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Thiolate-Capped PbS Nanocrystals in Water: Sensitivity to O_2, pH and Concentration, an Alternate Pathway for Crystal Growth and a Top-Down Synthesis

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SUPPORTING INFORMATION

1. Figures

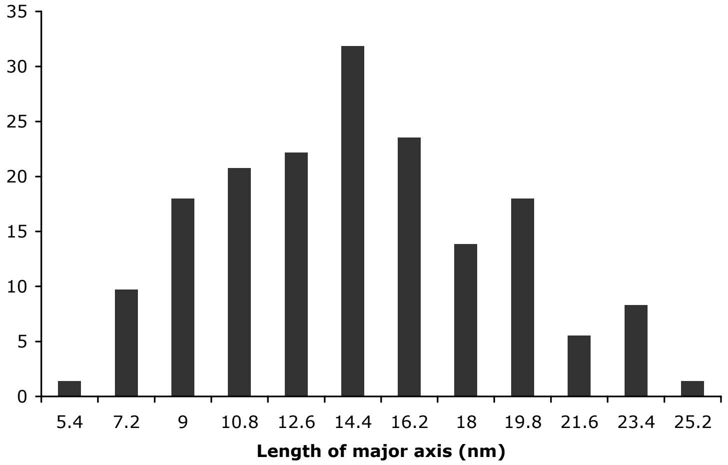

Figure S1. Particle size distribution as measured by TEM of PbS nanocrystals reaulting from the dissolution of PbS powder in an aqueous solution containing TG (0.1 M), DTG (0.17 M) and Et_3N at pH 11.5. This distribution was determined from the micrograph from which Figure 4 in the main body of the paper was created.

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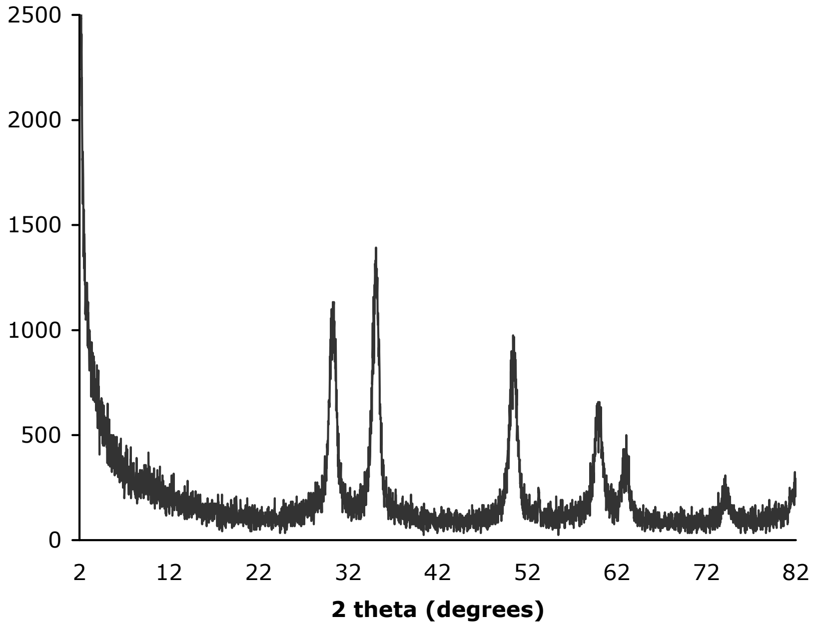

Figure S2. Powder X-ray diffraction pattern of PbS nanocrystals produced by the top-down method ([TG] = 0.1 M, [DTG] = 0.17 M). Only the first six reflections of the FCC lattice are shown due to limitations of the instrument. The 2θ values (°) and Miller indices of the peaks are: 30.38 (111), 35.12 (200), 50.52 (220), 60.06 (311), 63.06 (222), 74.12 (400). These data correspond to those of the reference pattern of PbS (#05-0592 in the Powder Diffraction File from the International Centre for Diffraction Data).

2. Experimental Section

2.1 General Considerations

The ligands, thioglycerol (3-mercapto-1,2-propanediol, TG) and dithioglycerol (1,2-dimercaptopropan-3-ol, DTG), and the metal salts, $Pb(OAc)_2$ and PbS, were obtained from commercial sources and used as supplied. Preparations of PbS nanocrystals were conducted in distilled H_2O under N_2 at 0 °C unless otherwise specified. These solutions were stored in sealed Schlenk tubes under N_2 and exposed to ambient laboratory lighting. UV-Visible absorption data were obtained using a Cary 300 Bio UV-Visible spectrometer with a deuterium/tungsten two-lamp system; solutions were diluted to a concentration of *ca.* 8.3×10^{-3} M using distilled water. Hydrodynamic diameters were determined using a Melvin Nano-S type Zetasizer equipped with a 532 nm laser for solutions of nanocrystals dispersed in H_2O (refractive index = 1.330); analyses were performed at 20°C using disposable plastic cuvettes. TEM measurements were conducted on a Phillips CM10 microscope operating at 80kV with a 40 μm aperture. Samples were deposited onto a carbon-coated copper grid by wicking away solvent from small droplets of solutions containing PbS nanocrystals. Powder X-ray diffraction data were collected using a Rigaku diffractometer employing Co Kα radiation (λ = 1.79926 Å). NMR spectra were recorded at 20 °C on a Varian Mercury 400 spectrometer (400.089 MHz for ^{1}H and 100.613 for ^{13}C) using D_2O as solvent.

2.2 Assays for disulfide production

a. For PbS colloids produced in the "top-down" fashion. A D_2O (30 mL) solution containing TG (3.0×10^{-3} mol, 0.260 mL) and DTG (1.08×10^{-3} mol, 0.108 mL) was prepared in a 100 mL Schlenk flask, which had been wrapped tightly in black plastic so as to minimize exposure to light. The pH of this solution was increased to *ca.* 11 by the addition of Et_3N (1 mL). The solution was degassed by purging with N_2 for *ca.* 10 min before being split into two equal aliquots. To one of these was added PbS (1.25×10^{-4} mol, 299 mg). Both aliquots were stored at r.t. in the dark and stirred vigorously (1200 rpm) for 24 to 48 h. Undissolved PbS was then removed from the appropriate aliquot by centrifugation under N_2. Each of the PbS-containing and PbS-free aliquots were further divided into two equal fractions, one being placed into a 50 mL Schlenk flask, which had been wrapped tightly in black plastic, and one into a flask without wrapping. All four fractions were then opened to the air. The two wrapped flasks were stored in a dark cupboard, while the two flasks without wrapping were stored in the fumehood and exposed to constant illumination from a 15 W halogen desk lamp from which the UV filter had been removed. The solutions were stirred at 1200 rpm at r.t. for a maximum of 3 h during which aliquots were removed at 30 min intervals for analysis by ^{1}H NMR spectroscopy as detailed in **c** (below). Solutions containing PbS were centrifuged to remove black precipitates prior to analysis, and the blank solutions were treated in the same manner.

b. For PbS colloids produced in the "bottom-up" fashion. A stock thiol solution was prepared in the same manner as **a** (above) and split into two equal aliquots. To one of these was added $Pb(OAc)_2$ (2.5×10^{-4} mol, 95 mg). This solution was stirred at 1200 rpm and cooled on ice for *ca.* 10 min. A solution of Na_2S (0.1M), also prepared in D_2O, was then added rapidly (1-2s) with continuous stirring. Both aliquots were stored at r.t. in the dark and stirred vigorously (1200 rpm) for *ca.* 24 h. The remainder of the experiment was then conducted in the same manner described in **a**.

c. Analysis. The formation of disulfides was monitored quantitatively using ^{1}H NMR spectroscopy in $CDCl_3$ solution with Et_3N serving as an internal standard. Prior to exposure to O_2, the solutions showed characteristic TG peaks at δ 2.36 (dd, CH_2SH, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 6.5 Hz), 2.41 (dd, CH_2SH, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 6.5 Hz), 3.35 (dd, CH_2OH, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 6.5 Hz), 3.46 (m, $CHOH$), 3.56 (dd, CH_2OH, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 3.7 Hz). The oxidation of TG to di(thioglycerol)disulfide ($\{CH_2(OH)CH(OH)CH_2S\}_2$, DTGDS) was characterized by the gradual disappearance of these peaks, combined with the simultaneous appearance of five multiplets at δ 2.57, 2.75, 3.38, 3.47 and 3.78. The extent of oxidation was determined from the ratio of the integration of the TG methylene peaks centred at δ 2.38 to that of the Et_3N methylene peak at δ 2.98.