

Supplementary Information

Nanoenergetic Materials: Boron Nanoparticles from the Pyrolysis of Decaborane and their Functionalization

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Experimental Section

All experiments were carried out under vacuum or under argon by using standard Schlenk or dry box techniques. The starting materials B₁₀H₁₄ (Aldrich), Br₂ (99.5+ %, Aldrich), and XeF₂ (Aldrich) were used as received. Solvents were distilled from sodium-benzophenone (benzene, pentane) or from sodium (toluene) and saturated with Ar before use. Microanalyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois.

TEM images were acquired either on a field emission JEOL 2010F (S)TEM instrument, or on a JEOL 2010 LaB₆ TEM. The XPS data was collected on a PHI 5400 instrument, and XPS depth profiles were carried out by means of argon sputtering. TOF-SIMS measurements were performed on a PHI Trift III from Physical Electronics. X-ray diffraction data were collected on a Bruker small angle X-ray scattering instrument in the George L. Clark X-ray facility at the University of Illinois at Urbana-Champaign. TGA/DSC experiments were carried out at Pennsylvania State by placing the samples into a ceramic crucible and collecting data on a Q2010 TGA/DSC from TA Instruments. The heating rate was 20 K per minute and all measurements were performed in an atmosphere of pure oxygen.

Synthesis of boron nanoparticles. A glass reservoir charged with decaborane (0.45 g, 4.0 mmol) was heated to 100 - 105 °C and the vapor transported by means of an argon carrier (1

atm; 0.5 SCFH) through a vertical quartz tube maintained at 700 °C or 900 °C until all the decaborane was consumed (6 hrs). The fine dark grey brown powder that accumulated downstream of the hot zone was collected. Yield: 0.159 g (40 %). Anal: B, 97.2; C, 0.42; H, 0.0.

Fluorination of boron nanoparticles. Boron nanoparticles (0.100 g, 9.25 mmol) were suspended in 20 mL of benzene were treated with XeF₂ (0.100 g, 0.591 mmol) dissolved in 20 mL of benzene. The mixture was stirred at room temperature for 72 h. Removal of the solvent under reduced pressure yielded a grey solid. Yield: 40 mg. Anal. B 93.0; C, 0.81; H 0.00; F 1.30%.

Bromination of boron nanoparticles. Boron nanoparticles (0.115 g, 10.6 mmol) were suspended in 20 mL of benzene were treated with Br₂ (3.12 g, 18.8 mmol). The mixture was stirred at room temperature for 12 h. Removal of the solvent and bromine under reduced pressure at 30° C yielded a black solid. Yield 93.2 mg Anal B 71.7, C 4.04, H 1.03, Br 4.12%.

Synthesis of boron nanoparticles by sodium reduction of boron tribromide. The material obtained by Na reduction of BBr₃, followed by addition of n-octanol, is reported to be a yellow oil whose ¹¹B NMR chemical shift is similar to that of molecular B(OR) compounds (A. L. Pickering, C. Mitterbauer, N. D. Browning, S. M. Kauzlarich and P. P. Power, *Chem. Commun.*, 2007, 580-582). We find that the yellow oil consists predominantly of tri(n-octyl)borate, as judged from micro-analytical data (calc for B(OC₈H₁₇)₃: C, 72.4; H, 12.8. Found: C, 73.8; H, 14.2) and mass spectroscopy (calc for B(OC₈H₁₇)₃: 398.4. Found (base peak): 398.4). Elemental boron must be a minor constituent (<5% by weight) of the yellow oil. Although alkoxide groups are claimed to be attached to the particle surfaces, the analytical data presented are more consistent with the alkoxide groups being present as trialkylborate.

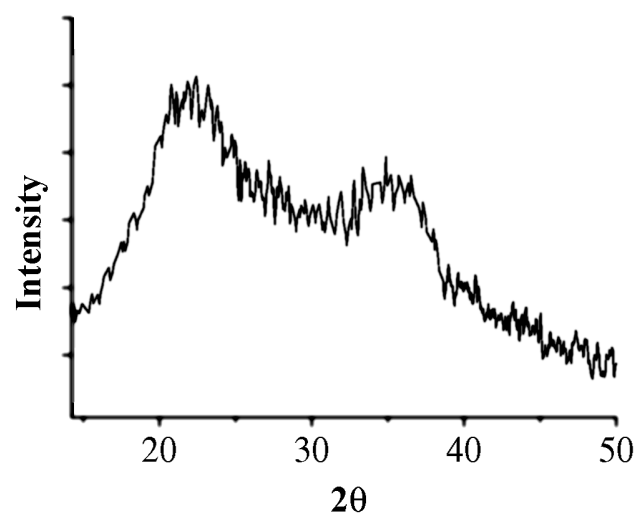


Figure S1. XRD profile (Cu K α radiation) of the boron nanoparticles.