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

Supporting Information

Mechanistic insight into the nucleation and growth of oleic acid capped lead sulphide quantum dots

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Supporting results

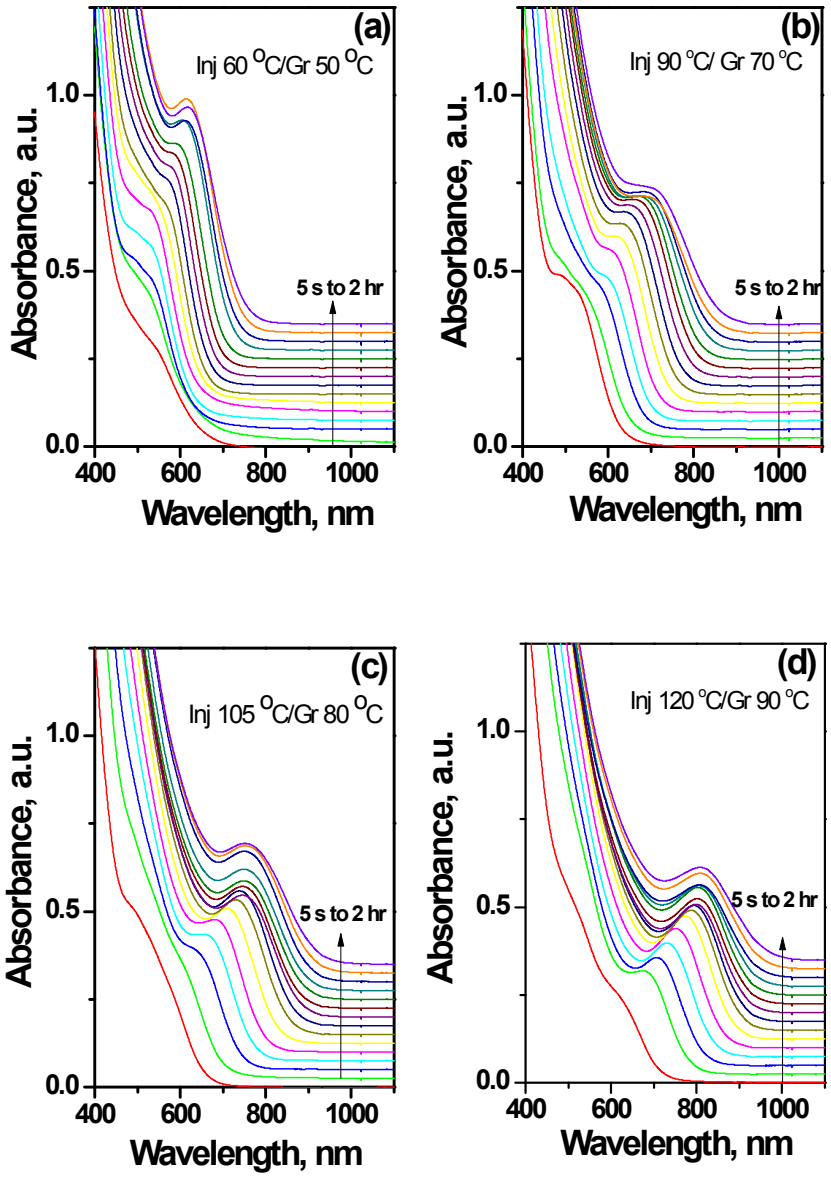

Figure S1. Temporal evolution of the absorption spectra of PbS QDs synthesized at various injection and growth temperatures.

(The wavelengths of the 1st exciton peak gradually increase with time indicating the increase in particle sizes. The particle sizes increase rapidly during the initial stage of the growth and gradually saturates as reaction time prolongs. The growth of the QDs ceases once the particle size reached optimal sizes)

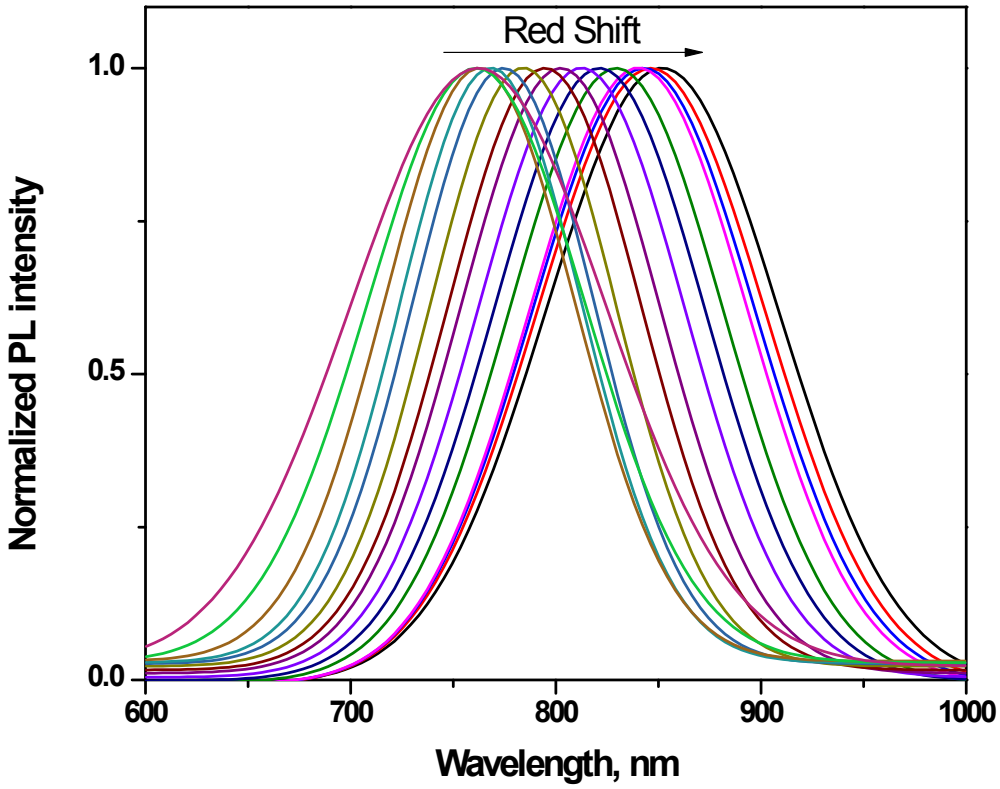

Figure S2. Photoluminescence (PL) spectra of PbS QDs. Synthesis condition - OA:Pb:S = 4:2:1, Injection temperature 90 ^{o}C and Growth temperature 70 ^{o}C.

(The red-shift of the PL peak indicates the increase in particle sizes).

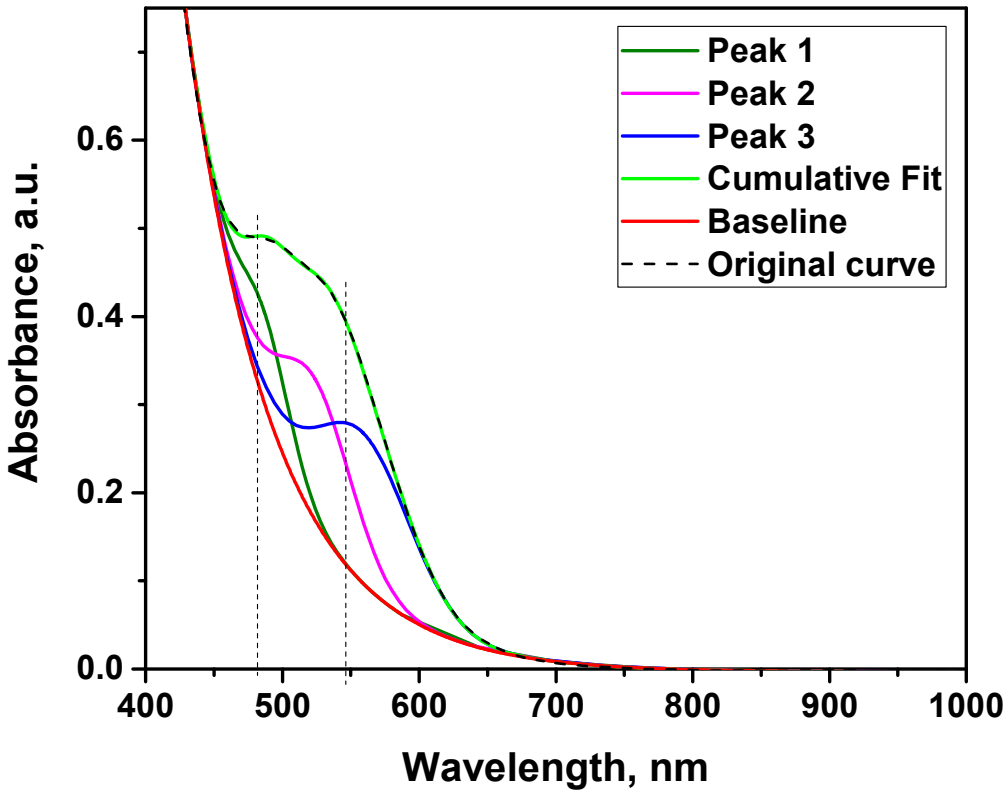

Figure S3. Peak fitting procedure to determine initial nuclei sizes.

(The absorbance spectra for 5 s aliquot for 90 ^{o}C injection and 70 ^{o}C growth condition was fitted to three Gaussian curves using the Origin Pro© software to determine the various nuclei sizes[1] Considering the bulk lattice parameter of PbS to be ~0.69 nm,[2] the various nuclei sizes were chosen to constitute 8-10 structural units per particle. For example, the nuclei with absorbance at ~480 nm (i.e. 1.4 nm particle diameter) would constitute 8 structural units of PbS per particle).

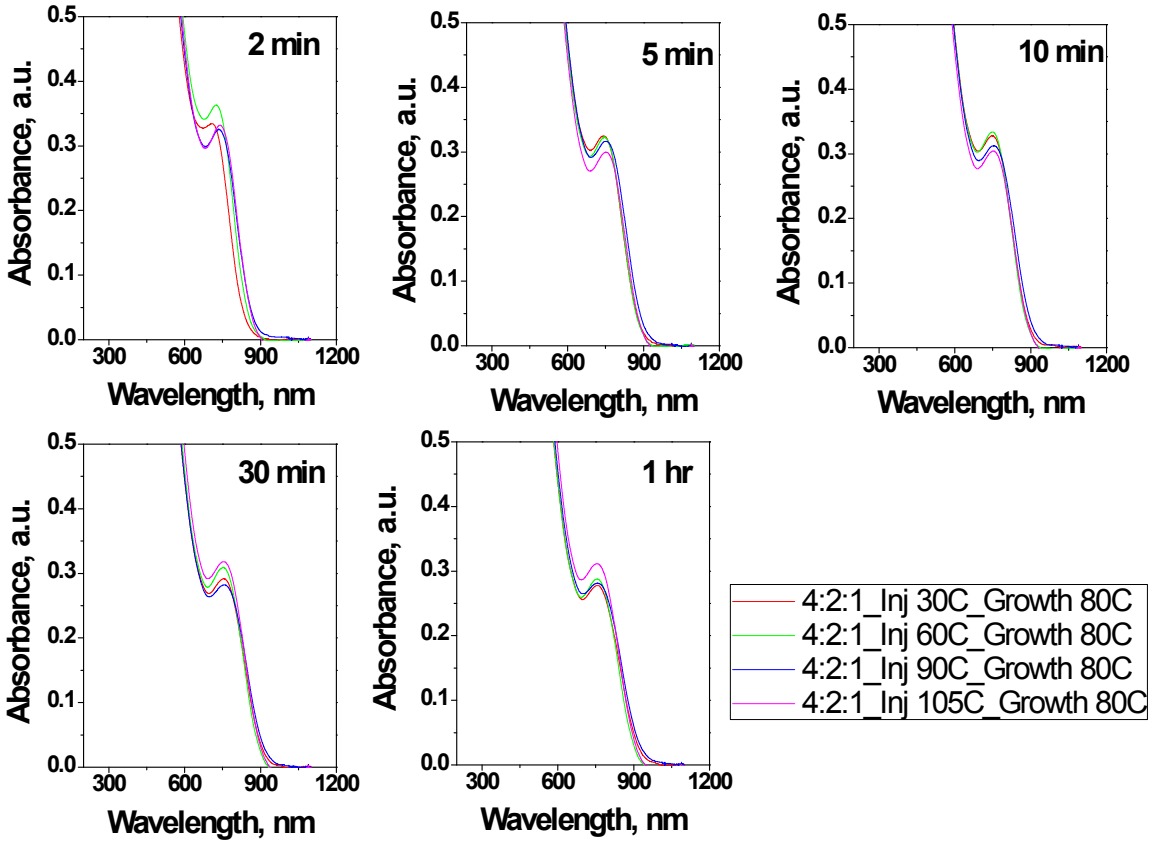

Figure S4. Absorption spectra for PbS QDs synthesis - different injection temperatures while maintaining the same growth temperature.

(The exciton peaks for all conditions saturate to the same position indicating the independence of nucleating temperatures on the final size of PbS QDs.)

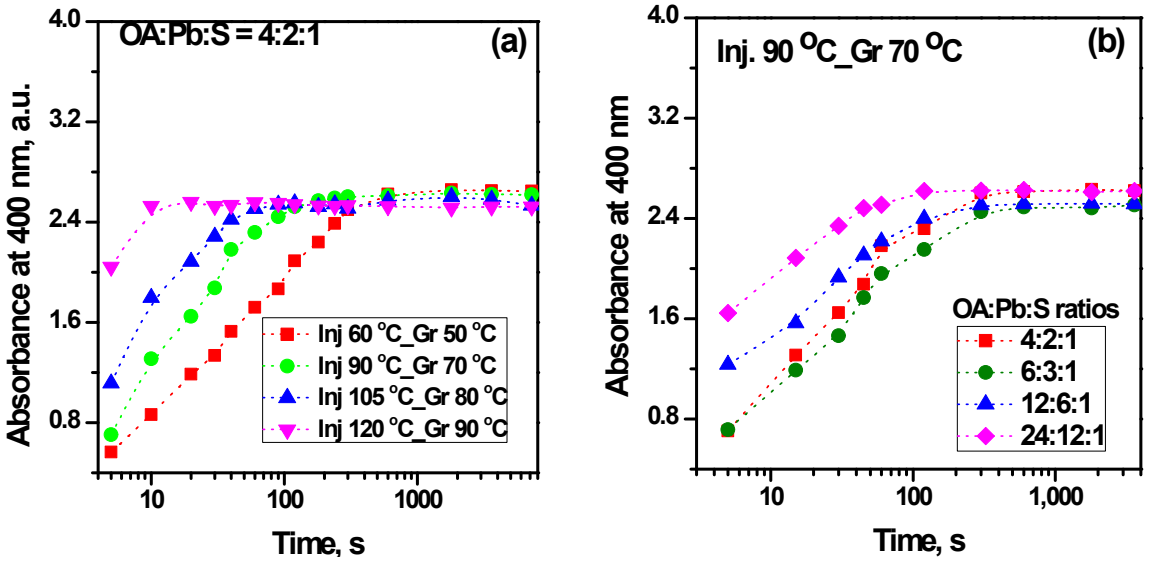

Figure S5. Temporal evolution of PbS QDs absorbance at 400 nm (a) at various injection and growth temperatures while the precursor ratio is maintained at OA:Pb:S=4:2:1 (b) at various ratios of lead precursor while keeping the same injection and growth temperatures (Injection temperature = 90 °C and Growth temperature = 70 °C growth). In both cases, the sulphur precursor concentration is kept the same.

(The formation of PbS QDs from precursor/monomers can be estimated from the absorbance spectra at 400 nm[2]. The molar extinction coefficient scales with nanocrystal volume at 400 nm and the precursor conversion to QDs can be estimated from the absorbance at 400 nm. We find that the higher temperature has a faster precursor conversion to QDs compared to lower temperature.)

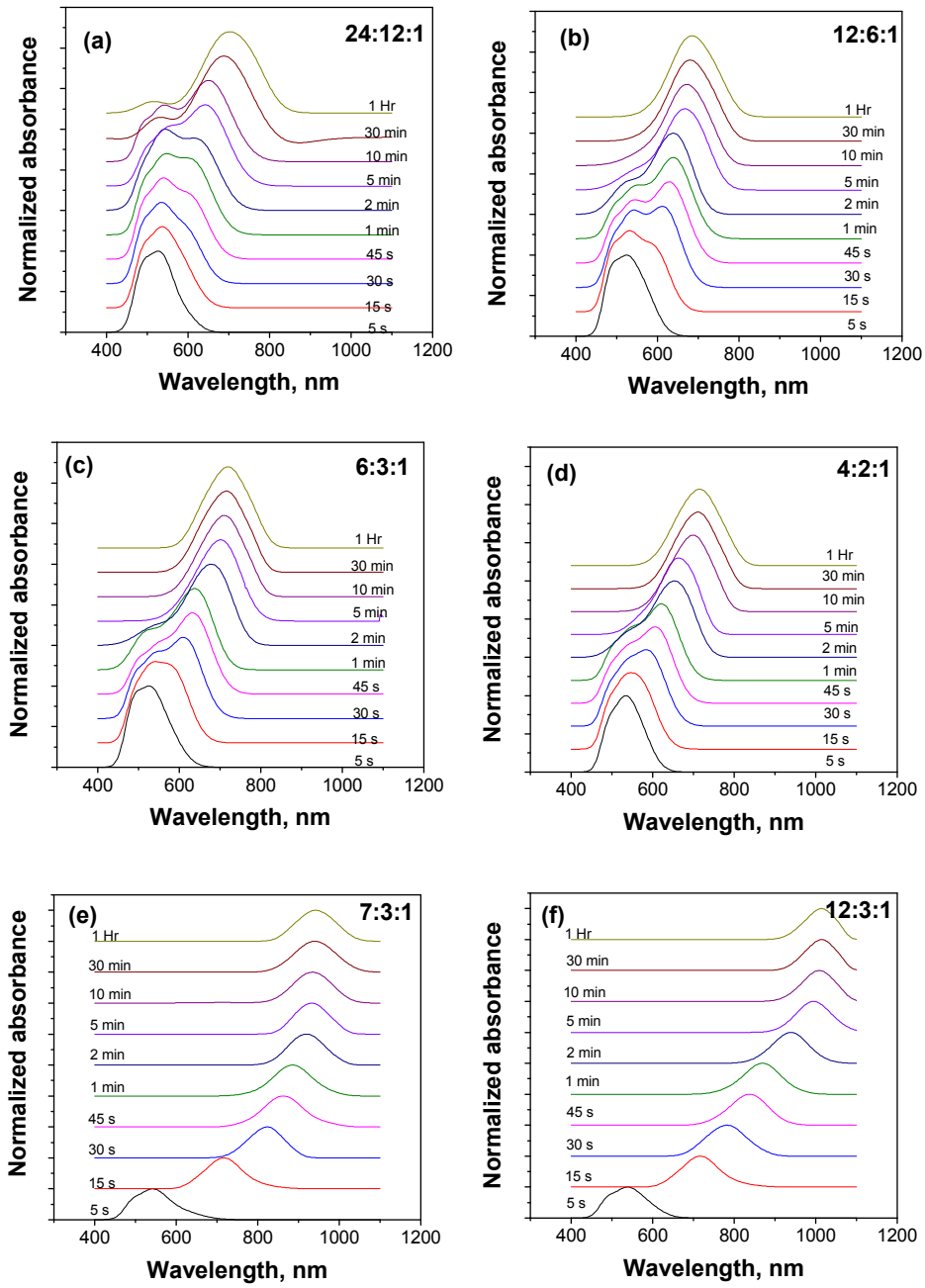

Figure S6. Absorption spectra fitting to a standard Gaussian distribution for various feed precursor ratios. Here, the precursor ratio are indicated as OA:Pb:S.

(The absorption spectra were fitted to the Gauss distribution using the curve fitting (spline function) in the Origin© software. It can been seen that at higher stoichiometric ratios OA:Pb forms the cluster of various sizes before focusing while in presence of free oleic acid i.e. at higher OA:Pb ratios no such clusters are formed.)

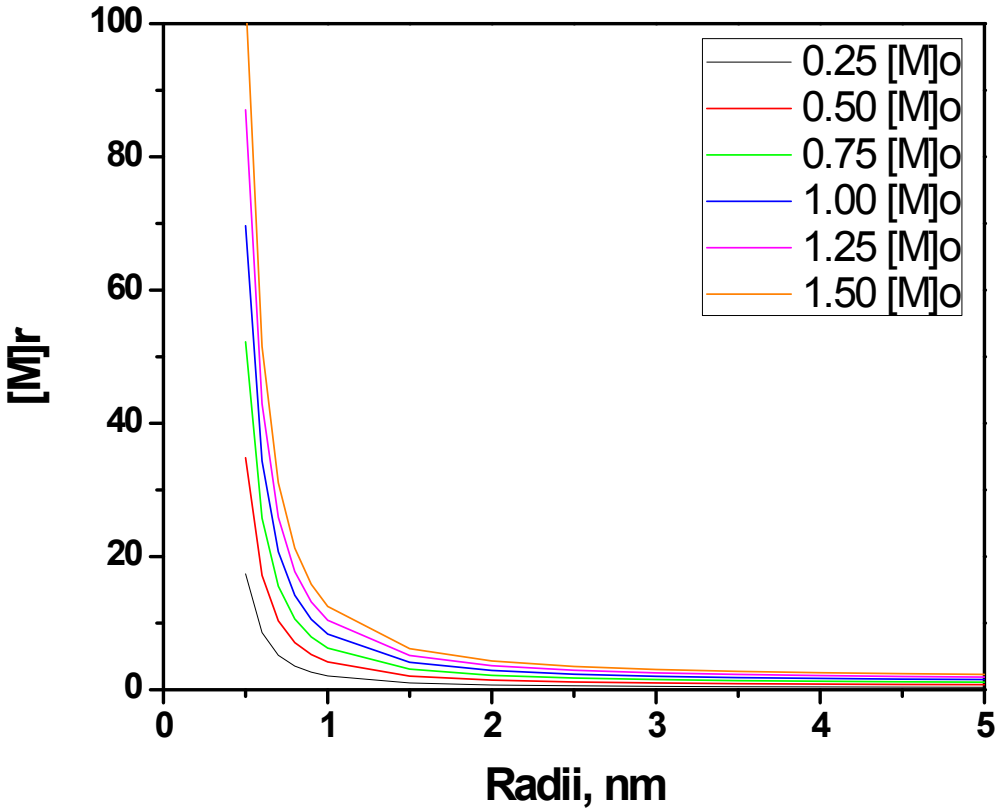

Figure S7. Change in solubility for various sized QDs particles with the change in equilibrium monomer solubility (Equation 3 main text).

(The simulation parameters are V_m = 3.15x10^{-5} m^3/mol, γ = 0.125 J/m^2, and R = 8.314 J/mol.K.)

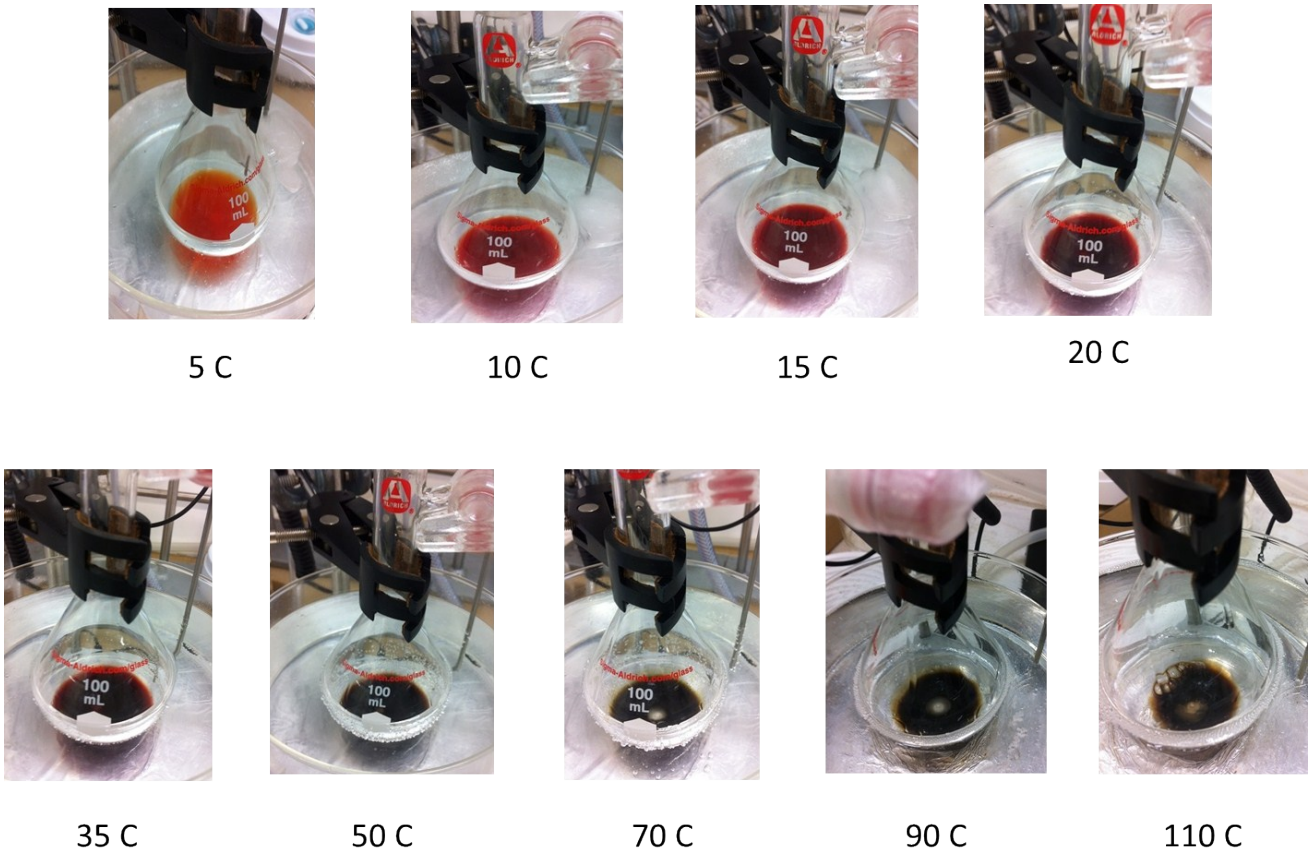

Figure S8. Snap shot of the synthesis of ultra-small PbS QDs at various growth temperatures

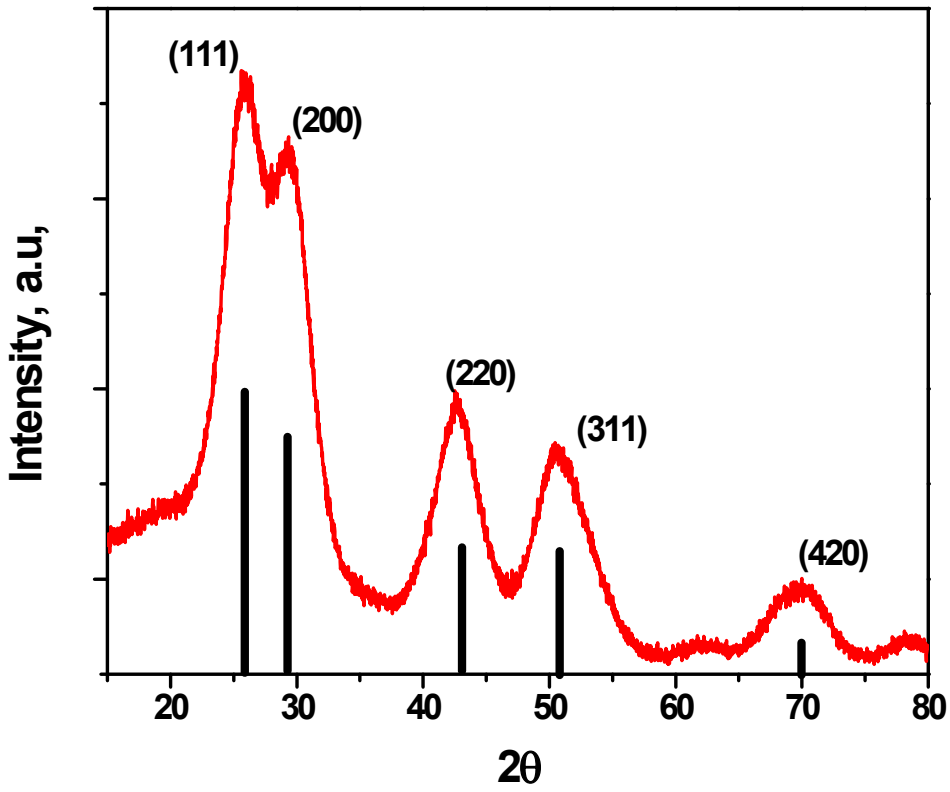

Figure S9. XRD spectra of ultra-small PbS QDs (~ 1.8 nm diameter and absorption peak at 600 nm)

Table S1. Designed experiments at various synthesis parameters. Each green shade indicates the reaction parameters (i.e. temperature and reactant ratios) used at a certain condition.

	Feed ratio (OA:Pb:S)	Injection (^{0}C)/Growth temperature (^{0}C)						
		120 ^{0}C/90 ^{0}C	105 ^{0}C/80 ^{0}C	90 ^{0}C/70 ^{0}C	60 ^{0}C/50 ^{0}C	90 ^{0}C/80 ^{0}C	60 ^{0}C/80 ^{0}C	30 ^{0}C/80 ^{0}C
Temperature Influence	(4:2:1)							
Lead precursor Influence	(4:2:1)							
	(6:3:1)							
	(12:6:1)							
	(24:12:1)							
Oleic acid (Ligand)Influence	(6:3:1)							
	(6.5:3:1)							
	(7:3:1)							
	(9:3:1)							
	(12:3:1)							
Sulphur precursor Influence	(6:3:1)							
	(6:3:0.5)							
	(6:3:1.5)							

Table S2. Natural logarithmic, standard Ostwald ripening (OR) model and orientation attachment (OA) model fitting for the exciton peak at various temperature as a function of time (min) for OA:Pb:S as 4:2:1

OA:Pb:S (4:2:1)				
	OR model fitting			OA model fitting
Temperature, ^{o}C	*SSE, n=2*	*SSE, n=3*	*SSE, n=4*	*SSE*
50 ^{o}C	0.0062	0.0017	0.0070	0.0544
70 ^{o}C	0.0264	0.0080	0.0337	0.1781
80 ^{o}C	0.0534	0.0185	0.0767	0.2797
90 ^{o}C	0.0745	0.0286	0.1174	0.3624

Table S3. Natural logarithmic, standard Ostwald ripening (OR) model and orientation attachment (OA) model fitting for the exciton peak at various temperature as a function of time (min) for OA:Pb:S as 5:2:1

OA:Pb:S (5:2:1)				
	OR model fitting			**OA model fitting**
Temperature, ^{o}C	***SSE, n=2***	***SSE, n=3***	***SSE, n=4***	***SSE***
24 ^{o}C	0.0013	0.0003	0.0014	0.0131
40 ^{o}C	0.0042	0.0011	0.0046	0.0386
50 ^{o}C	0.0081	0.0022	0.0093	0.0692
60 ^{o}C	0.0128	0.0036	0.0153	0.1054
70 ^{o}C	0.0192	0.0056	0.0236	0.1416
80 ^{o}C	0.0647	0.0234	0.0966	0.2803
90 ^{o}C	0.0712	0.0264	0.1088	0.2836

Table S4. Natural logarithmic, standard Ostwald ripening (OR) model and orientation attachment (OA) model fitting for the exciton peak at various temperature as a function of time (min) for OA:Pb:S as 7:2:1

OA:Pb:S (7:2:1)				
	OR model fitting			**OA model fitting**
Temperature, ^{o}C	***SSE, n=2***	***SSE, n=3***	***SSE, n=4***	***SSE***
24 ^{o}C	0.0039	0.0010	0.0043	0.0360
50 ^{o}C	0.0266	0.0081	0.0339	0.1784
60 ^{o}C	0.0327	0.0103	0.0430	0.2047
70 ^{o}C	0.0587	0.0205	0.0851	0.2508
80 ^{o}C	0.0638	0.0231	0.0954	0.2939
90 ^{o}C	0.1030	0.0432	0.1755	0.2427

Table S5. Natural logarithmic, standard Ostwald ripening (OR) model and orientation attachment (OA) model fitting for the exciton peak at various temperature as a function of time (min) for OA:Pb:S as 10:2:1

OA:Pb:S (10:2:1)				
	OR model fitting			**OA model fitting**
Temperature, °C	***SSE, n=2***	***SSE, n=3***	***SSE, n=4***	***SSE***
24 °C	0.0023	0.0006	0.0025	0.0223
40 °C	0.0096	0.0027	0.0112	0.0825
70 °C	0.0656	0.0238	0.0984	0.2919

References

[1] C. M. Evans, A. M. Love, E. A. Weiss, *Journal of the American Chemical Society* **2012**, *134*, 17298-17305.

[2] I. Moreels, K. Lambert, D. Smeets, D. De Muynck, T. Nollet, J. C. Martins, F. Vanhaecke, A. Vantomme, C. Delerue, G. Allan, Z. Hens, *ACS Nano* **2009**, *3*, 3023-3030.