

SUPPORTING INFORMATION

EXPERIMENTAL SECTION

Quartz powders were prepared by the dissolution of amorphous silica at elevated temperature and pressure. Reaction temperatures were controlled using a Parr 4843 programmable temperature controller providing ± 2 °C accuracy. When used, 500 nm silica spheres were prepared by the Stober method¹ with 0.29 M tetraethoxy orthosilicate (99%, Alfa), 1.19 M NH₄OH (reagent grade, 29.4% Fisher), and 7 M ultra-pure water (Milli Q UVPlus, Millipore) in ethanol (200 proof USP grade, Pharma).

Purification. Products were dialyzed in 3500-Dalton dialysis tubing (Spectra/Por 3, Spectrum Laboratories) against a 4 L bath of ultra-pure water to remove unreacted soluble silica. The dialysis bath was changed 2-3 times daily. Initially, due to sample-bath pH equilibration, the pH of the bath increased from 5.8 (pH of ultra-pure water which is acidified by the activated carbon filter) to 10.5. The initial pH of the sample was 12. Consecutive bath changes resulted in lower values of the final pH. Once the bath pH fell below 8 (after 3-4 bath changes), baths and samples were titrated to pH 8 following bath changes. Samples were dialyzed until, upon reaction of molybdic acid with a sample of the bath water, no color change was observed.^{2,3} This required 8-10 bath changes.

Molybdic Acid Test. Soluble silica concentrations were determined by reaction with molybdic acid, which is known to form a yellow complex with Si(OH)₄ monomer.^{2,3} 5 mL samples of either reaction product or dialysis bath water were acidified with 0.1 mL 6M HCl and combined with 0.2 mL molybdic acid. Color changes were evaluated either by eye (to evaluate the progress of dialysis) or by UV/Visible absorbance. Absorbance was measured at 410 nm (Ocean Optics ST2000) and standardized against curves generated from the absorbance of sodium silicate solutions prepared to specified concentrations. For the case of reaction products that were cloudy with dispersed solids, samples were centrifuged at 900 G for 10 minutes prior to testing.

Pre-filtration. After dialysis the samples were first filtered over coarse filter paper (Whatman 541) and then over a glass-fiber pre-filter (Millipore AP15). The pH was adjusted to 8 before filtration. Filter cakes were washed with ultra-pure water, which increased the sample volume roughly 50%. Up to 6 different samples were combined and concentrated 8× by rotary evaporation.

Final Size Selection. Samples were filtered over a smaller pore size (1.2 or 0.2 μm) nylon filter (Osmonics). Size selection of the smallest fractions reported was achieved by centrifugation (Marathon 22k, Fisher). Centrifuge times varied for different samples and are noted in the text and figure captions. The smallest sized fractions (fraction 3 and fraction 4) were always taken from the supernatant of a centrifuged dispersion.

X-Ray Diffraction. The powder diffraction patterns in Figure 1 were obtained on a Bruker-AXS General Area Detection Diffraction System (GADDS, CuK_α, 50 kV and 40 mA) at a sample-to-detector distance of 12.3 cm. The detector distance and 2θ spacing was calibrated (GADDS system software) using the d₁₁₁, d₂₂₀ and d₃₁₁ reflections from silicon powder (325 mesh, Aldrich). Broadening of the quartz d₁₀₁ peak-width was calibrated against the width of the silicon d₁₁₁ reflection. Reflections shown in Figure 5 were obtained using 14-keV synchrotron radiation at the Advanced Light Source (Beamline 7.3.3, Lawrence Berkeley Laboratories, Berkeley CA). An X-ray CCD detector was used. Spatial distortion and sample-to-detector distance was calibrated (FIT2D two-dimensional data analysis program⁴⁻⁶) using the d₀₁₂, d₁₀₄, d₁₁₀, d₁₁₃, d₀₂₄, and d₁₁₃ reflections from alumina (NIST standard). Instrumental line broadening was calibrated using the d₁₀₀ reflection from LaB₆ (Sigma, <10μm). Peak widths were measured by least squares refinement of Voigt fits (Peak Fit v4, Jandel Scientific Software). Grain sizing was done by the Scherrer method⁷ according to:

$$t = \frac{0.9\lambda}{B \cos \theta_B} . \quad [1]$$

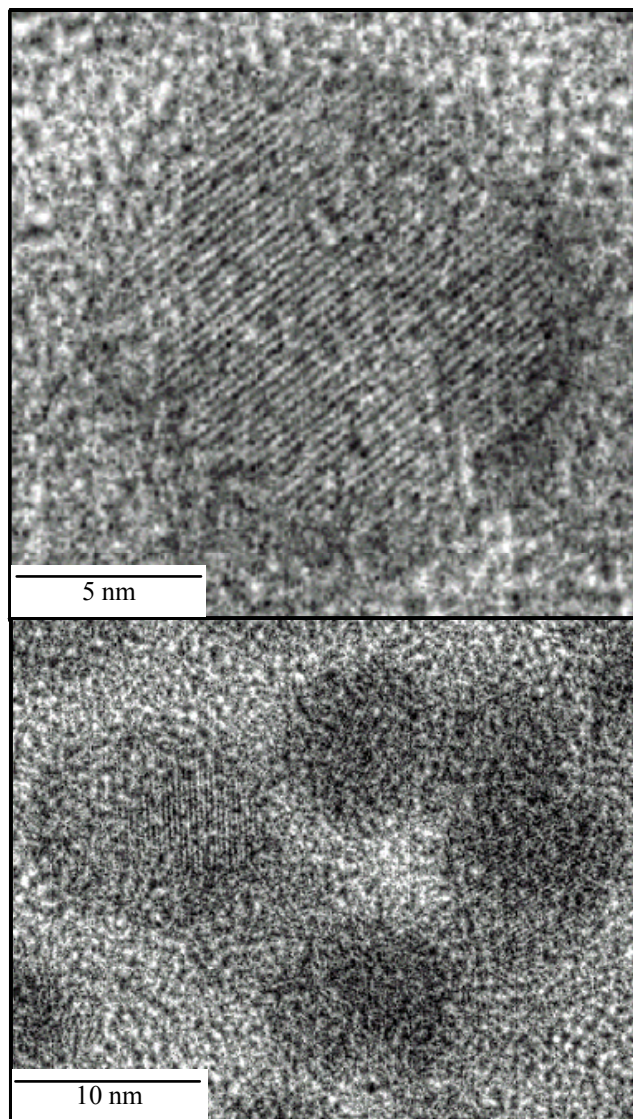
t is the crystallite size in angstroms, λ is the x-ray wavelength, B is the Full Width at Half Maximum (FWHM) and θ_B is the peak position. For Debye-Sherrer powder diffraction, B can be taken as the difference of the observed peak width and the peak width of a standard whose average grain size is well beyond 1000 Å (LaB₆, above)⁷.

Microscopy. Transmission electron microscopy was performed on a JEOL JEM 2010 operating at 200kV. Samples were prepared by placing a drop of dilute water dispersion on a 300 mesh copper grid that was coated with approximately 8 nm of amorphous carbon (Electron Microscopy Sciences). The droplet was allowed to completely dry on the grid. Scanning electron microscopy was performed on a JEOL JSM 6500F. Samples were dried onto silicon wafers and sputter-coated for 15 seconds with Au.

Energy Dispersive X-ray Analysis (EDX). EDX was performed on a Philips XL30 Environmental Scanning Electron Microscope equipped with an EDAX ES3030 detector. Samples were embedded in Eponate-12 resin (Ted Pella) and polished using a Leica UCT Ultramicrotome. They were then mounted onto aluminum holders (Electron Microscopy

Sciences) and sputter-coated for 15 seconds with Au.

SUPPLEMENTAL FIGURE 1



Supplemental Figure 1. High resolution transmission electron micrograph of nanocrystals from fraction 4. The reaction conditions are 3.5 g. fumed silica in 100 mL 0.1 M NaOH at 300 °C for 2 hr. This sample was dialyzed and concentrated. It was prefiltered and then filtered over a 0.2 μm Nylon filter. It is the supernatant after centrifuging for 8 minutes at 3313 G.

(1) Stober, W.; Fink, A.; Bohn, E. *J. Colloid and Int. Sci.* **1968**, 26, 62.

- (2) Franson, M. A., Ed. *Standard Methods for the Examination of Water and Wastewater*; 7 ed.; American Public Health Association, American Water Works Association, Water Pollution Control Federation: Washington, DC, 1971.
- (3) Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979.
- (4) Hammersley, A. P. "FIT2D: An Introduction and Overview," European Synchrotron Radiation Facility, 1997.
- (5) Hammersley, A. P.; Svensson, S. O.; Hanfland, M.; Fitch, A. N.; Hausermann, D. *High Pressure Research* **1996**, *14*, 235.
- (6) Hammersley, A. P.; Svensson, S. O.; Thompson, A. *Nucl. Instr. Meth.* **1994**, *A346*, 312.
- (7) Klug, H. P.; Alexander, L. E. *X-Ray Diffraction Procedures For Polycrystalline and Amorphous Materials*; Wiley: New York, 1954.