SUPPORTING INFORMATION FOR

Controlled Growth of Nanoparticles from Solution with *In Situ* Liquid Transmission Electron Microscopy

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EXPERIMENTAL PROCEDURES:

Lead sulfide precursor solutions for *ex situ* and *in situ* growth: Lead acetate [$Pb(CH_3COO)_2{\cdot}3H_2O$] (Sigma Aldrich), thioacetamide [C_2H_5NS] (Sigma Aldrich), and polyvinyl alcohol [MW 6,000] (Sigma Aldrich) were dissolved in water to stock concentrations of 0.5 M, 0.5 M, and 5% w/v respectively. Isopropyl alcohol [C_3H_8O] (Sigma Aldrich) was used undiluted and the thioacetamide was adjusted with acetic acid to pH 2.8. For the 1x *ex situ* experiment, 500 µl of lead acetate was combined with 125 µl of isopropyl alcohol, 125 µl of polyvinyl alcohol and 500µl of thioacetamide in order. Thioacetamide decomposition can be accomplished either by illumination with high-energy electrons [1], thermal degradation [2, 3], or intense optical stimulation between 330 and 532 nm [4, 5]. The different solutions used for these experiments were either irradiated with UV light at 355 nm or heated to 80 °C to verify growth of PbS nanoparticles *ex situ*. For *in situ* experiments, the stock solutions were further diluted (1,000-5,000x) in ddH_20 prior to mixing in ratios described above. The amount of thioacetamide was kept constant for the experiments comparing variable chemical composition.

In situ environmental chamber assembly and sample loading: We utilized two continuous flow *in situ* liquid stages for the experiments in this paper: one stage is compatible with an aberration corrected JEM-2100F/Cs microscope while the other is compatible with a JEOL JEM-2000FX microscope modified as a Dynamic TEM. Both stages incorporate the same reusable environmental chamber design (Hummingbird Scientific). After cleansing the tip with an acetone wash to ensure a pristine environmental chamber, the inlet and outlet lines for the stage were primed with reactant solution. Two square silicon chips containing silicon nitride membranes were then loaded into the tip of the continuous flow *in situ* liquid stage with membranes facing each other. The silicon chips have electron transparent 50 nm thin film silicon nitride membranes (50 x 200 μm) residing on silicon substrate (2.60 x 2.60 x 0.3 mm). Gold spacers deposited on the four corners of one chip (50-200 nm tall) dictate the nominal fluid path length for imaging. Prior to placing the upper window into the holder tip, a 1 μl sample of the diluted reaction solution was deposited directly on the surface of the lower window. After final assembly the tip was tested for maintaining vacuum in a Pfeiffer vacuum test chamber.

Scanning Transmission Electron microscopy: The *in situ* liquid stage was inserted into a JEM–2100F/Cs with a spherical aberration corrector. Prior to sample insertion the microscope was aligned to 1-angstrom resolution using the standard Platinum/Iridium calibration sample for the CEOS corrector system. STEM images were collected simultaneously on Bright Field and Dark Field detectors with dwell times of 2 μs or 10 μs per pixel.

Dynamic Transmission Electron Microscopy: The Dynamic Transmission Electron Microscope (DTEM) incorporates a time resolved pump-probe experimental modality by integrating two lasers with the electron optics of a conventional TEM (JEOL JEM-2000FX) as shown in Supplementary Figure 1. The sample drive laser illuminates the specimen with a tunable wavelength to initiate a reaction within a sample prior to, or during, imaging with electrons either in a pulsed or continuous wave (conventional TEM equivalent) imaging mode. Following a variable temporal delay (ranging from nanoseconds to milliseconds), a cathode drive laser

initiates the photoemission of electrons from a photocathode source inside the gun of the TEM. The emitted electrons are bunched within a 15 ns pulse that are focused via the electron optics of the TEM and subsequently image the specimen. Prior to insertion, the electron optics, cathode drive and sample drive lasers were all aligned with sacrificial thin Ti foils. The electron dose exposed to the fluid cell within the Dynamic TEM was below the detection limit of 0.5 pA/cm^2. The low dose imaging condition provided by pulsed imaging mode helped mitigate generation of hydrogen gas bubbles from radiolysis damage within the solution. This low dose condition was obtained through 200 keV pulse mode of the cathode laser stimulating 15 ns electron pulses at 8 Hz. Images were obtained before and after continuous cathode pulsing as well as after the conclusion of PbS nanocrystal growth at varied time intervals ranging from 1 pulse to 10 seconds. Continuous pulsing of the cathode laser onto the windowed reaction was recorded for a 20 min interval. After setting the sample drive laser to a wavelength of 532 nm, we were able to acquire images of nanoparticle growth initiated by laser-induced decomposition of thioacetamide. The initiation of the reaction was initiated with the drive laser aimed directly at the windowed cell, the holder being tilted 10° toward the drive laser entry port. Drive laser was stable throughout the experiment at 532 nm wavelength, $1/e^2$ radius of 30 μm and 0.60 ± 0.02 μJ energy. Images were obtained at 1,200x magnification at the corners of the fluid cell to limit bulging effect by SiN thin film membranes.

SUPPLEMENTARY FIGURES AND FIGURE LEGENDS:

Figure S1: Schematic of the continuous flow *in situ* liquid stage. A) Picture overview of the *in situ* stage. B) Diagram showing arrangement of electron transparent windows and flow of fluid, path of electron pulse and sample drive laser representative of the Dynamic TEM system. C) STEM image highlighting (circles) the smallest observable nanoparticle nuclei corresponding (from top to bottom) to 1.26, 2.11 and 0.84 nm, respectively. Scale bar represents 10 nm. D) Illustration showing the relevant details for the Dynamic TEM.

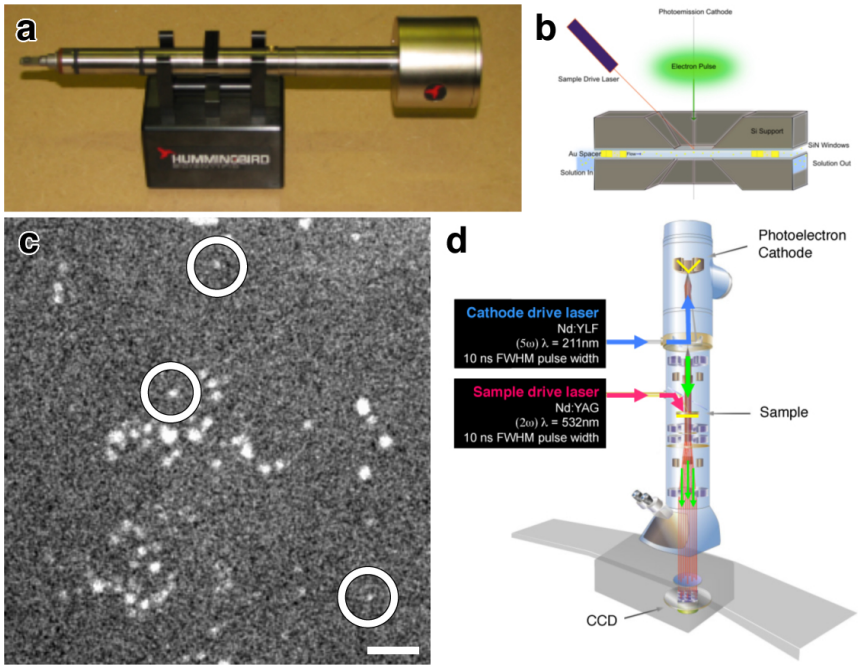


Figure S2: Tracking nanoflower growth. Correlated image series showing the growth of a single nanoflower over 5 minutes. Scale bars represent 20 nm.

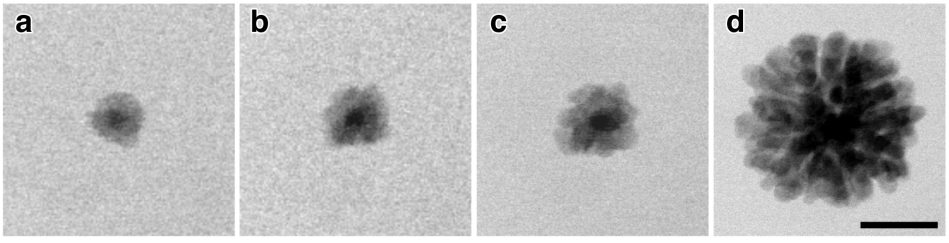
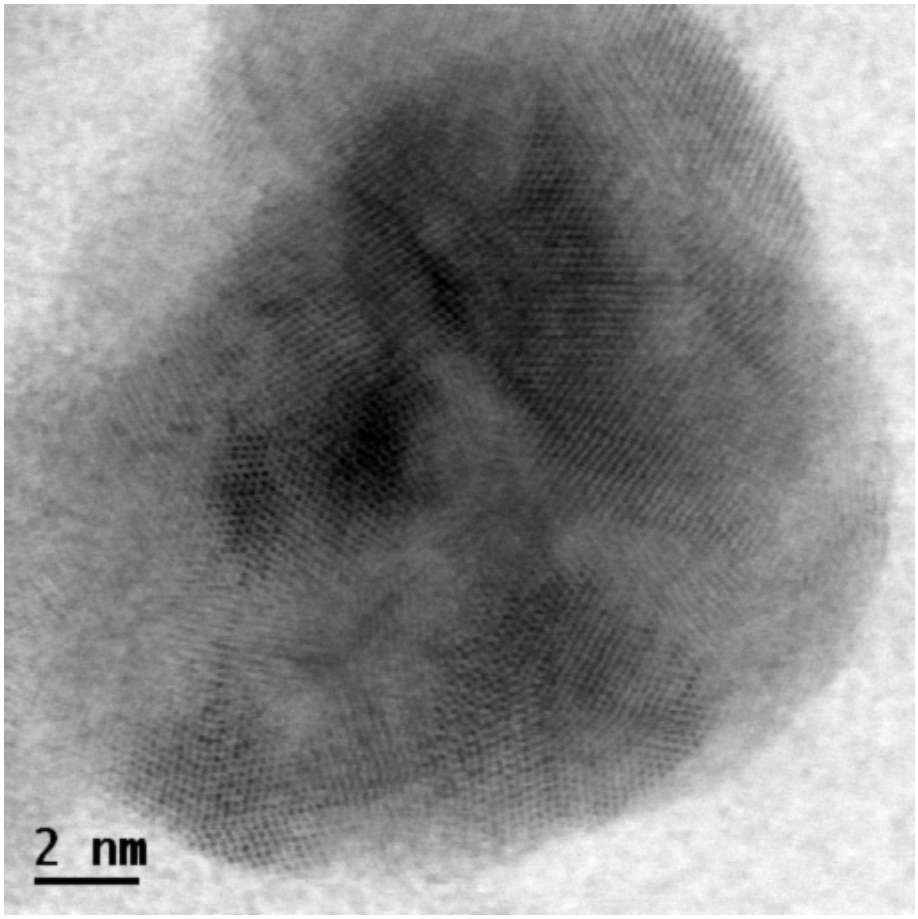


Figure S3: Postmortem analysis of PbS nanoparticles grown *in situ*. Postmortem analysis of an *in situ* grown nanoparticle from the 2:1 (Pb:S) condition using aberration corrected STEM.



Movie S1: Movie depicting nanoparticle growth in real-time. This movie shows the same growth sequence as visualized by time snapshots in Figure 2a-c and the plot in Figure 2e.

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