Synthesis, Structure, and Properties of Mesoporous B/C/N Microspheres

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Dedicated to Professor Arndt Simon on the Occasion of His 70 Birthday

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Abstract. Reaction of low surface area carbon with a mixture of urea and boric acid at 930 °C yields a composition close to BC₄N with a graphitic structure. BC₄N was characterized by electron energy loss spectroscopy, X-ray photoelectron spectroscopy, transmission electron microscopy, Raman spectroscopy, and X-ray diffraction. BC₄N is a porous ceramic with a surface area of 428 m²·g⁻¹, and shows a CO₂ uptake of 40 wt-%. The layered structure of BC₄N involves a random

Introduction

Several efforts to prepare materials containing boron, carbon, and nitrogen atoms $(B_x C_v N_z)$ with different compositions were carried out. One of the objectives of such studies is to tune and alter the properties of graphene through doping with a suitable element such as boron and nitrogen [1]. Whereas graphene exhibits fascinating electronic and vibrational properties and has a great potential for a variety of applications, its potential for use as a semiconductor in nanoelectronic circuits is limited because of its vanishing bandgap. Nanotubes containing boron, carbon, and nitrogen of variable compositions were reported [2]. For example, nanotubes with separated layers of carbon and boron nitride were prepared by the arc discharge method, laser ablation and chemical vapor deposition (CVD) [3–7]. $B_r C_v N_z$ nanotubes were also obtained by the pyrolysis of a BH₃-trimethylamine adduct [8]. Nanotubes of graphitic carbon and carbon nitride were employed as templates to obtain BCN nanotubes of varying compositions [9, 10]. Singlewalled BCN nanotubes with indefinite compositions were ob-

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distribution of boron, carbon, and nitrogen atoms and shows high thermal stability up to 1000 °C. A comparative analysis of the structure and properties of BC₄N and graphene using first-principles pseudopotential based density functional theoretical calculations is presented. The calculations predict it to be an insulator. The bulk modulus of BC₄N exhibits an interesting dependence on the ordering of boron and nitrogen on the graphene lattice.

tained by the hot filament CVD method [11]. CVD [12, 13], laser ablation [14, 15], ion beam assisted deposition [16], and magnetron sputtering [17-19] were employed to deposit $B_x C_y N_z$ films on solid substrates. A crystalline composition of B₄CN₄ is reported to occur on direct nitridation of B₄C with nitrogen in the 1600 to 2250 °C range [20, 21]. Amorphous B₄CN₄ was obtained by the pyrolyzation of a xerogel consist of B-trichloroborazene and bis(trimethylsilyl)carbodiimide [22, 23]. Attempts have been made to prepare high surface area BCN by heating mesoporous carbon with B₂O₃ at high temperatures in a nitrogen environment [24]. Porous carbon materials doped with boron and nitrogen are reported to be formed by the pyrolysis and carbonization of gels containing boric acid and citric acid in a nitrogen atmosphere [25], the compositions varying between of BC₁₆N and BC₆N. A solid with the composition of BC₄N seems to be formed on the thermal decomposition of the BH3-C5H5N complex at high temperatures [26].

Nitridation of boric acid and carbonization of saccharose in molten urea is reported to give a material with the bulk composition of BC₄N, but the material was not adequately characterized with respect to composition and properties [27]. Reaction of amorphous carbon nanotubes with boric acid and urea was shown to yield nanotubes with the approximate composition of BC₄N [28]. It was our desire to find a means of carrying out a large scale synthesis of BC₄N with desirable properties. In order to accomplish this, we made use of amorphous carbon spheres, obtained from the hydrothermal treatment of glucose, as the starting material. By the reaction of the carbon spheres with boric acid and urea at high temperatures we obtained bulk quantities of BC₄N with interesting properties. BC₄N is found to be a ceramic with high thermal stability, containing both micro and mesopores.



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In this article, we present the synthesis and characterization of BC_4N and describe some of the properties through a combination of experimental and theoretical studies.

Results and Discussion

Amorphous carbon spheres prepared [29] by the hydrothermal treatment of aqueous glucose solution were used as the starting material for the synthesis of $B_x C_v N_z$. Diameters of the carbon spheres were in the 150 nm to 500 nm range as can be seen from the FESEM image in Figure 1a. A TEM image of a typical carbon sphere is shown in Figure 1b. The images reveal the smooth surface of the spheres. The BET surface area of these carbon spheres was 85 $m^2 \cdot g^{-1}$. The reaction of the carbon spheres with urea and boric acid at 930 °C gave a product containing boron, carbon, and nitrogen. The product consisted of spherical particles as shown in the FESEM image in Figure 1c, diameters of these spheres remaining in the 150-500 nm range. From the TEM image in Figure 1d, it is obvious that unlike the smooth surface of carbon spheres, the BC₄N spheres show contrast variations originating from the presence of pores at the surface with uneven depth.



Figure 1. (a) FESEM image and (b) TEM image of carbon spheres. (c) FESEM image and (d) TEM image of $B_x C_v N_z$ spheres.

XPS core level spectra of the $B_xC_yN_z$ product is shown in Figure 2. The carbon 1s spectrum shows a peak centered at 286 eV, which can be deconvoluted into two bands at 283 and 287 eV. The band at 283 eV is assigned to a carbon atom bonded to boron and the band at 287 eV ascribed to a carbon atom bonded to another carbon and nitrogen atoms [7, 20, 21, 30, 31]. The nitrogen 1s signal can be deconvoluted into two bands at 399 and 400 eV, of which the former corresponds to a nitrogen atom bonded to boron and the latter to a nitrogen atom bonded to carbon [7, 20, 21, 31, 32]. The boron 1s signal appears as a broad feature with shoulders on either side. This band can be deconvoluted into three bands centered at 188, 190 and 193 eV, of which the first two can be assigned to a boron atom bonded to carbon and nitrogen, respectively [7, 20, 21, 30, 32]. The weak feature at 193 eV is assigned to a boron atom bonded to oxygen, probably arising from a small amount of unreacted B_2O_3 . Based on the capture cross sections and intensities of boron, carbon, and nitrogen signal in Figure 2, we estimated the composition to be $B_{1,4}C_4N$ or $B_4C_{12}N_3$. Whereas the XPS spectra of the product obtained in the present study look somewhat different from the corresponding spectra of the BC₄N nanotubes [28], the main features are comparable.



Figure 2. XPS of BC₄N spheres.

In order to establish the composition of the $B_x C_y N_z$ product, we carried out electron energy loss spectroscopy (EELS) measurements on the K edge absorptions bands of boron, carbon, and nitrogen of the entire-sphere as well as different parts of the sphere were carried out in a high resolution transmission electron microscope. A representative spectrum in Figure 3a shows the K shell ionization edges around 188, 284, and 401 eV, which are characteristic of boron, carbon, and nitrogen, respectively. Each core edge fine structure shows two peaks corresponding to the π^* and σ^* bands, because of the sp²



hybridization [7]. Based on the EELS data, we got an average chemical composition of B_{1.4}C_{3.7}N, which is in agreement with the XPS results. This analysis corresponds approximately to B₄C₁₁N₃. For purpose of convenience, we shall indicate the composition as BC₄N throughout this paper. In Figure 3b, we show an EELS map of a small portion of BC₄N sphere, the red, green, and blue colors representing boron, carbon and nitrogen atoms, respectively. The colors are uniformly distributed throughout the sphere suggesting a reasonably homogeneous nature of BC₄N. The homogeneity of BC₄N is also indicated by the fact that oxidation of BC₄N at 650 °C in an oxygen environment does not yield BN as it was the found in the case of $B_r C_v N_z$ nanotubes with separate layers of BN and carbon [33]. The XRD pattern and Raman spectrum of BC₄N do not change significantly on oxygen treatment at high temperatures.



Figure 3. (a) EEL spectrum (inset core edge fine structure of nitrogen) and (b) EELS map of boron (red), carbon (green), and nitrogen (blue) of a small portion of a BC₄N sphere.

The XRD pattern of the BC₄N spheres in Figure 4a shows two broad reflections with d spacing of 3.4 Å and 2.1 Å corresponding to the [002] and [100] planes respectively. The pattern is similar to that reported earlier for BCN materials with different compositions [20, 21, 26-28]. This XRD pattern is typical of materials with a graphite-like structure with little or no sheet-to-sheet registry. The interlayer distance (d = 3.4 Å)of the BC₄N is slightly larger than that of graphite (3.33 Å)and h-BN (3.36 Å). In Figure 4b we show a TEM image of BC₄N to reveal the presence of fragments of layered structure. The Raman spectrum of BC₄N, recorded with the 633 nm line from a HeNe laser, shows two strong features centered around



Figure 4. (a) XRD pattern of BC₄N spheres (b) TEM image of BC₄N.

1324 cm⁻¹ and 1600 cm⁻¹, which are assigned to the D and G bands as in $B_x C_v N_z$ and graphitic materials [34, 35]. The broadness of the D band can arise from disorder in the BCN layers.

Reaction between B(OH)₃ and urea, a main synthesis route for pure BN has been well studied earlier [36, 37]. In a similar reaction, addition of amorphous carbon to the mixture of $B(OH)_3$ and urea yields BC_4N , on two-phase of heating. The initial reactions involved in the formation of BC₄N are the dehydration of B(OH)₃ and decomposition of urea:

$$2B(OH)_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

 $CO(NH_2)_2 \xrightarrow{\Delta} NH_3 + HNCO$

The overall stoichiometric reaction for the formation of BC₄N may be written as:

$$B_2O_3 + 2NH_3 + 8C \rightarrow 2BC_4N + 3H_2O.$$

In Figure 5, the thermogravimetric analysis curve of BC₄N is compared with that of the starting carbon spheres recorded in air. The carbon spheres get completely oxidized before 750 °C just like other carbon materials. The BC4N spheres, however, do not show any decomposition up to 1000 °C. This feature of BC₄N is noteworthy.



Figure 5. TGA of BC₄N spheres and carbon spheres.

Nitrogen adsorption-desorption isotherms of BC₄N at 77 K are shown in Figure 6. The specific surface area of the BC₄N spheres by the Brunauer-Emmett-Teller (BET) method is 428 $m^2 \cdot g^{-1}$. The isotherm shows type IV behavior with a H3 type hysteresis loop (as per IUPAC classification), associated with capillary condensation of nitrogen in the mesopores [38]. The sharp rise in nitrogen adsorption at low relative pressures (p/p) $p_0 < 0.01$) indicates the presence of micropores in the material. The pore size distribution, calculated from the adsorption branch of the isotherms using DFT (density functional theory) model confirms the presence of both micropores (1.4 nm) and mesopores (2.8 nm and 4.5 nm) in the BC₄N spheres (see inset of Figure 6). The release of gaseous species during the high temperature reaction appears to be responsible for the mesoand micropores in the BC₄N spheres, which in turn give rise to the higher surface area. Thus, the BC₄N spheres prepared by us exhibit properties of a porous ceramic.



Figure 6. Nitrogen adsorption-desorption isotherm of BC₄N spheres (inset pore size distribution).

CO₂ adsorption of the BC₄N spheres measured at 298 K and 40 bar shows 9 wt-% uptake (Figure 7a). The uptake, however, goes up to 40 wt-% of CO₂ at 195 K and 1 atmosphere. The adsorption and desorption isotherms (Figure 7b) follow exactly the same path, showing no hysteresis. The adsorption isotherm does not exhibit saturation even at $p/p_0 = 1$. Methanol adsorption measurements on the BC₄N spheres at room temperature and low pressures were carried out. The BC₄N spheres adsorbed about 200 mL (28 wt-%) of methanol at $p/p_0 = 0.9$. The H₂ adsorption isotherm of the BC₄N spheres at 77 K and 50 bar rises sharply and reaches saturation at 10 bar, with 1.1 wt-% of H₂ adsorption. At 77 K and 1 bar atmospheric pressure, the BC₄N spheres adsorb 0.8 wt-% of H₂.

To determine possible structures of a BC₄N layer, we carried out first-principles calculations by considering different ordering of boron and nitrogen substituted for one third of carbon atoms in the 6×6 unit cells (a supercell) of graphene, and relaxing the atomic positions and the periodic cell parameter *a* to minimum energy (see Figure 8). Whereas there are numerous possible configurations, we consider four [labeled (i) to (iv)] of them, in which boron is substituted for carbon on one sublattice and for nitrogen on another. This ensures that no two boron (or nitrogen) atoms are nearest neighbors. Whereas configuration (i) has a relatively more homogeneous distribution of boron and nitrogen, it is highest in energy. On the other hand, configuration (iv) is highly heterogeneous in the sense BN forms a continuous region (phase segregated), and lowest in energy among the four configurations. From the cohesive energies (Table 1), it is clear that BC₄N layers are less stable than pristine graphene by -2.5 to -6 %, and the configuration (i) of BC₄N is only 0.3 eV per atom higher in energy than the configuration (iv). In agreement with weakened binding, the graphene lattice expands by up to 0.4 % upon substitution of boron and nitrogen at 33 %, with the precise value depending on the ordering of boron and nitrogen. The configurations of the samples synthesized by us would depend on the kinetics and other experimental factors such as temperature that affect the growth. Clearly, configurational entropy would favor a homogeneous distribution of boron and nitrogen, as in configuration (i), which may be the most stable form if the samples are grown at high temperatures. Luo et al. [39] show that the hexagonal BC4N structure stacked with one B-N layer and two C-C layers has the lowest total energy among all constructed

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Figure 8. (left) Energy as a function of lattice constant of BC_4N for configurations with different ordering of boron and nitrogen on carbon lattice, and (right) structures of configurations with the highest (top) and lowest energy (bottom) of the four. Note that the energies are of the whole supercell that contains 72 atoms.



Figure 7. CO₂ adsorption-desorption isotherm of BC₄N spheres (a) at 298 K and 40 bar (b) at 195 K and 1 atm.

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 BC_4N structures. However, we do not seem to have B-N and C-C layers.

Table 1. Lattice parameter (*a*), bulk modulus (*B*), and cohesive energy (E_{coh}) of graphene and BC₄N in different configurations.

Configuration	a /bohr	B /GPa•m	$E_{\rm coh}$ /eV per atom
BC ₄ N (i)	28.36	1.81	8.63
BC ₄ N (ii)	28.28	2.06	8.81
BC ₄ N (iii)	28.28	1.66	8.84
BC ₄ N (iv)	28.24	1.61	8.93
Graphene	28.04	1.74	9.16

The electronic structure of BC₄N is sensitive to the ordering of boron and nitrogen (Figure 9). Whereas a small gap of about 0.17 eV opens up in configuration (i) because of different on-site potentials felt on the two sublattices of graphene, configuration (iv) exhibits a larger bandgap of 1.1 eV. A detailed examination of the band structure reveals that both configurations (i) and (iv) exhibit a direct bandgap. The larger bandgap of configuration (iv) correlates well with its greater structural stability.



Figure 9. Electronic density of states as a function of energy for BC_4N in configurations (i) and (iv), and graphene.

The bulk modulus of each configuration was determined using the second derivative of energy with respect to unit cell area from the energy curves. Configurations (i) and (ii) with a homogeneous distribution of boron and nitrogen atoms exhibit a higher bulk modulus (by 10 %) than that of graphene or of the energetically favorable configurations (iii) and (iv). Qualitatively, the BC₄N synthesized by us is a harder material relative to graphite.

Conclusions

It was possible to synthesize a ceramic of the composition BC_4N starting with amorphous carbon spheres, obtained from the hydrothermal treatment of glucose. The reaction of amorphous carbon spheres with urea and boric acid yields bulk quantities of BC_4N spheres. The boron, carbon, and nitrogen atoms are homogeneously distributed in the structure. BC_4N is a porous ceramic with high thermal stability. BC_4N has a

graphite type layered structure and gives an X-ray diffraction pattern and Raman spectrum expected of such structure. It has a high propensity for CO_2 uptake (up to 40 wt-%). First-principles density functional theoretical calculations were used to compare the structure and properties of BC₄N and graphene. It is found that BC₄N is stable and that electronic structure and elastic (bulk) modulus are sensitive to the ordering of boron and nitrogen atoms. An energy gap ranging from 0.17 to 1.1 eV is exhibited by various configurations of BC₄N augurs well for its possible applications as a semiconductor in nanoelectronics.

Experimental Section

Amorphous carbon spheres were prepared by hydrothermal treatment of a saturated solution of glucose [29]. In a typical procedure, an aqueous solution of glucose (20 mL, 0.5 M) was sealed in a 22 mL Teflon seal autoclave and heated to 180 °C for 6 hours. The resulting black colored solution was centrifuged to obtain a solid that was washed with ethanol for several times by using sonication and centrifugation. The dark brown solid obtained as the final product after oven drying at 50 °C for 12 h was found to contain carbon spheres. This material was used as the starting material for the synthesis of $B_xC_yN_z$ spheres.

A mixture of boric acid (0.4 g), urea (4.7 g), and amorphous carbon spheres (1 g) in distilled water (40 mL) was heated to 60 °C until the solution became viscous. The product was separated by centrifugation and dried in air at 40 °C overnight. The dried sample was thermally treated at 930 °C for 10 h in a nitrogen atmosphere, and cooled to room temperature. The product was subsequently heated in an NH₃ atmosphere at 1000 °C for three hours to give black-colored BC₄N spheres.

Characterization

X-ray diffraction (XRD) patterns were recorded at 25 °C with a Rich-Siefert 3000-TT diffractometer employing Cu- K_{α} radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ESCALAB MKIV spectrometer employing $Al-K_{\alpha}$ radiation (1486.6 eV). Electron energy loss spectra (EELS) were recorded with a transmission electron microscope (FEI, TECNAI F30) equipped with an energy filter for EELS operating at 300 kV. Raman spectra were recorded with a LabRAM HR with a 633 nm line from HeNe laser. Thermogravimetric analysis was performed with a Mettler Toledo Star system. Low pressure gas adsorption properties were measured using a QUANTACHROME AUTOSORB-1C surface area analyzer. Surface areas were obtained from nitrogen adsorption-desorption isotherms at 77 K. High-pressure gas sorption isotherm measurements were carried out on BELSORP-HP, BEL JAPAN high pressure instrument. The dead volume of the sample cell was measured with helium gas of 99.999 % purity. Non-ideal correction for hydrogen gas was made by applying virial coefficients at the respective measurement temperature. The adsorption isotherm of MeOH (at 298 K) was measured in the gaseous state by using BELSORP-aqua volumetric adsorption instrument from BEL, Japan.

Computational Methods

We used plane wave self consistent field (PWSCF) [40] implementation of density functional theory (DFT), with a generalized gradient

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approximation (GGA) [41] to exchange correlation energy of electrons and ultrasoft pseudopotentials [42] to represent interaction between ionic cores and valence electrons of boron, carbon and nitrogen. Kohn– Sham wave functions are represented with a plane wave basis with an energy cutoff of 25 Ry and charge density with a cutoff of 150 Ry. To facilitate a direct comparison, both BC₄N and graphene were simulated using 6×6 unit cells in the *ab* plane and a periodic supercell with a vacuum of 16 Å in the third direction. Integration over the Brillouin zone was sampled with a $5 \times 5 \times 1$ Monkhorst-Pack mesh [43] of *k* points and occupation numbers were smeared with a Methfessel-Paxton scheme [44] with a broadening of 0.003 Ry.

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