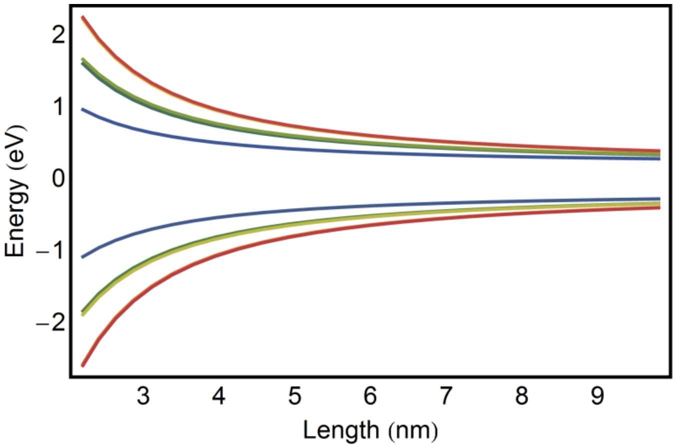


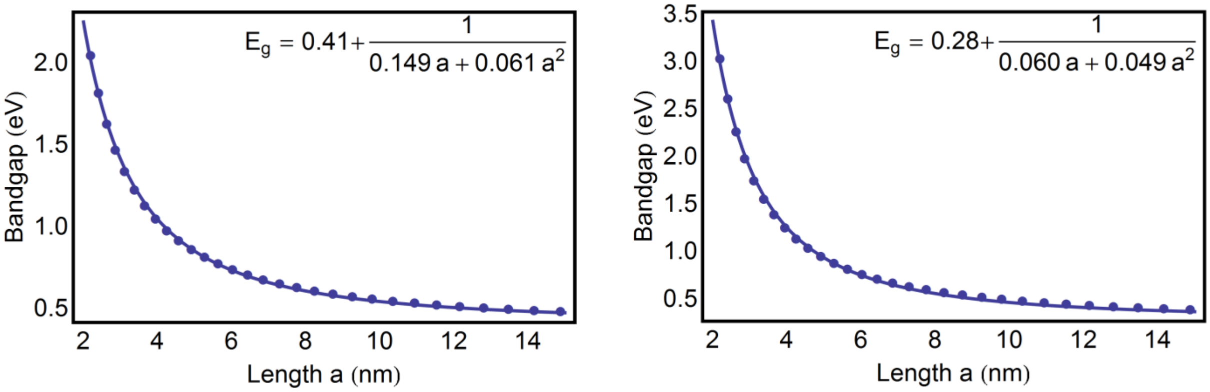
Figure S3: Energies for the first 14 states for electron and hole as a function of length for PbS cube.

We also try to find a simple analytic expression that can describe the bandgap reasonably well, to facilitate future comparison. In figure S4(a), calculated bandgaps (blue dots) are fitted to the function

$$E_g = 0.41 + \frac{1}{0.149a + 0.061a^2}$$

where a is the length of the cube. We also calculate bandgap for PbSe cubes (Figure S4(b)) for future reference, and fitted it to

$$E_g = 0.28 + \frac{1}{0.060a + 0.049a^2}$$



(a) (b)

Figure S4: (a) Fitting of PbS cube bandgap with an analytic expression. (b) Fitting of PbSe cube bandgap with an analytic expression.

Quasi-Spherical PbS NCs Synthesis

Quasi-spherical PbS NCs were synthesized according to the literature procedure.[3] In a typical synthesis of ca. 7 nm PbS NCs, a mixture of 0.45 g PbO and 20 mL oleic acid (HOA) was heated to 110°C under nitrogen until solution is clear. Reaction flask was vacuumed to remove water. The solution was then reheated to 135°C. In a glovebox, 252 µL bis(trimethylsilyl)sulfide (TMS) was mixed with 12 mL octadecene (ODE) to prepare TMS-ODE solution. TMS-ODE (10 mL) was then injected into the reaction solution and allowed to react for 30s. The solution was cooled down by water bath and ethanol was added to the solution to precipitate out NCs, which was separated by centrifugation and washed twice with hexanes/ethanol. The purified NCs were dissolved in hexanes. The PbS NCs size can be controlled by varying the reaction temperature or PbO:HOA ratio.

Treat Quasi-Spherical PbS NCs in Oleylamine Only

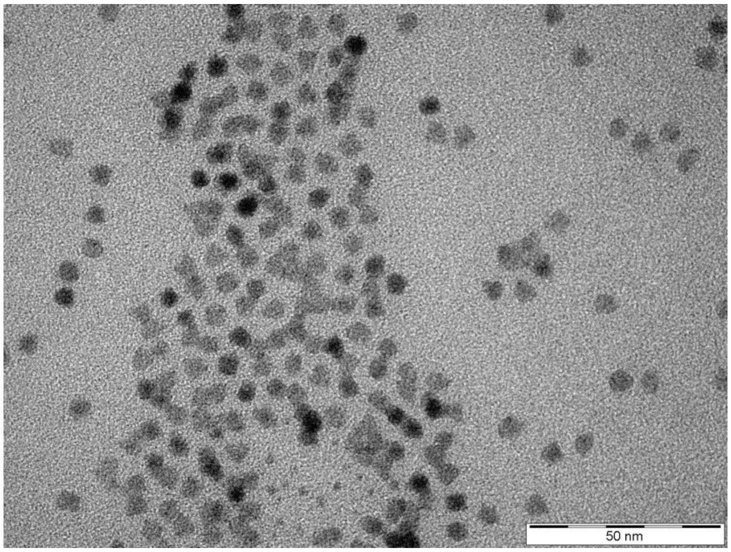


Figure S5. TEM image of ca. 5.5 nm Quasi-spherical PbS NCs after treatment in oleylamine: 15 mg NCs in a mixture of 4 mL hexanes and 4 mL oleylamine were stirred for 30 mins at room temperature. No shape transformation from quasi-sphere to cube was observed during this process.

References

1. J. C. de Mello, H. F. Wittmann and R. H. Friend, *Advanced Materials*, 1997, **9**, 230-232.
2. I. Kang and F. W. Wise, *Journal of the Optical Society of America B*, 1997, **14**, 1632-1646.
3. M. A. Hines and G. D. Scholes, *Advanced Materials*, 2003, **15**, 1844-1849.