Room temperature synthesis of surface-functionalised boron nanoparticles

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Received (in Berkeley, CA, USA) 3rd October 2006, Accepted 1st December 2006
First published as an Advance Article on the web 11th January 2007
DOI: 10.1039/b614363f

Capped boron nanoparticles have been synthesized at room temperature by a simple route that does not involve the use of flammable boranes.

Known routes to boron nanoparticles are few and employ gas phase decomposition of the toxic and flammable gas diborane. We now report a room temperature, solution synthesis of organo-capped boron nanoparticles *via* the reduction of BBr_3 with sodium naphthalenide in dry dimethoxyethane. This results in a reactive bromide-capped intermediate, which can be conveniently reacted with octanol to form the first organo-capped boron nanoparticles. Scanning transmission electron microscopy (STEM) in combination with electron energy-loss spectroscopy (EELS) was used on individual nanoparticles and shows the particle composition to be boron. It is expected that this work will provide a platform for the synthesis of innumerable organically capped boron nanoparticle compounds with a variety of applications.

Boron is a light element that has a diverse range of industrial applications in areas such as semiconductors, protective coatings, pyrotechnic flares, high-density fuels and refractory materials.[1–3] Boron is also an essential nutrient for most living organisms,[4,5] and boron compounds have been used in medicinal applications such as neutron capture therapy.[6–8] Molecular boron chemistry has a rich history of cluster formation and much attention has recently been focused on the electronic properties and controlled synthesis of a range of interesting morphologies, including tubes,[9–12] wires[13–15] and ribbons.[16] In contrast, very little has been published on the subject of boron nanoparticles.

The synthesis of metal and metalloid nanoparticles is a subject of ever-increasing interest, and has been achieved by a variety of different routes, including deposition methods,[17,18] aerosols,[19–21] emulsions,[22–24] and micelles.[25–27] Reduction routes to metallic particles were reported as early as 1857, when Faraday observed a ruby coloured solution of gold nanoparticles by reduction of an aqueous gold salt,[28] and have been exploited to produce particles from metals such as silicon,[29–31] gold[32–34] and platinum.[35–37] High purity amorphous boron nanoparticles with a wide size distribution (25–500 nm) were first synthesised by the furnace heating of diborane (700 °C).[38] It has also been shown that laser heating of diborane (1400 °C) produces amorphous boron nanostructures, with a large size distribution that includes predominantly non-uniform globules with some spherical particles.[39] The first relatively narrow size distribution of amorphous boron nanoparticles was achieved by arc decomposition of diborane to produce spherical particles with diameters between 55 and 95 nm.[40]

Thus far no synthetic route to functionalised boron nanoparticles has been published. Here, a convenient, room temperature solution synthesis is reported that shows potential to be versatile in the use of a variety of capping agents.

The synthesis of the boron particles follows a solution reduction route (Fig. 1) previously used by our groups to produce silicon nanoparticles with a narrow size distribution.[29] The reaction stoichiometry used in this case is 14Na : 15Br, theoretically resulting in small particles with a boron atom to capping agent ratio of 5 : 1. The reduction of the trisubstituted boron yields a reactive halide-capped nanoparticle that serves as a convenient precursor for reaction with alcohols such as octanol. Further compounds have been synthesised with B–NR_2 and B–OR (R = butyl, octyl) linkages at the boron nanoparticle surface, and are currently under investigation. The octyloxy-capped boron nanoparticles are obtained as a sticky, pale yellow oil, and the long aliphatic chains of the octyloxy-capping agents prevent aggregation of particles during the subsequent work-up and analysis. The B–OR linkage appears to be stable during the extraction of salt (washing with water) as well as removal of the naphthalene *via* sublimation (*ca.* 100 °C, 10^{-3} mbar). The material was shown to be amorphous by powder X-ray diffraction experiments (performed on an INEL CPS120 diffractometer using Cu Kα radiation) which yielded no discernable diffraction peaks. Solution ^{1}H NMR indicates the presence of the octyloxy-capping groups on the surface of the nanoparticles, which is further supported by FTIR analysis with absorbances corresponding to alkyl C–H groups between 2800 and 3000 cm^{-1} and B–OR groups at *ca.* 800 cm^{-1}. The ^{11}B NMR spectrum shows a resonance at 18.5 ppm with respect to $BF_3{\cdot}OEt_2$ (0 ppm), which is consistent with results obtained for molecular B–OR compounds[41] and

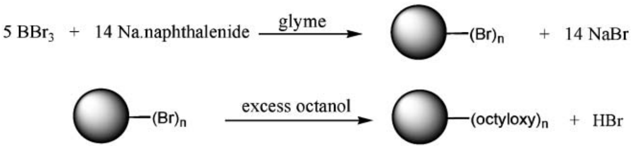

Fig. 1 Schematic of the reduction route to organo-capped boron nanoparticles.

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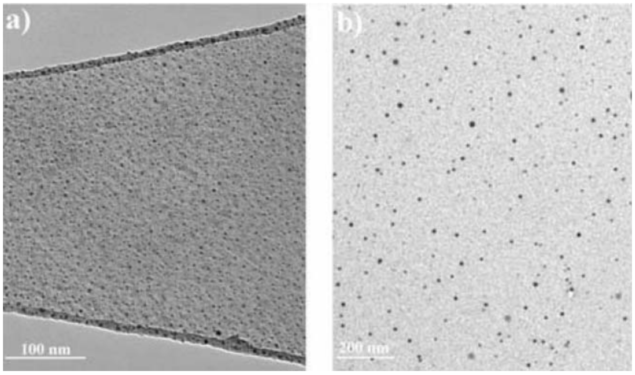

Fig. 2 Low magnification, bright field TEM images showing examples of a) 2–4 nm boron particles and b) 18–20 nm boron particles.

provides further evidence of B–O bonding on the surface of the particles.

TEM samples were prepared by dipping holey carbon-coated, 400-mesh electron microscope grids into a (sonicated) hexane solution and subsequent drying at *ca.* 100 °C. Fig. 2 shows TEM micrographs of a number of the octyloxy-capped boron nanoparticles. The size distribution of the particles was determined by measuring 937 nanoparticles from different regions of the grid using Digital Micrograph software. Analysis of the particle size distribution indicates that the particles lie in the range 1 to 45 nm (with 1.8% lying in the range 30 to 45 nm). The majority of particles are 1–3 nm (54%), with the remaining particles quite evenly distributed between 4 to 20 nm. Elemental analysis *via* EDS (electron dispersive X-ray spectroscopy) is very difficult on elements lighter than carbon, so a combination of STEM and EELS (Fig. 3) has been used to confirm the presence of boron in the particles.[9]‡

In summary we have described a convenient synthetic route to functionalised boron nanoparticles (exemplified here by the formation of B–Br and B–O–R capping). The reactive halide intermediate produced during the room temperature, solution synthesis has considerable potential for the synthesis of a variety of capping agents, and further examples of such compounds will be reported in a future publication. The production of the

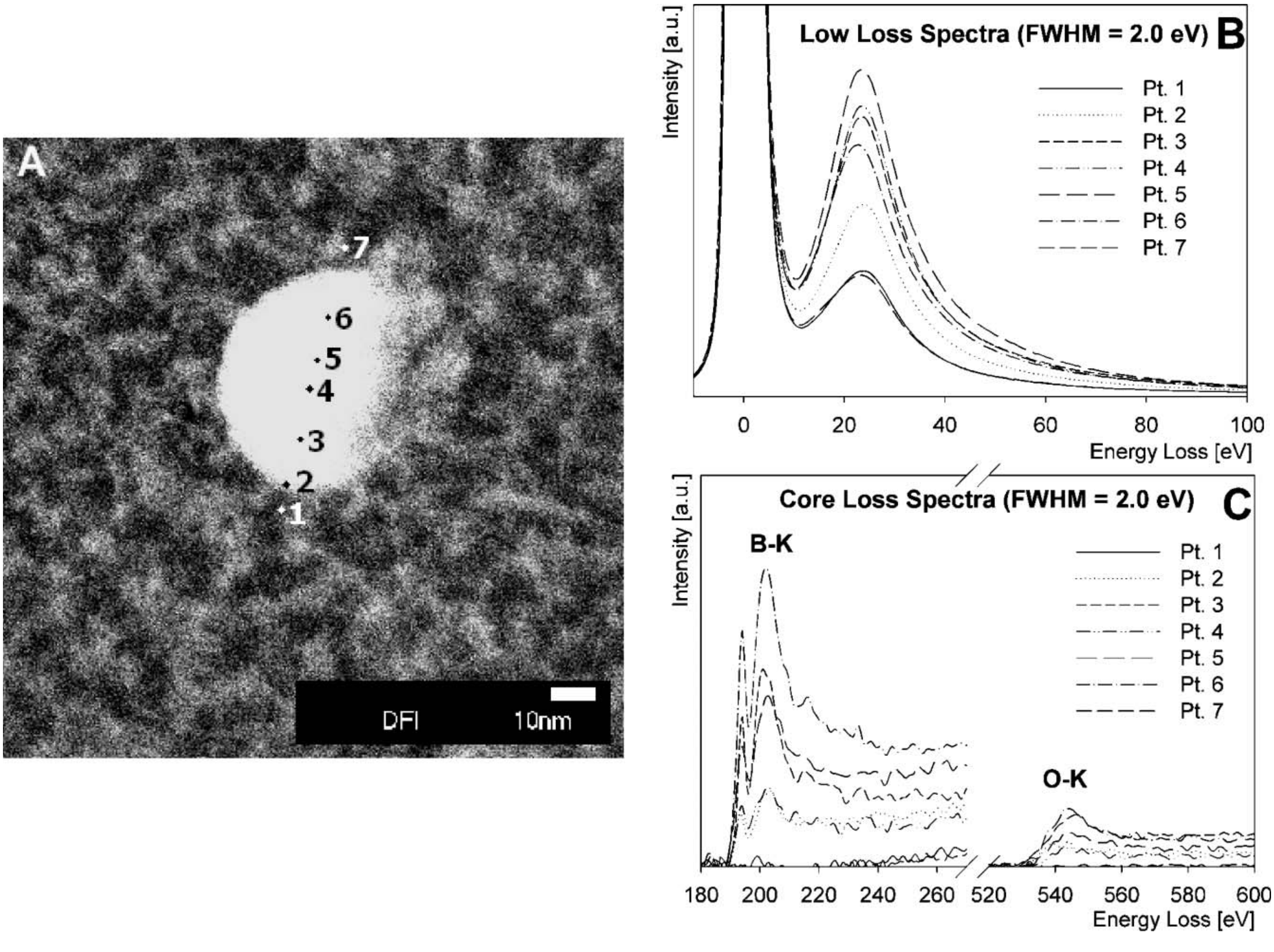

Fig. 3 (A) A STEM dark field image of the octyloxy-capped amorphous boron nanoparticle, with a diameter of approximately 37 nm. Measurements were also performed on particles of each size range (20 and 3 nm), and these confirmed the presence of boron in each. In (B) the low loss spectra are normalized to the height of the zero loss peak and trace the increased intensity of the plasmon peak (~24 eV) on the particle (points 3–6). The low loss region in EELS provides a quantitative measure of the specimen thickness. In the case of the measured boron nanoparticle the specimen thickness varies from 0.09 (points 1 + 7; on the carbon foil) to a maximum thickness of 0.20 t/λ inelastic (point 5). The core loss spectra (C) were background subtracted using a power low fit and corrected for multiple scattering using a Fourier-log deconvolution algorithm.[42] As expected, the intensity of the boron K edge increased to a larger extent towards the centre of the particle with respect to the oxygen K edge.

bromide-capped intermediate also facilitates safe and efficient hydrogenation at the surface, and investigations are underway to produce hydride-capped boron nanoparticles for application as hydrogen storage vessels. These products may also be suitable for hydroboration reactions. Variation of the reaction conditions such as concentration and reducing agent may also facilitate further control over the size distribution of the nanoparticles.

The authors would like to thank the DOE's Center of Excellence for Chemical Hydrogen Storage for funding and acknowledge financial support for C. Mitterbauer by the U.S. Department of Energy, Grant # DE-FG02-03ER46057, and the National Science Foundation, Grant # CTS-0321356. We are grateful to D. Neiner for useful discussions.

Notes and references

‡ Transmission electron microscopy (TEM) analyses of the nanoparticles were performed on a Philips CM-120 microscope operating at 80 keV. STEM results were obtained using a JEOL JEM-2500SE STEM/TEM, equipped with a Schottky field-emission source operated at 200 kV and a post column Gatan imaging filter (863 GIF Tridiem) for EELS. The microscope and GIF spectrometer were set up for a convergence semiangle (α) of x mrad and a spectrometer collection semiangle (θc) of y mrad, resulting in a probe size of 1 nm. The full width at the half maximum at the zero loss peak (FWHM at the ZLP) is 2.0 eV using a spectrometer dispersion of 0.5 eV/pixel and an acquisition time of 0.01 s (low loss) and 10 s (core loss spectra), respectively.

Materials: 1,2-Dimethoxyethane (glyme) (Acros, $> 99\%$) and hexane (Aldrich, $> 99\%$) were dried through a Seca Solvent Systems column purification system by Glass Contours. Octanol ($C_8H_{18}O$; EM Science) was dried over molecular sieves. Naphthalene ($C_{10}H_8$; Fisher, 99.98%) and boron tribromide (BBr_3; Acros, 99+ %) were used without further purification. HPLC-grade water (EM Science) was used as received. All chemicals were handled either in a N_2-filled glovebox or on a Schlenk line using standard anaerobic and anhydrous techniques. Sodium naphthalenide (11.4 mmol, prepared from the reaction of sodium metal with naphthalene in dry, degassed glyme (70 ml) overnight) was added rapidly *via* canula to a stirred solution of BBr_3 (4.07 mmol) in dry, degassed glyme (120 ml) and the mixture was stirred for 1 h at room temperature. To the cloudy white solution was added an excess of octanol (6 mmol) and the reaction mixture was stirred overnight. The solvent was removed under reduced pressure and the naphthalene was collected on a liquid nitrogen cooled probe. The oily residue was dissolved in hexane (20 ml) and washed three times with HPLC grade water to remove sodium chloride impurities. Removal of all solvent yielded octyloxy-capped boron nanoparticles as pale yellow oil. ^{11}B NMR (500 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ standard): δ/ppm 18.5 (br, s); ^1H NMR (300 MHz, $CDCl_3$): δ/ppm 3.76 (t, 2H), 1.52 (quin, 2H), 1.28 (m, 10H), 0.88 (t, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ/ppm 63.44, 32.10, 31.79, 29.61, 29.55, 26.07, 22.90, 14.29; FTIR: (KBr) ν/cm^{-1} 2955.15(s), 2885.85(s), 2853.75(s), 1459.40(w), 1410.06(w), 1325.13(m), 1259.50(w), 1092.12(w), 1018.59(w), 797.66(w), 663.29(w), 443.34(m); UV/vis: 320 ν/cm^{-1}.

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