

Supporting Information for “Rapid and facile synthesis of high-quality, oleate-capped PbS nanocrystals”

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Contents:

1. Detailed procedures for synthesis of PbS NCs of various sizes
2. Evidence for oleate capping of these PbS NCs
3. Stability of the PbS NCs

1. Detailed procedures for PbS NC synthesis of various sizes:

A. “Standard” synthesis of 7.4 nm PbS NCs with exciton absorbance peak near 1750 nm

In the “standard” synthesis, lead oleate was prepared by combining 335 mg (1.5 mmol) PbO with 1.13 g (4.0 mmol) HOIAc and 5.0 mL of ODE in a 25 mL, three-necked round bottom flask. A magnetic stir bar was added, after which one side neck of the flask was equipped with a thermometer, the middle neck was connected to a reflux condenser and inert gas/vacuum manifold, and the remaining side neck was sealed with a septum. The flask was thoroughly evacuated ($P < 0.1$ mTorr) and refilled with flowing, high-purity N₂ gas. Next, 3.0 mL of TOP, taken from an inert gas glovebox in a sealed syringe, was injected through the septum under the flowing N₂ gas. This mixture was heated with stirring to 95 °C under vacuum for 1 hour, until a clear solution of lead oleate was obtained. At that time, the flask was placed back under N₂ flow, and the temperature was lowered to 85 °C.

To prepare the sulfur precursor, 40 mg (~0.5 mmol) of TAA was thoroughly dissolved in 0.25 mL of DMF. After the TAA dissolved completely, 3.0 mL of TOP and 2.0 mL DPE were added, and the mixture was stirred until thoroughly mixed, approximately 10 minutes. This mixture was removed from the glovebox in a sealed, gas-tight syringe and

rapidly injected into the stirring lead oleate mixture at 85 °C. After the injection, the reaction was held at 85 °C for one hour.

B. Synthesis of 8.5 nm PbS NCs with exciton absorbance peak near 1870 nm

The “standard” synthesis outlined above in section A was followed exactly except that 1.55 g (5.5 mmol) HOIAC was used in the lead oleate preparation step.

C. Synthesis of < 5.0 nm PbS NCs with exciton absorbance peak near 1325 nm

The “standard” synthesis outlined above in section A was followed exactly except that 30 mL of ODE was added into the flask at the outset instead of 5 mL.

D. Synthesis of 5.7 nm PbS NCs with exciton absorbance peak near 1500 nm

The “standard” synthesis outlined above in section A was followed exactly except that 1.55 g (5.5 mmol) HOIAC and 30 mL of ODE were added into the flask at the outset.

E. Synthesis of 7.0 nm PbS NCs with exciton absorbance peak near 1700 nm

The “standard” synthesis outlined above in section A was followed exactly except that 1.156 g (1.5 mmol) of dry lead oleate was substituted for the PbO and HOIAC used in that reaction. The pure, dry lead oleate was prepared according to the method of Hendricks *et al.*¹

F. Synthesis of 9.4 nm PbS NCs with exciton absorbance peak near 1950 nm

The “standard” synthesis outlined above in section A was followed exactly. During the one hour growth period, a second TAA injection solution, identical to the first, was prepared in the glove box and loaded into a syringe. A syringe pump was used to gradually inject this solution at a rate of 130 µL/minute while the temperature was held constant at 85 °C. Once the second injection was completed, the heat was removed and the sample allowed to cool to room temperature.

¹ M. P. Hendricks, Campos M. P., Cleveland G. T., Jen-LaPlante I., Owen J. S. *Science*, 2015, **348**, 1226.

2. Evidence for oleate capping of PbS NCs

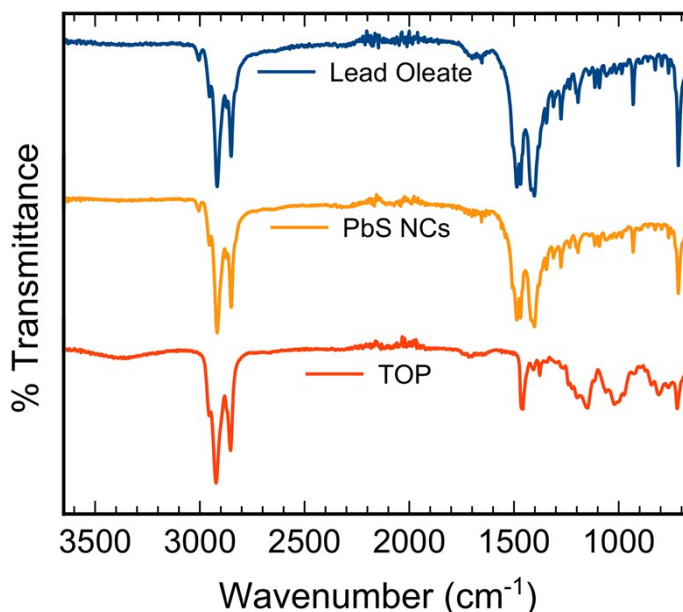
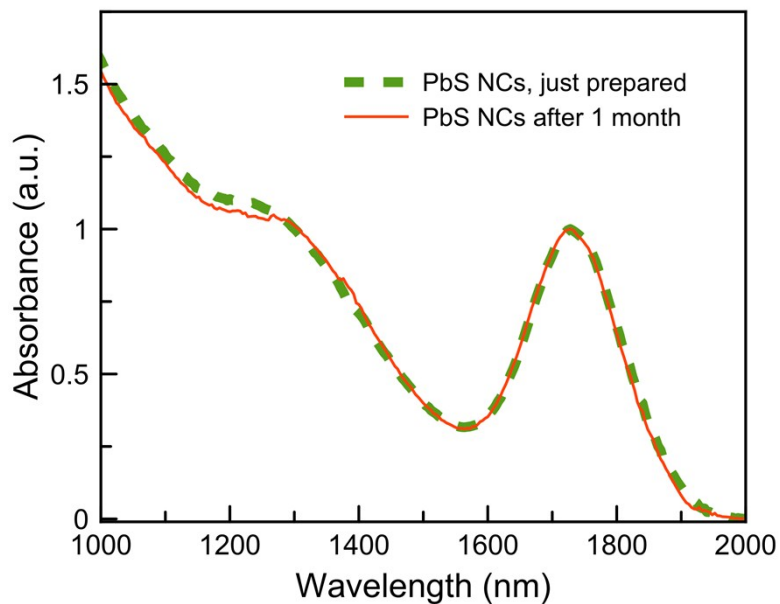


Figure S1. FTIR spectra from solid lead oleate (top, blue curve) and from solid, purified PbS NCs (middle, orange curve). The lead oleate was synthesized according to the method of Hendricks et al. as explained in the text of the article. The data above were collected in attenuated total reflectance mode on an HP model FTIR. The two curves are almost identical, down to the fine structure in the fingerprint region (below 1500 cm⁻¹). For comparison, a spectrum of tri-*n*-octylphosphine (TOP) is also shown (bottom, red curve), and there is no evidence that the PbS NC spectrum contains much, if any, contribution from surface-bound TOP. Although the C-H stretching region looks similar for all of these spectra due to the dominance of aliphatic chains, a key difference in the oleate spectrum are the presence of a small peak on the high energy side, near 3000 cm⁻¹, which we attribute to the presence of C=C double bonds. This feature is absent in the TOP spectrum, so the similar amplitudes of this feature in the top two spectra suggest that the ratio of C=C double bonds to C-C single bonds in the PbS NCs is similar to that in the pure lead oleate sample. From these data we conclude that oleate is the primary, dominant surface capping ligand in these NCs and TOP is present at most at a very low surface coverage. The spectra have been offset for clarity.



3. Long-term air stability

Figure S2. Absorbance spectra of PbS NCs shortly after preparation (thick, green, dashed curve) and after being stored for one month in the reaction mixture without protection from air or light (thin, red, solid curve). The exciton peak began to blue-shift days later. Once started, the spectral shift was rapid, moving a few hundred nanometers within a few days. This type of behavior (apparent stability for a few weeks followed by rapid degradation) is typical of our PbS NC samples.