Electronic Supplementary Material (ESI) for Nanoscale
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SUPPORTING INFORMATION

Timing Matters: The Underappreciated Role of Temperature Ramp Rate for Shape Control and Reproducibility of Quantum Dot Synthesis

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Methods and materials:

Lead oxide (99.99%), selenium (99.999%, pellets), trioctylphosphine (90%, technical grade), diphenylether (> 99%), and oleic acid (90%, technical grade) were all purchased from Sigma-Aldrich and were used without purification. Common solvents such as hexane and ethanol were purchased from various sources and used without purification. Reaction temperature was controlled using a J-Kem Scientific 310 precision heater with a heating mantle. Time-temperature data was logged every 1 second using the temperature controller and the proprietary Kem-Net software.

X-Ray Diffraction was obtained using a Rigaku Smartlab X-Ray Diffractometer using Cu Kα radiation. Transmission electron microscopy was performed with a Tecnai T-12 microscope operating at 120 kV.

Synthetic Procedure:

Lead oleate stock solution is produced by dissolving 6 mmol of PbO in 48 mL of diphenyl ether (DPE) and 12 mL of oleic acid. The solution is heated to 150 ^{0}C and stirred under nitrogen for two hours. Once complete, this solution is cooled to room temperature and gently stirred with 3A molecular sieve under nitrogen for 1 day to remove any water produced during the lead:oleate formation.[1] This solution is filtered and stored under nitrogen for use in later reactions. Separately, 8 mL of molecular sieve dried DPE and 3 mL of 1M trioctylphosphine:selenide (TOP:Se) is heated to 200 ^{0}C under nitrogen for one hour, at which point 10 mL of lead oleate stock solution and 2 mL of room temperature DPE are rapidly injected into the TOP:Se solution, causing the temperature to dip below 140 ^{0}C. The solution is heated back up to 200 ^{0}C at varying rates determined by manipulating the power output of the temperature controller. Heating rates can be further increased by packing the outside of the flask with cotton insulation. 6 minutes after the lead:oleate injection, the reaction is quenched by submersing the flask in water. The particles are cleaned using hexane and ethanol as the solvent and anti-solvent respectively. After two rounds of cleaning, the particles are dissolved in hexane, and centrifuged. The supernatant of this solution is the well capped particles, and is retained. Typically, the well-dispersed product yield for this reaction is about 10%. For reactions reported in this work, all syntheses within a series were performed within 24 hours of each other and within 1 week of synthesis of the lead oleate stock solution.

In some cases, reactions were performed using solvents other than DPE. For these reactions, the same parameters were used, only the solvent was changed with a 1:1 replacement.

Reaction with Same Growth Temperature

A set of reactions were performed using the previously described method but with an extended reaction time (30 mins) that allowed all reaction to reach a final growth temperature of 180^{0}C. The effect of varying the temperature ramp rate was studied.

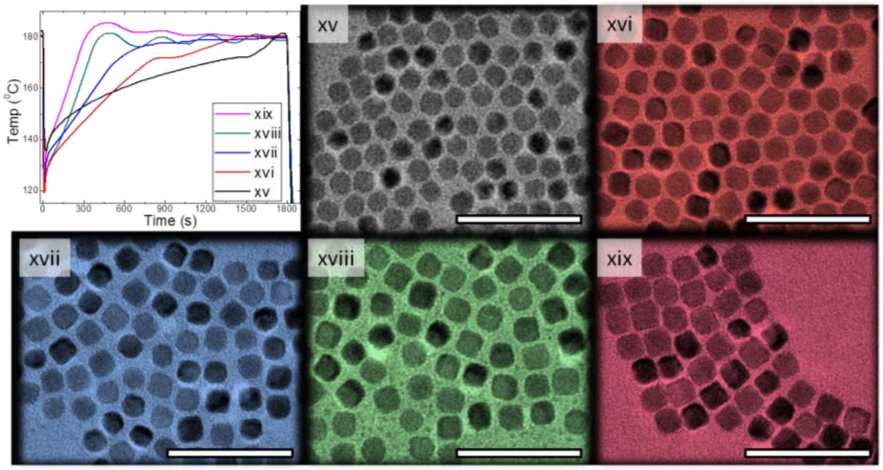

Figure S1. (upper left) The full time-temperature profile of reactions xv-xix, pictured in the TEM. Scale bar is 50 nm

Effect of Temperature Dip on Reaction

The magnitude of the temperature dip was adjusted by either heating the injection solution to different temperatures (to reduce the dip), or by increasing the amount of DPE in the injection volume (to increase the dip). When increasing the injection volume, less DPE was used in the initial reaction solution in order to maintain a consistent chemical composition within the reaction vessel.

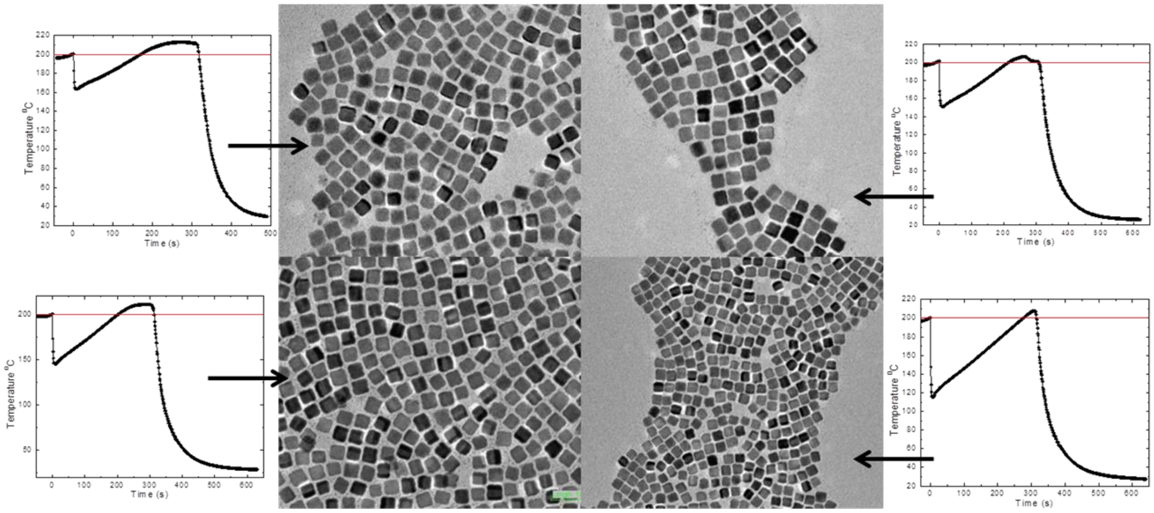

Figure S2a. 4 reactions are reported with different time-temperature profiles, varied primarily by adjusting the magnitude of the initial dip. Representative TEM images of these reactions are included. The scale bar represents 100 nm.

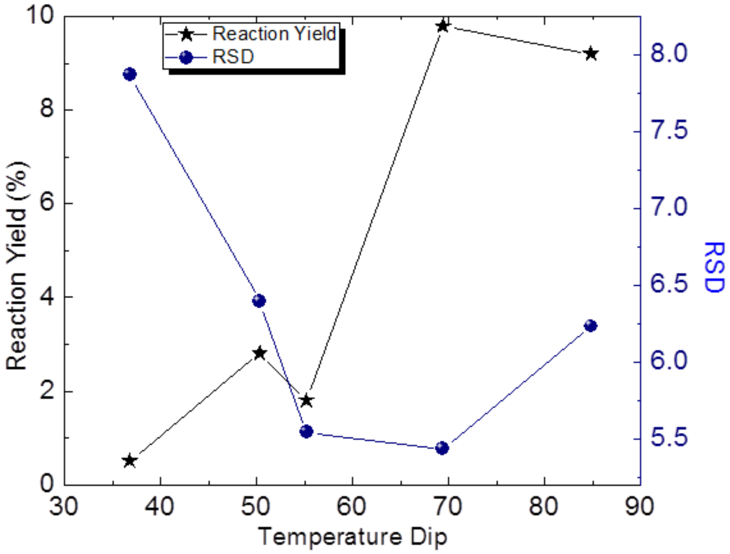

Figure S2b. Statistics on reactions with different magnitude of temperature dip. As the magnitude of the dip increases, the reaction yield (defined only as the well dispersed portion of the product) increases. The relative standard deviation of the diagonal length of the cubes also decreases with increasing temperature dip.

Effect of Water on Particle Shape

For certain reactions, we relaxed the drying requirements on solvents and the precursor solution. It was found that the most important solution to dry is the lead:oleate precursor solution. This is likely due to the formation of water during the reaction between lead oxide and oleic acid to form lead oleate. We also performed reactions in which water was deliberately introduced into the reaction mixture to observe its effect on particle shape.

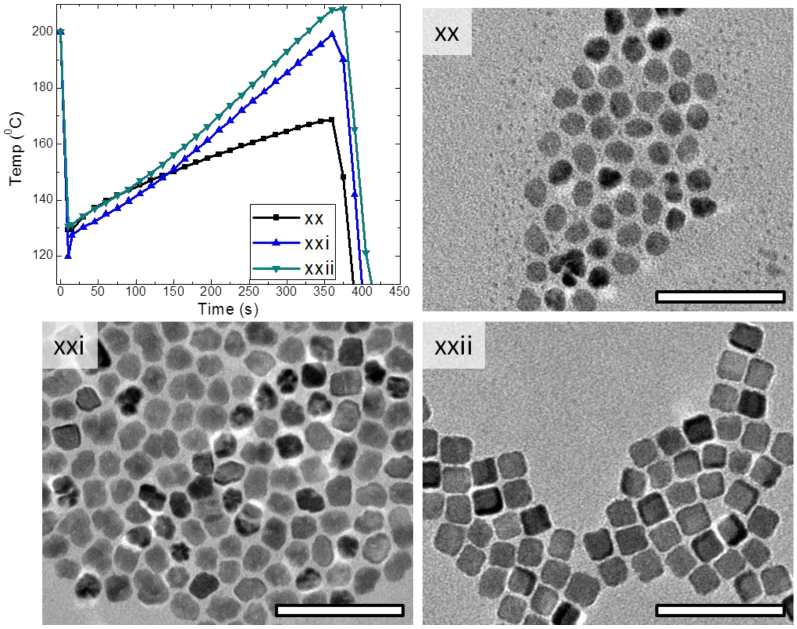

Figure S3a. Three reactions in which adventitious water from solvents and lead formation were allowed to exist within the reaction vessel were performed with differing post-injection ramp rates. TEM images from those reactions are provided. Scale bar is 50 nm.

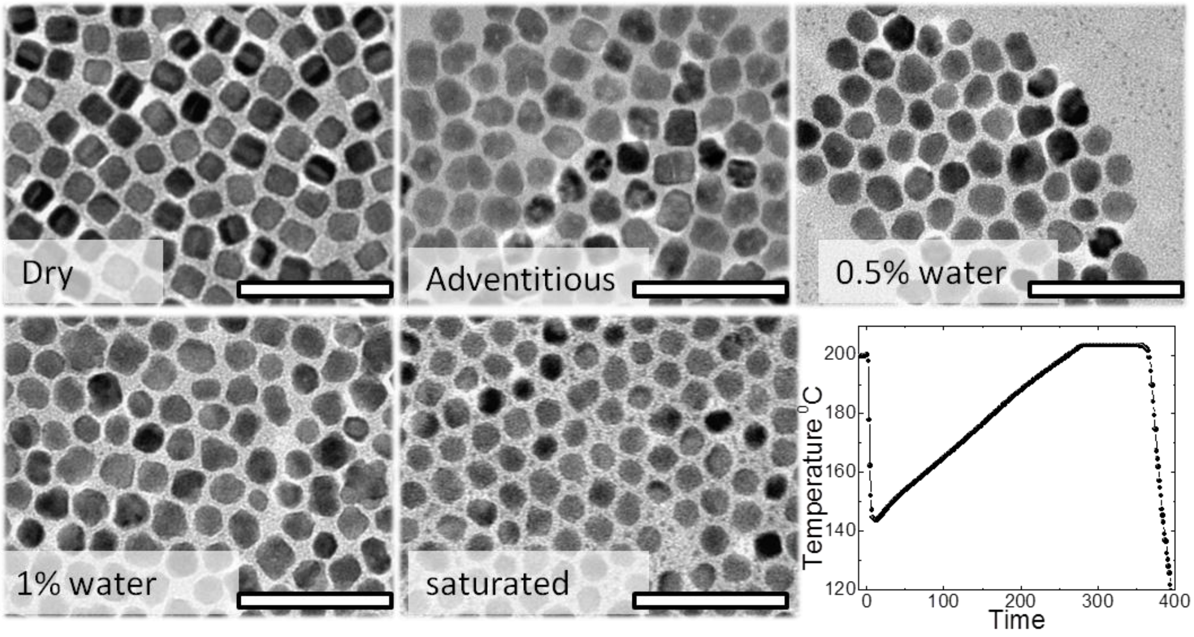

Figure S3b. TEM images from a series of reactions in which the amount of water in the solution is allowed to vary, along with a sample time-temperature profile. The time-temperature profile for these reactions are as close to identical s possible. Dry is defined as all solutions either dried with molecular sieve or extended heating. The adventitious water solution did not include any molecular sieve drying of any solutions. For the other reactions, water was deliberately introduced. The scale bar represents 50 nm.

Cube Reactions in other Solvents

PbSe Nanocubes reactions were carried out according to the described method but the diphenyl ether in the reaction was replaced with different solvents. We found that for the solvents studied, which include ethers, amines, and long chain alkenes, the reaction was insensitive to solvent. While the most monodisperse cubes were produced using diphenyl ether, it is possible to use dioctyl ether, trioctylamine, octadecene, and likely many other solvents.

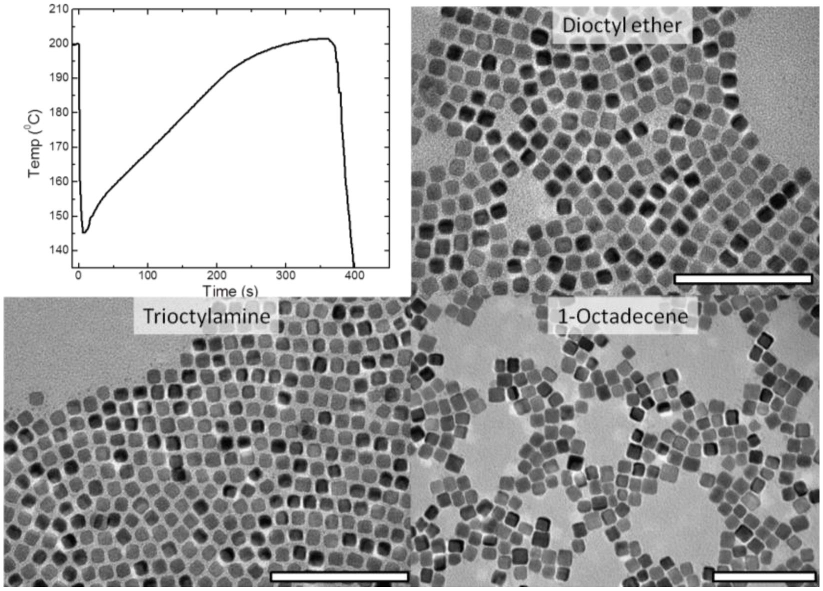

Figure S4. A representative time temperature profile for three reactions is given. Also provided are TEM images for nanocubes reactions performed using dioctyl ether, triocylamine, and 1-octadecene. Scale bar is 100 nm.

1. B. G. Williams, M. Lawton, *J. Org. Chem.* 2010, **75**, 8351.