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Research paper

# Properties of nanosheets of 2D-borocarbonitrides related to energy devices, transistors and other areas

M.B. Sreedhara, K. Gopalakrishnan, B. Bharath, Ram Kumar, G.U. Kulkarni, C.N.R. Rao *

*Chemistry and Physics of Materials Unit, New Chemistry Unit, International Centre for Materials Science, CSIR Centre of Excellence in Chemistry and Sheikh Saqr Laboratory, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, P.O., Bangalore 560064, India*

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ABSTRACT

We have prepared borocarbonitrides of various compositions with extended sheet morphology, by the reaction of few-layer graphene with boric acid and urea at 900 °C and characterized them in detail. Supercapacitor performance of the borocarbonitrides has been studied in detail, the composition containing more pyridinc nitrogen exhibiting a specific capacitance of 306 F/g at 0.2 A/g. This composition also shows good oxygen reduction reaction (ORR) activity with an electron transfer number close to 4. The extended sheet structures of the $B_xC_yN_z$ samples has enabled us to fabricate field-effect transistors. These materials also show reasonable UV photoresponse.

## 1. Introduction

Graphene, the two-dimensional sheet of $sp^2$ carbons, has received great attention due to its novel properties with potential applications in nanoelectronics and energy storage [1–3]. Electronic devices based on graphene are of interest due to its high carrier mobility and ballistic transport properties [4,5]. Field effect transistors (FETs) as well as photoresponse properties of suitably doped graphene have been reported [6,7]. Chemical doping of graphene with nitrogen and other hetero atoms alters the electronic and electrochemical properties [8,9] and theoretical calculations show that random doping of graphene with boron or nitrogen opens a small gap in the Dirac points [10]. Graphene sheets containing B and N over a wide compositional range results in borocarbonitrides, which are new materials with interesting electronic properties with applications in supercapacitors [8,11–13], oxygen reduction reaction (ORR) [14,15] and other areas [16].

There are several reports on B, N-doped graphene with different doping levels [8,17] and B, N-doped graphene films have been generated using a thermal catalytic CVD method [8,18–23]. Bulk borocarbonitrides, $B_xC_yN_z$, of different compositions have been prepared starting with mixtures of activated carbon, boric acid and urea [24]. Graphene with nitrogen (4.5 at.%) and boron (3 at.%) has been prepared using melamine diborate as the precursor [25]. Covalently cross-linked boron nitride and graphene with composition-dependent surface and electrical properties have been prepared recently [26]. Single and few-layer borocarbonitrides, $B_xC_yN_z$, containing hybridized bonds of B, C and N are reported to exhibit electronic and optical properties distinct from those of graphene and BN [24,27]. In the light of this observation, we have sought to prepare borocarbonitrides by the reaction of graphene sheets with the precursor of nitrogen and boron and study their properties.

Starting with graphene rather than other sources of carbon is expected to be advantageous in forming borocarbonitride nanosheets. We have successfully prepared varying compositions of $B_xC_yN_z$ by the reaction of few-layer exfoliated graphene (EG) with boric acid and urea at 900 °C in a nitrogen atmosphere and characterized them by thermogravimetric analysis, electron microscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM) and other techniques. We have investigated the supercapacitor and oxygen reduction reaction performance of these materials and have fabricated field effect transistors and examined photo-response properties.

## 2. Experimental

Few-layer graphene, EG, containing 8–9 layers prepared by the thermal exfoliation of graphene oxide (GO) [28], and was reacted with varying proportions of urea and boric acid [24] to obtained $B_xC_yN_z$ samples of different compositions. Thus, the molar ratio of

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* Corresponding author.
*E-mail address:* cnrrao@jncasr.ac.in (C.N.R. Rao).

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boric acid and urea was varied from 1:100 to 1:25 keeping the amount of EG constant. Gravimetric compositions of $B_xC_yN_z$ samples were determined by thermogravimetric analyses carried out in an oxygen atmosphere with a Metler Toledo TGA-850 TG analyzer. Elemental mapping of B, N and C using energy dispersive X-ray spectroscopy (EDX) and morphology of nanosheets were obtained using scanning electron microscopy Nova NanoSEM 600 FESEM (FEI Company). Elemental compositions and chemical nature of the samples were determined by X-ray photoelectron spectroscopy (XPS) using a Omicron nanotechnology spectrometer, with a monochromatic Mg $K_\alpha$ as X-ray source ($E$ = 1253.6 eV). Elemental analysis was carried out with a Thermo Scientific™ FLASH 2000 Series CHNS Analyser. Atomic force microscope (AFM) images were obtained on Si substrates in tapping mode using Bruker Innova instrument. Transmission electron microscopy (TEM) images were recorded with a FEI Tecnai $G^2$ S-Twin operated microscope at an accelerating voltage of 200 kV, fitted with a Gatan CCD camera. High resolution TEM images and electron energy loss spectra (EELS) were recorded using Titan (cube) FEI aberration-corrected transmission electron microscope with an accelerating voltage 300 kV.

Powder X-ray diffraction patterns were collected using a Bruker D8 Discover diffractometer using Cu $K\alpha$ radiation with accelerating voltage 40 kV and current 30 mA. Raman spectra were recorded at different spots in the backscattering geometry using a 632 nm HeNe laser with a Jobin Yvon LabRam HR 800 spectrometer. Fourier transform infrared spectra (FTIR) were recorded in a Bruker FTIR specrometer in KBr mode. $^{13}C$ and $^{11}B$ solid state MAS NMR spectra were collected with a Bruker Avance ||| HD 400 MHz spectrometer. $N_2$ sorption isotherms at 77 K were recorded using a Quantachrome Quandasord-*SI* analyzer. Prior to measurements, the samples were heated at 120 °C under vacuum for 12 h. Optical reflectance spectra were recorded on Perkin–Elmer, Lambda 750 UV–Vis spectrometer from 800 to 200 nm wavelength range.

Supercapacitor measurements were performed on PGSTAT 262A (Techno Science Instruments) electrochemical workstation in 1 M $H_2SO_4$ aqueous electrolyte solutions under three-electrode assembly with Ag/AgCl reference electrodes. The working electrode was fabricated by dispersing 3 mg of sample in 1 mL ethanol–water mixture (1:1) from that 10 μL was drop casted on glassy carbon electrode followed by 10 μL of 0.05 wt.% nafion solution was used as the binder. The electrodes were dried in air at 60 °C for 30 min.

Field effect transistors were fabricated on $SiO_2$ (300 nm)/Si substrates by thermally depositing Au to form source and drain electrodes. The channels with BCN flakes as active elements were defined by patterning AZ photoresist (~1.4 μm thick) using a maskless optolithography instrument (Intelligent Micro patterning Ltd., 365 nm). The device characteristics were measured using a Keithley 4200 semiconductor characterization system. The gate current was typically below 1 nA in each case.

## 3. Results and discussion

Borocarbonitrides (BCN) of three different compositions were prepared by heating urea and boric acid with few-layer graphene (EG) at 900 °C. The molar ratio of the precursor employed, gravimetric compositions and surface areas of the samples are presented in Table 1. Of the three compositions, designated as BCN-1, BCN-2 and BCN-3, BCN-1 is most carbon-rich and BCN-3 has the least proportion of carbon. Thermogravimetric curves of the borocarbonitrides in comparison with EG are shown in Fig. S1. EG exhibits sharp weight loss of more than 90% in the temperature 350–500 °C, and followed by gradual weight loss. BCN-1, BCN-2 and BCN-3 showing weight loss at 397, 440 and 488 °C respectively corresponding to the combustion of the carbon component. The gravimetric compositions of the samples (Table 1) were calculated from the residual weight remaining above ~700 °C. The thermal stability of the BCN samples is seen to be higher in comparison with that of EG, BCN-3 with the largest contents of B and N showing highest thermal stability (Table S1) [29].

**Table 1**
Compositions and surface areas of the borocarbonitrides along with molar ratios of the precursors used for synthesis.

| Sample | Boric acid (mg) | Urea (g) | EG (mg) | Gravimetric composition | Composition from XPS | Surface area ($m^2/g$) |
|---|---|---|---|---|---|---|
| BCN-1 | 5 | 0.5 (1:100) | 60 | $(BN)_{0.28}C_{0.72}$ | $B_{0.06}C_{0.73}N_{0.21}$ | 419 |
| BCN-2 | 10 | 0.5 (1:50) | 60 | $(BN)_{0.48}C_{0.52}$ | $B_{0.13}C_{0.49}N_{0.38}$ | 437 |
| BCN-3 | 40 | 1 (1:25) | 60 | $(BN)_{0.72}C_{0.28}$ | $B_{0.26}C_{0.22}N_{0.52}$ | 254 |

To examine bonding in the BCN samples and the nature of doping, XPS measurements were carried out by drop casting the samples on Si substrates. Fig. 1(a–c) show B 1s, C 1s and N 1s spectra of BCN-2. The B 1s feature of this composition can be deconvoluted into two peaks centered at 191.2 eV and 192.3 eV corresponding to B—C and B—N bonds [24]. High resolution C 1s spectra can be fitted in to four peaks at 283.7, 284.4, 285.4 and 286.5 eV due to B—C, $sp^2$ carbons (C=C), C—N and C—O bonds respectively. The N 1s spectra has been fitted into three major feature at 398.2 eV, 399.4 and 400.4 corresponding to N—B bonds, the pyridinic nitrogen and pyrollic nitrogen. Core-level spectra of BCN-1 and BCN-3 (Fig. S2) exhibit similar features, suggesting the presence of a random network of BCN along with the domains of graphene and BN. It is noteworthy the intensity of the signal at 399.4 eV is substantial even when the borocarbonitride has small proportion of boron suggesting the originate from being C—N bonds. The ratio of intensities of N 1s signals at 399.4 and 400.4 eV of the two types of nitrogen, indicates that pyridinic nitrogen dominates the BCN samples. The percentage of carbon and nitrogen in the samples were also obtained by a chemical analyses using CHNS analyser (Table S2). The results are in close agreement with those from XPS and thermogravimetric analyses. Elemental mapping using energy dispersive X-ray analysis (EDX) shows uniform distribution of B, C and N which confirms the homogeneity (Fig. S3).

Electron energy loss spectra of BCN-1, BCN-2 and BCN-3 in Fig. S4 show the K-shell ionization edges of B, C and N respectively. The splitting of $\pi^*$ and $\sigma^*$ levels in B 1s, C 1s and N 1s spectra indicates $sp^2$ hybridization of these atoms as in BN and graphene. The EEL spectrum of boron has a peak at 191.5 eV due to the transition 1s electron to $\pi^*$ antibonding orbitals associated with planar $sp^2$ hybridization and a peak at 198.7 eV due to the transition of the 1s electron to the $\sigma^*$ antibonding orbital. The K-shell ionization edges of carbon at 282.7 eV and 293 eV correspond to $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions of graphene respectively [30]. Similarly, the nitrogen K-shell ionization spectrum shows peaks at 397.5 and 405.3 eV refers to $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transition of BN [31]. The broad signals around 214 eV and 321 eV arise from extended energy-loss fine structure (EXELFS) due to backscattering from nearest neighbour of B and C respectively [32]. The atomic composition obtained by EELS measurements summarised in Table S3 and were in good agreement with the results from other methods.

Electron microscope images of EG and BCN-2 are shown in Fig. 2. The nanosheets are transparent and wrinkled. High resolution transmission electron microscope (HRTEM) images of BCN-2 clearly show the presence of few layers in BCN with the interlayer separation of 0.35 nm which is only slightly higher than graphene