

Hidden Role of Anion Exchange Reactions in Nucleation of Colloidal Nanocrystals

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Supporting information

Methods and Materials

Chemicals used:

Lead oxide (99.9%) and Lead acetate trihydrate (99.9%) were purchased from Alfa Aesar. Selenium (99.99%), Trioctylphosphine (TOP)(technical grade, 90%), 1-octadecene (ODE)(technical grade, 90%), oleylamine (technical grade, 70%), oleic acid (technical grade, 90%), Sodium hydroxide(97% ACS reagent) were purchased from Sigma Aldrich. All chemicals were used without further purification.

Synthesis

PbSe QDs:

Lead oxide (0.892 g, 4 mmol), oleic acid (5 ml, 9.5 mmol) and ODE(12 ml) were added into a round bottom(RB) flask and the flask was heated to 180°C under Argon atmosphere for 1.5 hr. 4 ml of 2 M TOPSe was injected into RB. 2 M TOPSe was prepared by dissolving 1.248 g of selenium in 8 ml of TOP. The reaction was quenched by adding 10ml of toluene once the QDs achieved desired size. QDs were cleaned QDs by repeated centrifugation with methanol, ethanol and isopropanol.

Unless otherwise stated, reactions using lead acetate as a lead source were performed in a similar manner, except that the conversion to lead oleate was performed at 100 °C under vacuum. The conversion time was varied from 1.5 hours to 8 hours with no detectable effect on the quality of the final material that was universally found to be extremely poor.

PbSe Magic Sized Nanocrystals(MSNCs):

Lead oxide (0.892 g, 4 mmol), oleic acid (5 ml, 9.5 mmol) and ODE(12 ml) were added into a RB and then heated to 150 °C under Argon for 1.5 hours. The flask was then cooled to RT and 4ml of 2M TOPSe was injected at room temperature(RT). The mixture was left at RT for 4hr. After 4hrs the solution turned from transparent to brown. This indicates the formation of PbSe MSNCs. MSNCs were purified by precipitation and centrifugation with methanol, ethanol and isopropanol. MSNCs were redissolved in hexane prior to each successive addition of alcohol. After the final step, the precipitate was allowed to dry before redissolution in the appropriate nonpolar solvent.

Unless otherwise stated, reactions using lead acetate as a lead source were performed in a similar manner, except that the conversion to lead oleate was performed at 100 °C under vacuum. The conversion time was varied from 1.5 hours to 8 hours with no detectable effect on the quality of the final material that was universally found to be extremely poor.

Lead Oxide synthesis by colloidal method:

Synthetic procedure was reported by Cattley *et. al.*^[1] Briefly, 5 mmol each of oleic acid and lead acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$) were placed in a three neck flask with 3 ml of octadecene. The reagents were degassed under vacuum. Subsequently this mixture was heated under argon flow to 150 °C for 1 hour while being continuously stirred. This solution is almost colorless. Into this solution, 5 mmol of oleylamine was injected. After mixing the reagents thoroughly, the temperature was rapidly increased to 190 °C at which point argon flow was halted. At this point the contents of the flask are seen to have an orange color. A syringe filled with 20 ml air was injected into the solution. The colour is observed to deepen and change from orange to brownish orange. This temperature was maintained for 5 minutes after which the solution was rapidly cooled in an ice bath. This temperature was then maintained for 1 hour to allow for ageing of the nanoparticles.

Lead Oxide synthesis by aqueous method:

Aqueous Lead Oxide (PbO) nanoparticles were prepared as follows. 60 ml of aqueous 1.0 M lead acetate trihydrate was heated to 90°C. This solution was added to an aqueous solution of 50 ml of 19 M NaOH in a beaker and stirred vigorously. Upon adding the lead (II) acetate, the solution eventually turns yellow orange. At this point, stirring was stopped, and the precipitate was allowed to settle

down and separated by decantation. The precipitate was washed with de-ionized water repeatedly, and dried overnight at 90°C.

Synthesis of PbSe NQDs using synthesized PbO nanocrystals in organic medium:

Procedure: 2 M TOPSe stock solutions were added to the PbO reaction mixture (without purifying PbO NQDs) and stirred at room temperature. The solution turned deep brown after 45min.

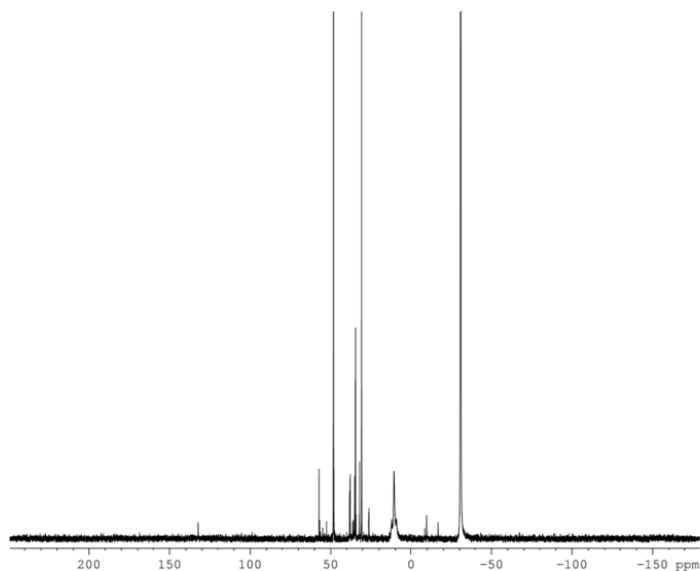


Figure S1: NMR spectra of TOP, tech. The presence of dialkyl phosphines has been previously noted by other workers.

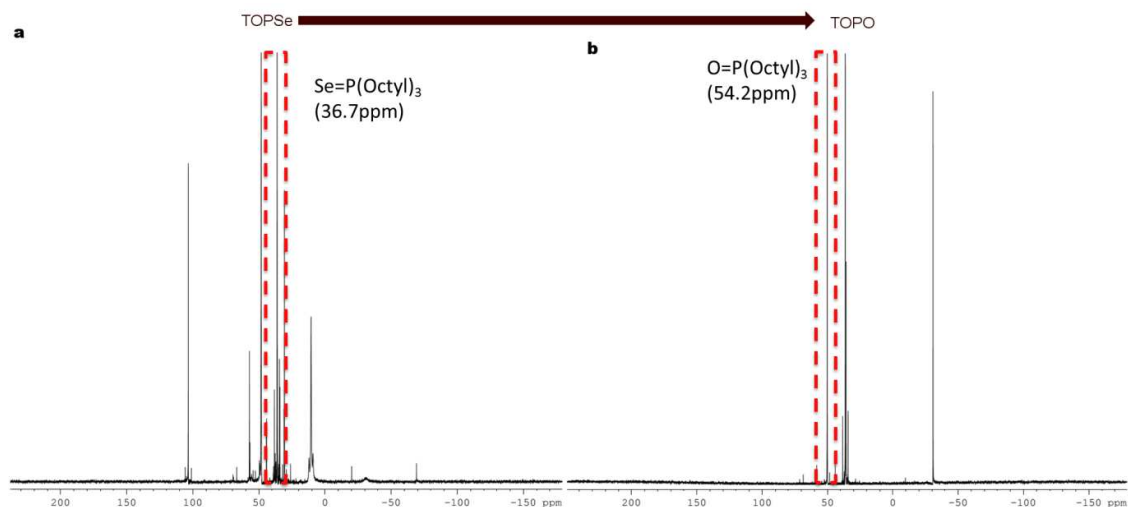


Figure S2: **a.** NMR spectrum of starting trioctyl phosphine selenium (TOPSe). **b.** NMR spectrum observed after treating with PbO QDs synthesized via an organic route. Note that the spectra indicate disappearance of the TOPSe feature (red box, figure S2a) as well as the simultaneous appearance of a TOPO feature (red box, figure S2b). This suggests the exchange reaction of the form $PbO + TOPSe \rightarrow PbSe + TOPO$. Impurity peaks corresponding to Selenized dialkyl phosphines are also observed to evolve and transform into the corresponding oxides. This suggests that the exchange reaction may also consume partially alkylated selenophosphines. Note that the reaction has been performed in absence of atmospheric oxygen. TOPSe is observed to be stable under these conditions indefinitely. PbO is thus the only viable oxygen source. The simultaneous appearance of PbSe has been tracked optically as well as through XRD (see main MS).

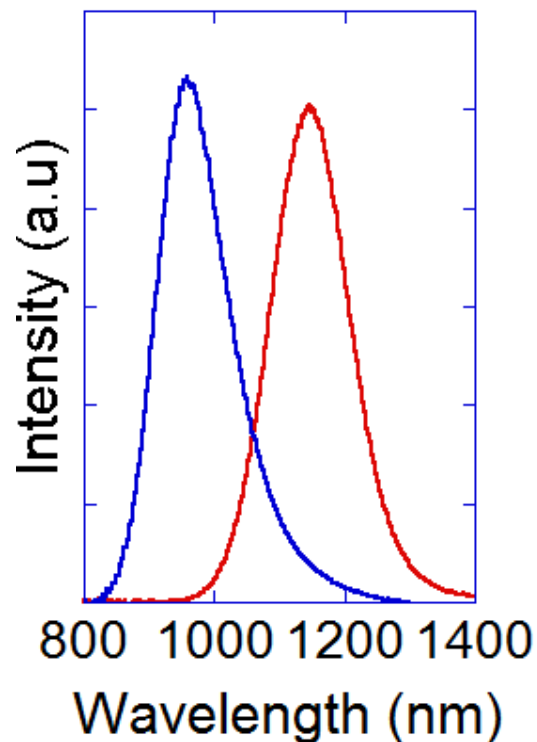


Figure S3: Photoluminescence spectra of two different sized PbSe Samples. Blue gaussian: photoluminescence spectrum of magic sized PbSe dots (Quantum yield is 36 %). Red gaussian: Spectrum of PbSe/CdSe dots (Quantum yield is 28%). The Quantum yields have been determined through an absolute measurement. These dots have been made through the procedure in figure 3b of the main manuscript. We find both procedures 3a and 3c to QDs with negligible emission, presumably due to improper surface passivation.

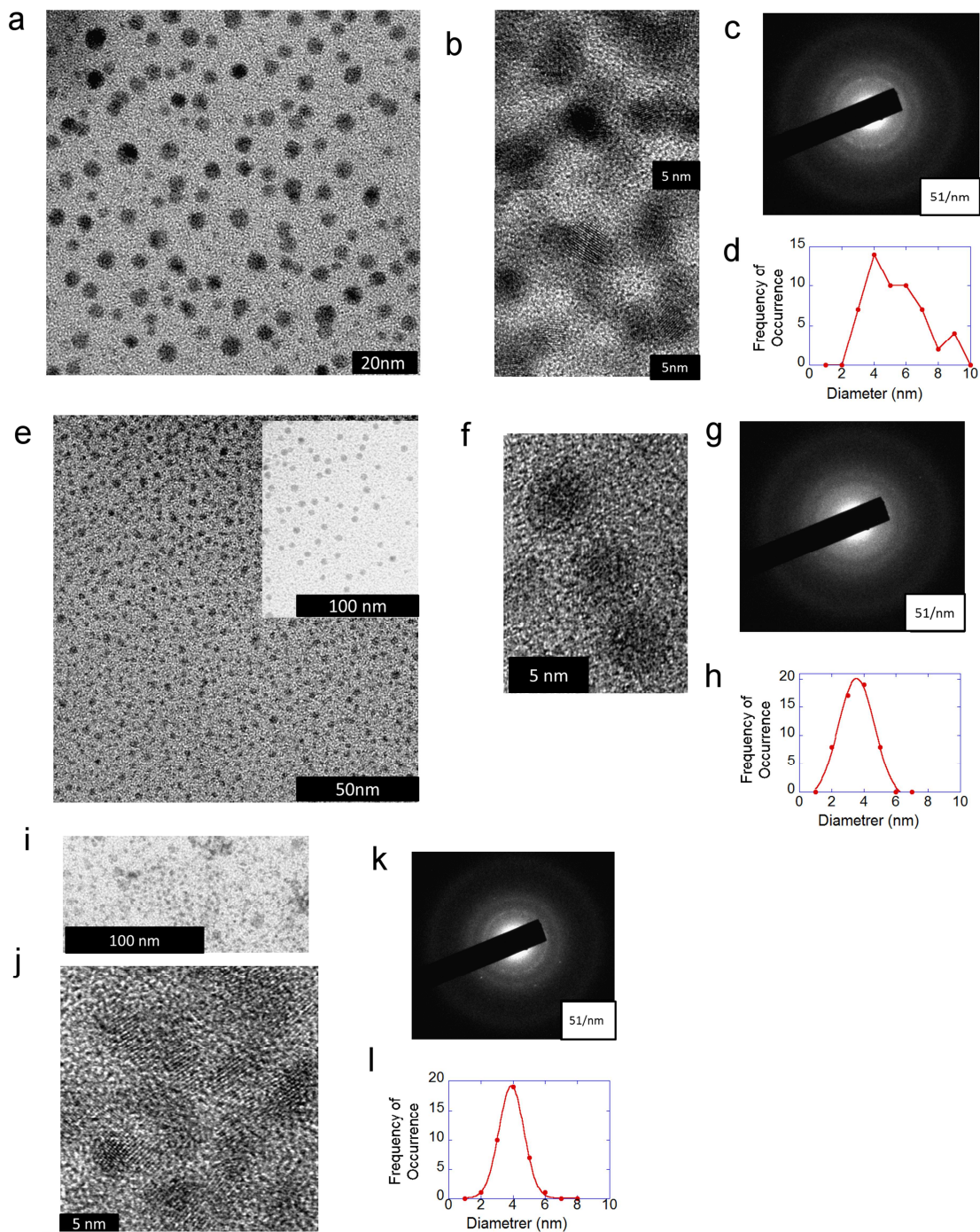


Figure S4: Transmission Electron Micrographs (TEM), High Resolution Transmission Electron Micrographs (HRTEM), Selected Area Electron Diffraction (SAED) and Size Histograms of PbSe samples, which are synthesized via the methods described in figure 3a b and c of the main manuscript. **a,b,c, d.** are the TEM, HRTEM, SAED and Histogram of the PbSe samples synthesized via figure 3a. These PbSe QDs were prepared by heating lead acetate at 100°C in presence of solvent

and oleic acid. Lead oleate was then cooled to RT and TOPSe was injected. The histogram suggests a poor size distribution. **e,f,g, h.** are the TEM, HRTEM, SAED and size Histogram of the PbSe samples synthesized following figure 3b. These PbSe QDs were prepared by heating lead oleate at 180°C for 30 minutes before the actual selenium addition. TOPSe was injected after cooling to RT. The size histogram suggests a good size distribution. **i,j, k, l.** are the TEM, HRTEM, SAED and size Histogram of the PbSe samples synthesized following figure 3c. These PbSe QDs were prepared by treating lead oleate with NaOH prior to addition of TOPSe at RT. The size dispersion is seen to be even sharper than the QDs synthesized through the procedure in figure 3b. We do observe some extent of clumping of the QDs, possibly suggesting a poorer surface passivation due to the presence of NaOH.

PbS Magic Sized Nanocrystals (MSNCs):

Lead oxide (0.892g, 4mmol), oleic acid (5ml, 9.5mmol) and ODE (12ml) were added into a RB and then heated to 150°C under Argon for 1.5 hours. The flask was then cooled to RT and 4ml of 2M TOPS was injected at RT. The mixture was left at RT for 4hr. After 4hrs the solution turned from transparent to brown. This indicates the formation of PbS MSNCs. MSNCs were purified by precipitation and centrifugation with methanol, ethanol and isopropanol. MSNCs were redissolved in hexane prior to each successive addition of alcohol. After the final step, the precipitate was allowed to dry before redissolution in the appropriate nonpolar solvent.

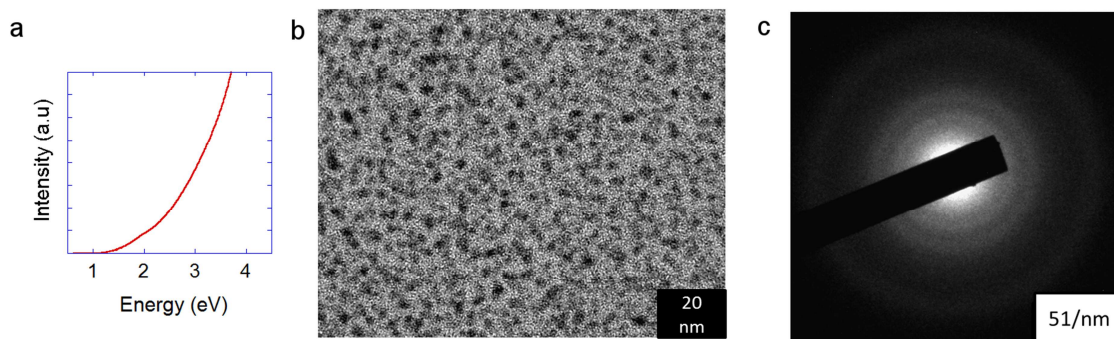


Figure S5: **a.** Absorption spectra of PbS MSNCs. **b.** TEM image of PbS MSNCs. **c.** SAD image of the PbS MSNCs.

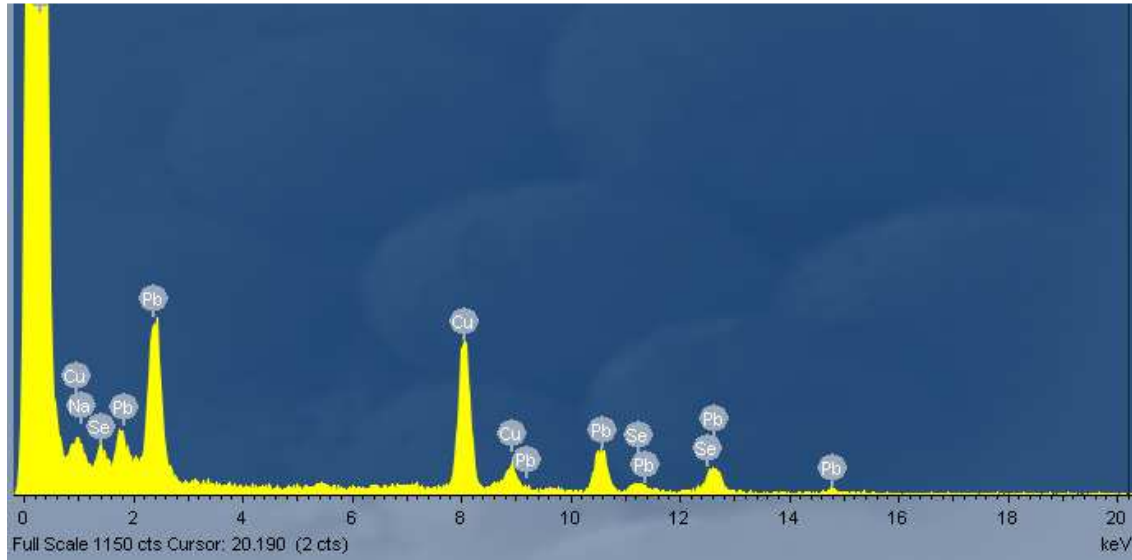
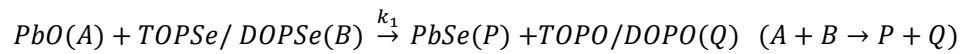


Figure S6: Energy-dispersive X-ray spectroscopy pattern of PbSe based QDs

Reaction scheme:

1. Nucleation of PbSe QDs



Rate of formation of PbSe is given by $\frac{dP}{dt} = k_1 AB$

In this case A is solid. We therefore set its activity to unity for the initial phases of the reaction.

Following its consumption, its activity drops to zero, and the reaction ceases instantaneously. This allows us to write the following equations for the early part of the reaction, when $A = 1$.

$$\frac{dP}{dt} = k_1 B \quad (1)$$

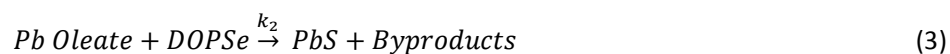
Then, rate of consumption of B is

$$\frac{dB}{dt} = -k_1 B \quad (2)$$

At $t=0$, $B=B_0$ and $P=0$, implying that in general $B(t) = B_0 e^{-k_1 t}$.

Solving for P using equation 1, $P = B_0 [1 - e^{-k_1 t}]$.

2. Growth of PbSe QDs



PbSe nanocrystals grow by the deposition of PbSe on top of existing PbSe nuclei. In general, surface catalyzed/surface deposition reactions usually exhibit a zero order. In particular, for the reaction studied here, the rate determining step would be a reactive collision of Pb Oleate and TOPSe on the surface of a PbSe QD. This is clearly independent of reagent concentrations over a broad range. This suggests that growth step follows zero order kinetics. We thus write

$$P = \begin{matrix} B_0 [1 - e^{-k_1 t}] + k_2 t & \text{Before Exhaustion of PbO} \\ k_2 t & \text{After Exhaustion of PbO} \end{matrix}$$

Because $k_2 \ll k_1$, we can further write

$$P(t) = \begin{matrix} B_0 [1 - e^{-k_1 t}] & \text{Before Exhaustion of PbO} \\ k_2 t & \text{After Exhaustion of PbO} \end{matrix} \quad (4)$$

We have used equation (4) to fit the kinetic data obtained from the experiment in figure 4a, main manuscript. The first part of equation (4) has also been used to generate the fits in figure 3e, f, g. We further note that within the noise in the experimental data, it is not possible to determine the reaction orders particularly for the second step with complete certainty. The excellent agreement between the observed and predicted trend however suggests a small or near vanishing reaction order.

References:

- [1] C. A. Cattley, A. Stavrinadis, R. Beal, J. Moghal, A. G. Cook, P. S. Grant, J. M. Smith, H. Assender, A. A. R. Watt, *Chemical Communications* **2010**, 46, 2802-2804.