

Nanoenergetic materials: boron nanoparticles from the pyrolysis of decaborane and their functionalisation†

Brian J. Bellott, Wontae Noh, Ralph G. Nuzzo* and Gregory S. Girolami*

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The surfaces of boron nanoparticles 10–150 nm in diameter, prepared by gas phase pyrolysis of decaborane vapour at 1 atm and 700–900 °C, can be halogenated by treatment with Br₂ or XeF₂; the surface halogenation somewhat increases the onset temperature for the oxidation of the particles under O₂.

Elemental boron is a highly attractive fuel for propellants and explosives.^{1,2} Of all the chemical elements, boron has the highest volumetric heat of combustion (140 kJ cm⁻³) and the third highest gravimetric heat of combustion (59 kJ g⁻¹), after H₂ and Be. These values are over 3 times higher per unit volume, and 1.4 times higher per unit mass, than those of hydrocarbon fuels.³

In order to increase the rate of energy release during the combustion of boron and make it a more attractive fuel for propellants and explosives, it is advantageous to prepare it in a nanoparticulate form. Boron nanoparticles have been obtained previously from diborane by thermolysis at temperatures between 700 °C and 2250 °C, although often the size distribution produced is broad or the particles are extensively aggregated.^{4,5} Boron nanoparticles have also been obtained by reduction of boron trihalides with H₂⁴ or sodium naphthalenide.⁶ Boron nanowires⁷ and thin films^{8,9} have been grown by a variety of methods.

To incorporate nanoparticles into larger assemblies and to stabilise them for long term storage under ambient conditions, it is desirable to functionalise their surfaces. In addition, derivatisation of boron nanoparticles with fluorine-containing groups could lead to significant increases in energy release, owing to both the kinetics and thermodynamics of BF₃ formation.¹ Although there has been one previous report of the surface-modification of boron nanoparticles,⁶ the yield is low and there is only indirect evidence that the functional groups were actually resident on the particle surfaces.† Here we describe the preparation of boron nanoparticles by a new method, and reaction chemistry that clearly results in derivatisation of the particle surfaces.

Decaborane, B₁₀H₁₄, is an air stable crystalline solid that was at one time produced industrially on a scale of >1000 tons per year. It is known to decompose on surfaces at temperatures as low as 200 °C to give boron films.⁸ By adjusting the experimental procedure, we find that decaborane

can also serve as a convenient starting material for the laboratory-scale preparation of boron nanoparticles. Passage of decaborane vapour in an Ar carrier at 1 atm through a hot zone at 700–900 °C affords a grey-brown, non-pyrophoric powder. The powder consists of >97% boron and is free of hydrogen as judged by combustion analysis. The particles are easily suspended in organic solvents such as toluene and pentane, and the resulting suspensions settle slowly over the course of a few hours.

Transmission electron microscopy images show that the majority of the particles have diameters in the range 10 to 150 nm, and that they are textureless and quasispherical (Fig. 1). Two broad peaks at *d*-spacings of 2.5 Å ($2\theta = 35.0^\circ$) and 4.0 Å ($2\theta = 22.5^\circ$) are present in the Cu K α XRD pattern. A Scherrer analysis of the XRD peak widths suggests that the crystalline domains are about 25 Å in size. The small crystalline domain size is expected, because the nanoparticles are synthesised at temperatures far below the 2075 °C melting point of boron.¹⁰ The *d*-spacings and intensities are consistent with those of the α -rhombohedral phase of boron.^{11,12} We cannot rule out the possibility that amorphous boron may also be present. The XPS spectrum of the as-prepared particles shows a signal at 189 eV (B 1s); the value is higher than the reported value owing to charging effects.¹³ Most notably, no evidence of any boron oxide phase is observed, which suggests that the as-synthesised boron particles are relatively inert towards oxidation at room temperature. (S)TEM-EELS analysis of the as-synthesised boron particles gives a signal at 210 eV that is also characteristic of pure boron.

DSC experiments conducted on the boron nanoparticles under pure oxygen show that an exothermic reaction occurs with an onset temperature of 530 °C (Fig. 2). The amount of heat released, 17.2 kJ g⁻¹, indicates that, under these mild conditions, the oxidation of the nanoparticles is incomplete, and only the surfaces of the particles are oxidised.

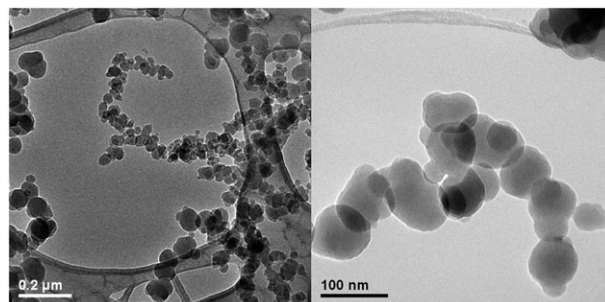


Fig. 1 TEM images of the boron nanoparticles. The large net-like structure is the carbon grid used to support the sample.

School of Chemical Sciences, University of Illinois at Urbana-Champaign, 600 South Mathews Avenue, Urbana, IL 61801, USA. E-mail: girolami@scs.uiuc.edu

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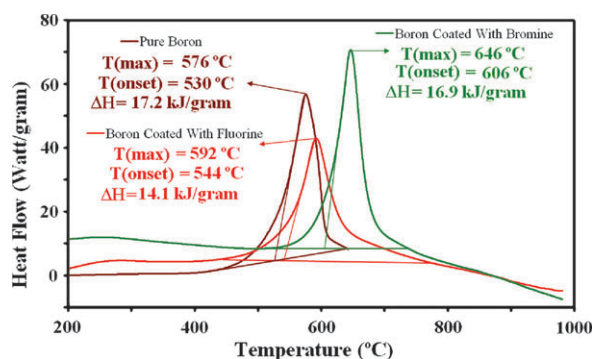


Fig. 2 DSC results for boron nanoparticles as-prepared (brown), surface-fluorinated (red), and surface-brominated (green).

(S)TEM-EELS studies of boron nanoparticles heated in air for 4 h at 600 °C show that a thin oxide shell (~ 7 nm thick) is present, with the core being pure boron (Fig. 3).

Treatment of the boron nanoparticles with bromine in benzene for 12 h affords black nanoparticles with a bromine content of 4.1%. Similarly, treatment with a benzene solution of XeF_2 for 72 h affords grey particles whose surfaces are fluoride terminated. The XPS spectrum of the fluorinated particles shows signals at 189 eV (B 1s) and 691.0 eV (F 1s) due to bulk boron and to surface fluoride, respectively. As judged from an XPS depth profile study and a TOF-SIMS sputtering experiment, the fluorine atoms are confined to the surfaces of the particles, whereas the interiors remain pure boron.

DSC experiments show that the surface-halogenated particles are slightly passivated toward combustion under pure oxygen relative to the untreated material. The onset temperature for oxidation is 544 and 606 °C, respectively, for the fluorinated and brominated nanoparticles. The amount of heat released is 14.1 and 16.9 kJ g^{-1} for the F- and Br-terminated boron particles, respectively.

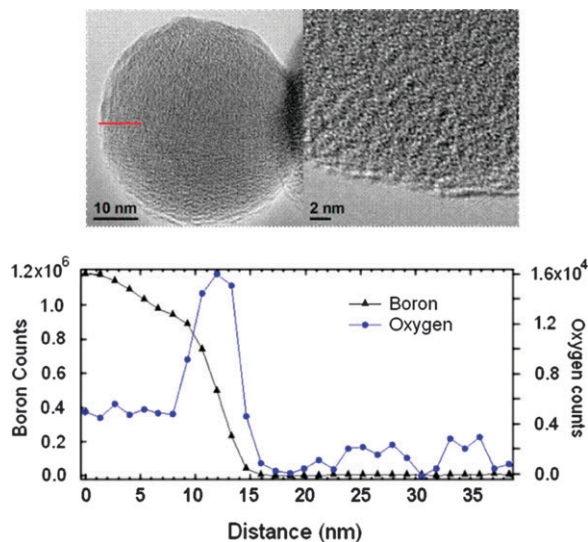


Fig. 3 Above: TEM images of boron nanoparticles after oxidation. Red line shows the approximate thickness of the resulting boron oxide overlayer. Below: EELS line profile showing composition of oxidised boron nanoparticles from centre of particle outward. Note that the scales for the boron and oxygen contents are different.

The present results show that highly pure boron nanoparticles can be synthesised by the gas phase pyrolysis of decaborane. The surface of the particles can be further functionalised by halogenation. Thermal analysis studies of the particles show that an exothermic combustion reaction takes place at temperatures above 500 °C, and that surface halogenation somewhat passivates the particles against further oxidation. Studies are underway to further exploit this new ability to prepare surface-functionalised boron nanoparticles.

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