Supporting Information

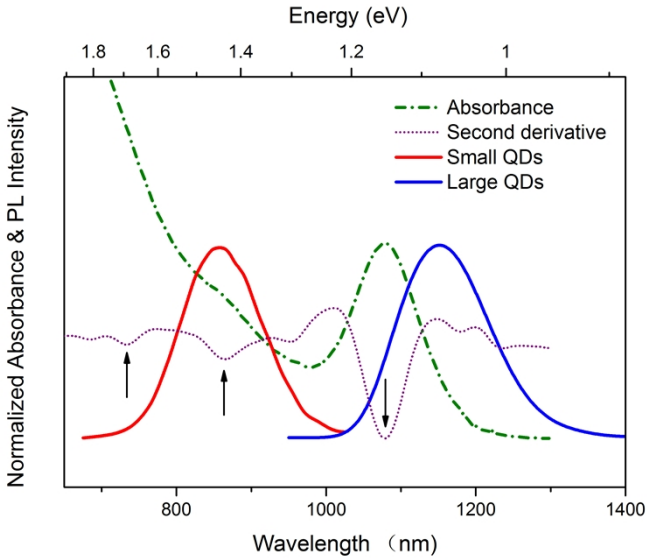

Fig.S1. PL spectra of 120℃PbSe QDs. Absorption spectra and its second derivative of the PbSe QDs are shown in dash dot line and dots, respectively.

Fig.S1 shows the PL and absorption spectra of 120℃ QDs. The emission peak of small QDs (plotted in red) locates at 856nm (1.45eV) while the peak of large QDs (plotted in blue) locates at 1151nm (1.07eV). A stokes shift of 80meV is observed between absorption and emission of large QDs. However, the absorption of small QDs cannot be observed probably because the absorption of large QDs overlaps the small QDs. An analysis of second derivative is applied to determine the absorption of small QDs, which is shown in a dot line. The valley at 1078nm (1.15eV) represents the first exciton peak of large QDs, which is assigned to the $1S_h$-$1S_e$ state transition.[2, 3] Another valley at 862nm (1.43eV) should be a second optical transition of $1P_h$-$1P_e$ state of PbSe QDs.[4] It is known that the Stokes shift always gives a red-shift (50-150 meV) of the emission peak behind the first absorption peak.[2] Hence, the second peak could be excluded for small QDs because two peaks are too close (1.43eV vs. 1.45eV). Besides, a weak but distinguishable valley at 738nm (1.68eV) is also observed, which could

be attributed to the first optical transition of the small QDs. However, considering the increasing absorbance in higher energy of photons, signals of small QDs are overlapped and thus difficult to analysis. A calculation result via tight binding method also reveals that the energy of 1.68eV corresponds to an average diameter of 2.23nm, which is consistent with TEM results (~2.3nm for small QDs).

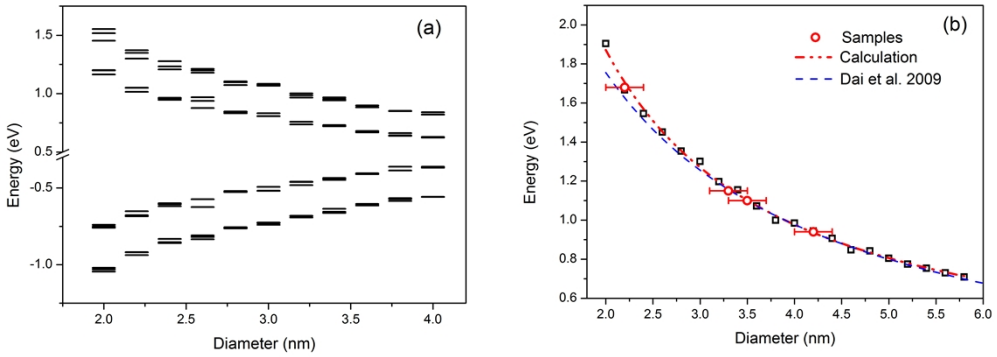

Fig.S2. (a) Calculated energy levels of PbSe QDs by a tight-binding approach. (b) Calculated energy gaps of the $1S_h$-$1S_e$ state as a function of particle size (dash-dot line).

The electronic structure of rock salt PbSe QDs was calculated by a tight-binding approach that was developed by G.Allan and C.Delerue.[5] A spherical model was applied on the PbSe QDs. The Hamiltonian matrix is written in a $sp^3d^5s^*$ basis. The first nearest neighbor tight binding parameters for PbSe were obtained from the Ref. 5. Calculation of energy levels of PbSe QDs with different particle sizes is performed. The results only display the energy states close to the valence band maximum and the conduction band minimum, which includes 1S and 1P states of electrons and holes. The relation of particle size versus energy gap of PbSe QDs is plotted in Fig.S2 (b). Previously reported data on single-size PbSe QDs by Dai and co-workers are given in the Fig.S2 (b) which was determined by optical absorption

spectral measurements.[6] Our tight-binding calculation shown in Fig.S2 (b) clearly explains the experimental data. Our tight-binding calculation of the energy gap (in eV) as a function of particle size is given below:

$$E_g(D) = E_g(\infty) + \frac{1}{0.0216D^2 + 0.2737D - 0.0053} \qquad \text{(eq1)}$$

References:

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