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Inorganic Analogues of Graphene

C. N. R. Rao*[a,b] and Angshuman Nag[a,b]

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The discovery of graphene has aroused great interest in the properties and phenomena exhibited by two-dimensional inorganic materials, especially when they comprise only a single, two or a few layers. Graphene-like MoS_2 and WS_2 have been prepared by chemical methods, and the materials have been characterized by electron microscopy, atomic force microscopy (AFM) and other methods. Boron nitride analogues of graphene have been obtained by a simple chemical procedure starting with boric acid and urea and have been characterized by various techniques that include surface area measurements. A new layered material with the composition BCN possessing a few layers and a large surface area discovered recently exhibits a large uptake of CO_2.

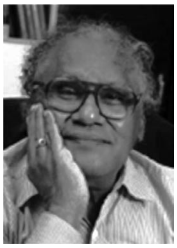
Introduction

The discovery of fullerenes[1] in 1985 prompted the discovery of fullerene-like structures of other layered inorganic materials, such as the dichalcogenides of tungsten and molybdenum by Tenne et al.,[2–4] which was soon followed by the fullerenes of BN and other nitrides.[5] Similarly, soon after the characterization of carbon nanotubes by Iijima et al.,[6] inorganic nanotubes of WS_2, MoS_2 and BN were prepared and characterized.[7–12] Graphene, which is a two-dimensional network of sp^2-hybridized carbon atoms has created a great sensation in the last few years because of the unique properties and phenomena exhibited by it. Graphene is fascinating not only academically but also promises numerous applications.[13–16] A natural extension of the study of graphene would be to synthesize graphene analogues of other layered inorganic materials, the obvious candidates being WS_2, MoS_2 and BN. These materials possess graphite-like layered structures in which the layers are held together by weak van der Waals forces. In this article, we present recent developments in the synthesis, characterization and properties of inorganic analogues of graphene, such as MoS_2, WS_2 and BN.[17,18] We also report the synthesis of an exciting new material with the composition BCN, which has graphene-like features.[19]

MoS_2 and WS_2

MoS_2 and WS_2 are quasi-two-dimensional compounds in which the atoms in the layer are bound by strong covalent forces, while van der Waals forces hold the layers together just as in graphite (Figure 1a). Intercalation of al-

[a] Chemistry and Physics of Materials Unit, International Centre for Materials Science, CSIR Centre of Excellence in Chemistry, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P. O., Bangalore 560064, India
E-mail: cnrrao@jncasr.ac.in
[b] Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560012, India



C. N. R. Rao obtained his Ph.D. degree from Purdue University (1958) and D.Sc. degree from the University of Mysore (1961). He is the National Research Professor and Linus Pauling Research Professor at the Jawaharlal Nehru Centre for Advanced Scientific Research and Honorary Professor at the Indian Institute of Science (both at Bangalore). His research interests are mainly in the chemistry of materials. He is a member of all the major science academies and the recipient of the Einstein Gold Medal of UNESCO, the Hughes Medal as well as the Royal Medal of the Royal Society, London. In 2005, he received the Dan David Prize for materials research and the first India Science Prize.

Angshuman Nag received his M.Sc. (Chemistry) degree from Indian Institute of Technology, Guwahati, in 2003. He obtained his Ph.D. degree from the Indian Institute of Science, Bangalore, in 2009. He is currently a centenary postdoctoral fellow at the Indian Institute of Science, Bangalore. He works on nanomaterials.

kali metals in layered metal dichalcogenides was reported sometime ago, but the products of exfoliation have not been studied adequately.[20] A graphene-like two-dimensional structure of WS_2 seems to have been obtained[21,22] by lithium intercalation and exfoliation, but the sample was characterized only by using X-ray diffraction (XRD). Such layered sulfides containing five layers or less do not exhibit the (002) reflection in the XRD pattern, and XRD is therefore not sufficient to estimate the number of layers. Preparation of graphene-analogues of MoS_2 was also attempted by lithium intercalation and exfoliation, but the characterization was only based on XRD.[23] MoS_2 samples prepared by lithium intercalation followed by exfoliation have been examined by employing scanning force microscopy and X-ray absorption fine structure spectroscopy,[24,25] but little information is available on the number of layers resulting from these preparations. Frindt at al.[26] reported that exfoliated MoS_2 forms aqueous suspensions of single layers wherein S atoms are bonded to Mo in an octahedral arrangement. Suspensions of layered chalcogenides have been used to prepare inclusion compounds with organic molecules[27,28] and to fabricate white-light-emitting diodes.[29,30] Optical properties of MoS_2 containing several layers prepared by micromechanical cleavage have been examined.[31,32] Rao et al.[18] have successfully carried out the reported the synthesis of few-layer MoS_2 and WS_2 by employing multiple chemical routes followed by unambiguous characterization involving different experimental techniques, including atomic force microscopy (AFM) and high-resolution transmission electron microscopy.

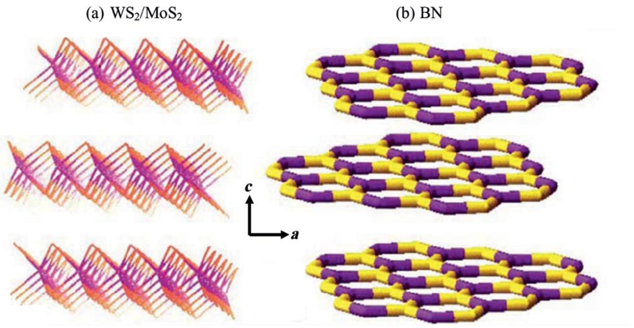


Figure 1. Layered structures of (a) WS_2/Mos_2 and (b) BN. In WS_2/Mos_2, the metal is in an octahedral coordination. Adapted from ref.[9]

Graphene analogues of MoS_2 and WS_2 can be synthesized by employing different chemical methods.[18] While methods (1) and (2) are common for both few-layer WS_2 and MoS_2, method (3) is applicable for only few-layer MoS_2. In method 1, bulk WS_2 or MoS_2 is intercalated with lithium followed by exfoliation of the layers by ultra sonication to form graphene analogues of MoS_2 and WS_2. In method 2, molybdic acid or tungstic acid is treated with excess thiourea. Graphene analogues of MoS_2 are produced by the reaction between MoO_3 and KSCN under hydrothermal conditions, as shown in the method 3; few-layer MoS_2 is formed.

$$\mathrm{MoS_2/WS_2} \xrightarrow[\text{Reflux in hexane, 3 d}]{n\mathrm{BuLi}} \mathrm{Li\text{-}MoS_2/Li\text{-}WS_2} \xrightarrow[\text{in water}]{\text{Exfoliation}} \text{Few-layer } \mathrm{MoS_2/WS_2} \tag{1}$$

$$\mathrm{H_2MoO_4/H_2WO_4} + 48\ \mathrm{NH_2CSNH_2} \xrightarrow[3\ \mathrm{h}]{500\ ^\circ\mathrm{C}} \text{Few-layer } \mathrm{MoS_2/WS_2} \tag{2}$$

$$\mathrm{MoO_3} + 2\ \mathrm{KSCN} \xrightarrow[180\ ^\circ\mathrm{C},\ 1\ \mathrm{d}]{\mathrm{H_2O}} \text{Few-layer } \mathrm{MoS_2} \tag{3}$$

The products obtained from the above reactions were characterized by employing TEM, AFM, Raman spectroscopy and XRD. The XRD patterns of few-layer WS_2 and MoS_2 along with the patterns of their bulk counterpart are shown in Figure 2a and b, respectively. WS_2 samples synthesized by methods 1 and 2 do not exhibit the (002) reflection, in contrast to the pattern of bulk WS_2 (see Figure 2a). The absence of the (002) reflection indicates that the material contains five or less layers of WS_2. The XRD patterns of the MoS_2 samples synthesized by all the three methods also do not exhibit the (002) reflection, which indicates the formation of few-layer MoS_2. Energy dispersive X-ray analysis (EDAX) shows the products to be stoichiometric.

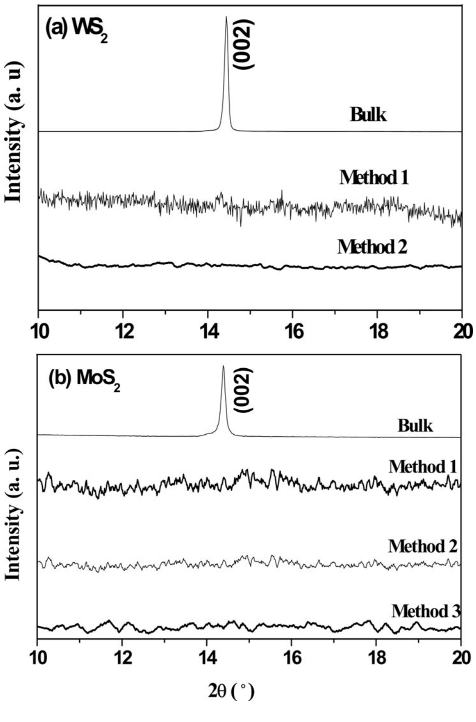


Figure 2. XRD patterns of (a) bulk WS_2 and few-layer WS_2 obtained by methods 1 and 2, and (b) bulk MoS_2 and few-layer MoS_2 obtained by methods 1, 2 and 3. Adapted from ref.[18]

The TEM images of the WS_2 and MoS_2 samples synthesized by the different methods are shown in Figure 3, which reveals that WS_2 obtained from both methods 1 and 2 mostly consists of single or bilayers. The interlayer separation between the WS_2 layers obtained from method 1 is in the range 0.65–0.70 nm (see inset of Figure 3a), and is slightly larger than the interplanar distance for the (002) plane of the bulk WS_2. However, WS_2 obtained by the thiourea method shows somewhat broken layers with an interlayer spacing of about 0.9 nm, and further studies are needed to understand the nature of these layers. The hexagonal atomic arrangement in a WS_2 layer is shown by the high resolution TEM image in the inset of Figure 3b. The MoS_2 samples synthesized by method 2 exhibit graphene-like layers (Figure 3c) with an interlayer separation of ca. 0.68 nm, which is slightly larger than the interplanar distance (0.62 nm) for the (002) plane of bulk MoS_2. The high resolution TEM image in Figure 3d shows the hexagonal atomic arrangement formed by Mo and S atoms with a Mo–S distance of 2.30 Å, which is in agreement with the known Mo–S distance in bulk MoS_2. It is to be noted that the MoS_2 samples prepared by all the three methods exhibit graphene-like layers, when examined by using high resolution TEM.

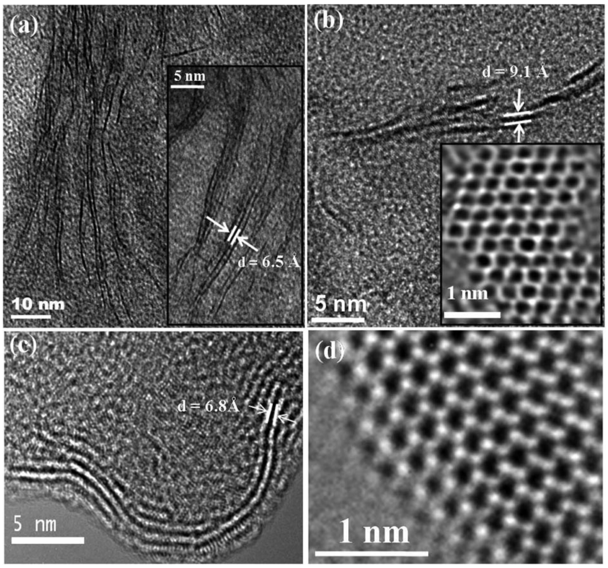


Figure 3. TEM images of WS_2 layers obtained from (a) method 1 and (b) method 2. (c) The TEM image of MoS_2 layers obtained from method 2; (d) the high-resolution TEM image of layered MoS_2 obtained from method 3. Adapted from ref.[18]

In addition to the TEM images, all the prepared WS_2 and MoS_2 samples were investigated by using AFM. Representative AFM images and the corresponding height profiles of the WS_2 sample prepared by method 1 are shown in Figure 4a and b, respectively. The AFM results confirm the formation of bilayer WS_2 with an average thickness of ca. 1.3 nm. AFM images of the MoS_2 samples similarly show graphene-like layers.

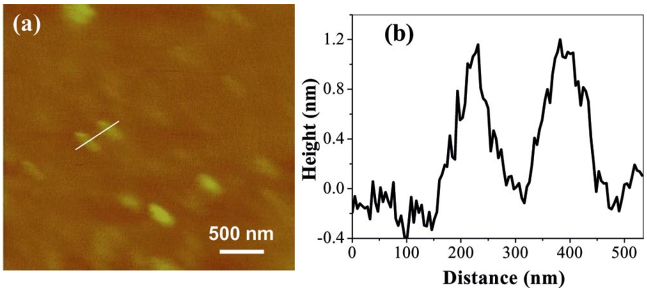


Figure 4. (a) AFM image and the corresponding (b) height profiles of WS_2 layers obtained by method 1. Adapted from ref.[18]

We compare the Raman spectra of graphene-like WS_2 and MoS_2 with those of their bulk counterpart. The spectrum for bulk WS_2 shows bands at 351 and 420 cm^{-1} arising from the E_{2g} and A_{1g} modes with FWHM values of about 7.8 and 2.4 cm^{-1}, respectively. However, the spectrum of WS_2 samples obtained from method 1 shows bands at 350 and 415 cm^{-1} with FWHM values of 13.7 and 8.4 cm^{-1}. A similar softening of the A_{1g} band and an increase in FWHM has been observed for few-layer WS_2 synthesized by method 2. Furthermore, the spectral width also increases in the spectrum of graphene-like WS_2. Figure 5 clearly shows that both the A_{1g} and E_{2g} modes soften in the graphene analogues of MoS_2 along with a spectral broadening compared to that seen for bulk MoS_2. The broadening of the Raman spectra occurs because of phonon confinement. We have prepared graphene-like MoS_2 by micromechanical cleavage of a MoS_2 single crystal by using the scotch-tape technique. Raman spectra of these samples exhibit a progressive softening of the A_{1g} and E_{2g} bands with a decrease in the number of layers. Thus, softening and broadening of Raman bands seem to be characteristic of few-layer MoS_2 and WS_2.

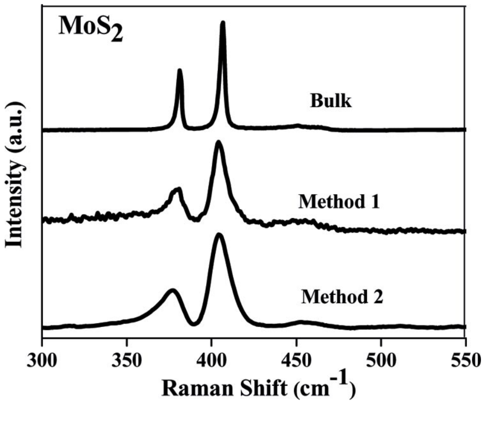


Figure 5. Raman spectra of bulk MoS_2 and few-layer MoS_2 obtained by methods 1 and 2. Adapted from ref.[18]

Boron Nitride

BN which is a layered material similar to graphite (Figure 1b) has a wide band gap. This material has received continuous scientific attention because of its remarkable mechanical, optical and electronic properties, with resistance to oxidation over a wide range of temperatures. A pair of boron and nitrogen is isoelectronic with a pair of carbon, and hexagonal boron nitride (h-BN) with a layered structure provides the motivation to prepare a graphene-analogue of BN, namely, mono- and few-layer BN. Mono- and few-layer BN has been prepared by peeling off BN layers from a bulk BN crystal by micromechanical cleavage,[33] by sonication[34] of BN particles, or by using a high-energy electron beam[35,36] inside a transmission electron microscope. We have been able to carry out the controlled chemical synthesis of graphene analogues of BN possessing a desired number of layers that can be used for the large-scale production of the material for the preparation of composites and for other applications.[17] In the course of this study, single-layer BN has been identified.

Graphene analogues of BN could be synthesized by employing the reaction of boric acid with urea at high temperatures.[37–39] Boric acid/urea mixtures with different molar ratios (1:6, 1:12, 1:24, 1:48 and 1:72) were used to obtain the desired number of BN layers.[17] The formation of BN is given by the following reactions (4), (5) and (6).[17]

$$2\,B(OH)_3 \xrightarrow{\triangle} B_2O_3 + 3\,H_2O \tag{4}$$

$$NH_2CONH_2 \xrightarrow{\triangle} NH_3 + HNCO \tag{5}$$

$$B_2O_3 + 2\,NH_3 \xrightarrow{\triangle} 2\,BN + 3\,H_2O \tag{6}$$

Characterization of few-layer BN was carried out by XRD, Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, TEM and AFM. The XRD patterns of the BN samples prepared with different boric acid to urea ratio exhibit two broad reflections with *d* spacings of ca. 3.51 Å and ca. 2.12 Å, which correspond to the (002) and (100) planes of h-BN, respectively. Interestingly, the width of the (002) reflection increases systematically with an increase in the proportion of urea in the starting reaction mixture. Also, the *d* spacing of the (002) plane increases slightly when the boric acid to urea ratio is 1:48, which suggests lower sheet-to-sheet registry in the sample. However, the Raman spectra of these samples remain unaltered with a band centred at 1373 cm^{-1} arising from the E_{2g} tangential mode.[40] The FTIR spectra show peaks at 1384 and 800 cm^{-1} assigned to the in-plane B–N transverse optical mode and out-of-plane B–N–B bending mode, respectively, along with the signature of the N–H stretching band from the amino groups on the surface.[41]

Electron energy loss spectroscopy (EELS) carried out in the transmission electron microscope reveals the π* and σ* peaks of the sp^2-hybridized B and N[42] and also that the composition of the product is stoichiometric. The TEM images in Figure 6 show the presence of single- as well as few-layer BN in the samples synthesized with different boric acid to urea ratios. The interlayer spacing is ca. 0.35 nm, which is slightly larger than that for the (002) planes of bulk h-BN (0.33 nm). The samples prepared with boric acid to urea ratios of 1:12 (Figure 6a) and 1:24 show the presence of eight and six layers of BN, respectively. Significantly, Figure 6b shows the presence of single layers along with two layers in the sample prepared with a ratio of 1:48 for boric acid/urea. The inset in Figure 6b shows the hexagonal atomic arrangement of the BN crystal. While the B–N bond length has been measured to be 1.44 Å, the separation between two nearest B atoms (or two nearest N atoms) is found to be 2.49 Å, both these values are in good agreement with the corresponding values for bulk h-BN.[34–36]

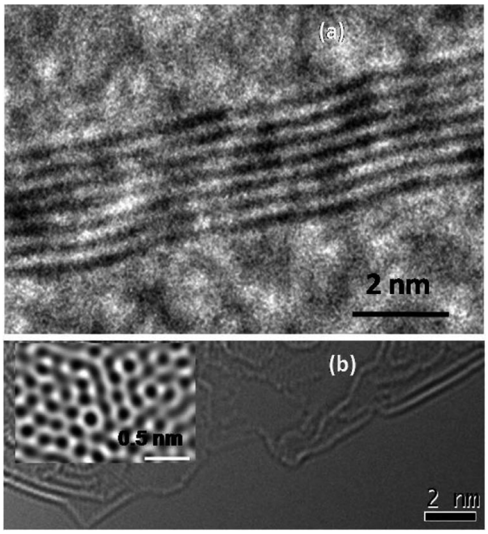


Figure 6. TEM images of few-layer BN prepared with boric acid/urea mixture with a ratio of (a) 1:12 and (b) 1:48. The inset in Figure 6b shows the HRTEM image of few-layer BN prepared with a 1:48 ratio for boric acid/urea. Adapted from ref.[17]

More reliable information on the number of layers in the BN samples was obtained by the AFM analysis, as shown in Figure 7. The AFM image of a BN flake prepared with a reactant ratio of 1:24 (Figure 7a) shows a steplike increase in the height from 0.4 to 0.8 nm, which corresponds to a single layer and bilayers. Figure 7b shows single-layer BN

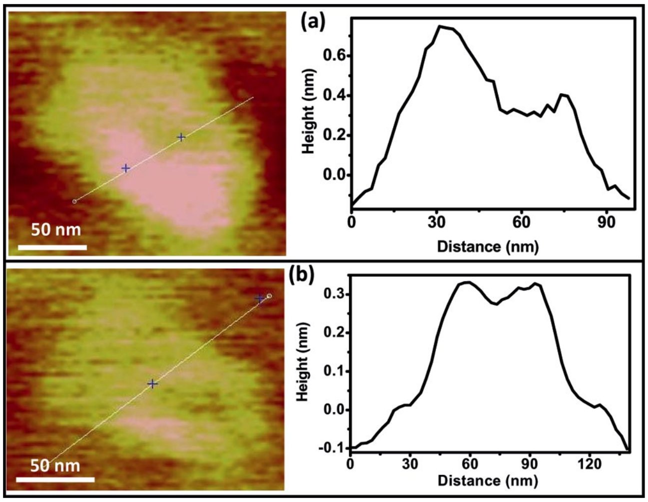


Figure 7. AFM images and corresponding height profiles of few-layer BN prepared with a (a) 1:24 and (b) 1:48 ratio for boric acid/urea. Adapted from ref.[17]

obtained from the sample prepared with a boric acid to urea ratio of 1:48. We prepared histograms of the thickness of the layer by analyzing AFM images of ca. 100 flakes for each sample synthesized with different urea content in the reaction mixtures, and the extracted average number of layers for different reactant ratios is plotted in Figure 8a. Clearly, the number of BN layers decreases with an increase in the proportion of urea in the starting reaction mixture. Thus, it is not surprising that the width of the (002) reflection in XRD increases with the proportion of urea in the reaction mixture; this graph is shown in the inset of the Figure 8a. A further increase in the boric acid/urea ratio of up to 1:72 does not result in thinner BN flakes relative to those obtained with a boric acid/urea ratio of 1:48. Recently, we have been able to synthesize few-layer BN using chemical vapour deposition techniques starting with a mixture of BBr_3 and NH_3.

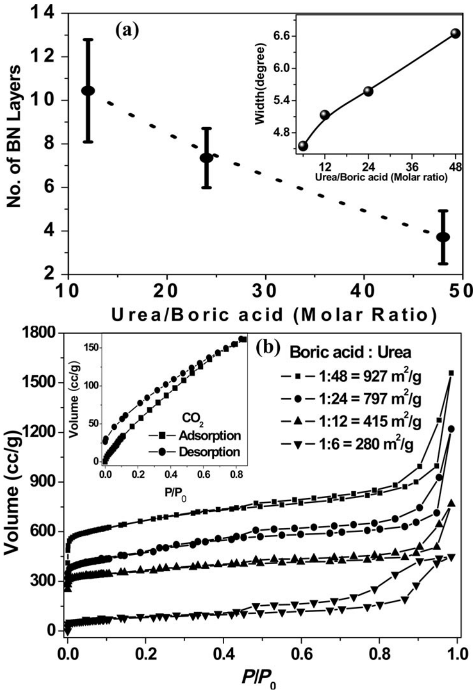


Figure 8. (a) Variation in the average number of BN layers obtained from AFM analysis vs. the urea/boric acid ratio. The inset shows the variation in the width of the (002) diffraction, obtained from XRD patterns, vs. the urea/boric acid precursor ratio. (b) Nitrogen adsorption–desorption isotherms of few-layer BN prepared with different boric acid/urea ratios in the reaction mixture. For a clear representation, plots for the ratios of 1:12, 1:24 and 1:48 have been moved vertically upward by 150, 270 and 400 units. The inset shows the CO_2 adsorption–desorption isotherms at 195 K and 1 atm for few-layer BN prepared with a boric acid/urea ratio of 1:48.

Figure 8b shows the N_2 adsorption–desorption isotherms of few-layer BN samples synthesized with different boric acid/urea ratios. Brunaure–Emmett–Teller (BET) surface areas of these samples calculated from the isotherms (Figure 8b) show an increase in the surface area with an increase in the proportion of urea in the reaction mixture. This systematic increase in the surface area is because of the decrease in the thickness of the layer with increasing urea content in the reaction mixture. To the best of our knowledge, the surface area of 927 m^2/g obtained with a boric acid to urea ratio of 1:48 is the highest value reported for BN so far. Remarkably, BN with the highest surface area adsorbs 32 wt.-% of CO_2 at 195 K and $p/p_0 = 0.85$, as shown in the inset of Figure 8b.

Solubilization of these inorganic graphenes is required for possible applications in composites and elsewhere. We have solubilized few-layer BN by interaction with Lewis bases.[43] The inherent electron deficiency of boron allows us to form Lewis acid/Lewis base adducts, by interacting few-layer BN with Lewis bases. Thus, adducts with trioctylamine (TOA) and trioctylphosphane (TOP) are soluble in nonpolar solvents such as toluene, while the as-prepared BN samples are insoluble in both polar and nonpolar solvents.

BCN – A New Graphene-Like Material

Similarly to h-BN and graphite, materials containing boron, carbon and nitrogen ($B_xC_yN_z$) also possess layered structures.[44–46] There are rare examples[47,48] of materials with compositions close to BCN, but their compositions and properties have not been investigated fully. We have recently been able to synthesize a graphite-like material with the composition BCN.[19] The material mainly consists of 2–3 layers of BCN, thus establishing a new graphene analogue.

Few-layer BCN could be synthesized by employing a reaction similar to that employed for few-layer BN. Activated charcoal with a high-surface area (1256 m^2/g) was used as a precursor for carbon. Addition of activated charcoal modifies reaction (7) to give BCN.[19]

$$B_2O_3 + 2\,NH_3 + 2\,C \xrightarrow{\Delta} 2\,BCN + 3\,H_2O \qquad (7)$$

Characterization of few-layer BCN was carried out by using XRD, Raman spectroscopy, TEM, AFM, X-ray photoelectron spectroscopy (XPS), EELS and thermogravimetric analysis (TGA). XRD and selected area electron diffraction (SAED) patterns show the (002) and (100) reflections of the graphite-like material. The obtained interlayer distance in BCN (3.46 Å) is slightly larger than that in both graphite (3.33 Å) and h-BN (3.36 Å). The Raman spectrum of BCN is similar to that of graphitic materials with a D band at 1324 cm^{-1} and G band at 1592 cm^{-1}.[49]

The unusual composition of BCN requires confirmation and verification by several means, in contrast to that of few-layer WS_2, MoS_2 and BN. TGA analysis carried out in air shows that BCN loses about 57% of weight at ca. 600 °C to leave a residue that is stable up to 1000 °C, while activated charcoal completely oxidizes before 600 °C. The XRD pattern of the BCN residue shows the presence of BN and C_3N_4, which suggests the presence of B, C and N in the final product. XPS core level spectra of few-layer $B_xC_yN_z$ products show broad signals for B 1s, C 1s and N 1s. The C 1s signal could be deconvoluted into three component spectra with binding energies of 283.1, 285.4 and 288.2 eV, which correspond to carbon bonded to boron, carbon and nitrogen, respectively.[42] The N 1s signal was deconvoluted into two bands with binding energies of 397.1 and 399.8 eV, which correspond to nitrogen bonded to boron and carbon, respectively.[42] Similarly, the B 1s signal was deconvoluted into two bands corresponding to boron bonded to carbon and nitrogen. The XPS spectra provide evidence for B–C, B–N, N–C and C–C bonds in the final product but also give an estimate of the composition to be $BC_{1.5}N_{1.1}$.

To have a more accurate estimation of the elemental composition and its homogeneity throughout the flake, we carried out EELS measurements on the K-edge absorption for B, C and N, as shown in Figure 9. K-shell ionization edges (Figure 9) at 188, 284 and 401 eV correspond to B, C and N respectively. The two peaks at each core edge suggest that all three elements are sp^2 hybridized, as expected in a graphite-like layered structure.[42] EELS measurements reveal the average chemical composition of the product to be $BC_{1.2}N$, which is in reasonable agreement with the XPS results. We conclude the composition to be similar to BCN. EEL mapping of boron, carbon and nitrogen showed that the composition is homogeneous throughout a BCN flake.

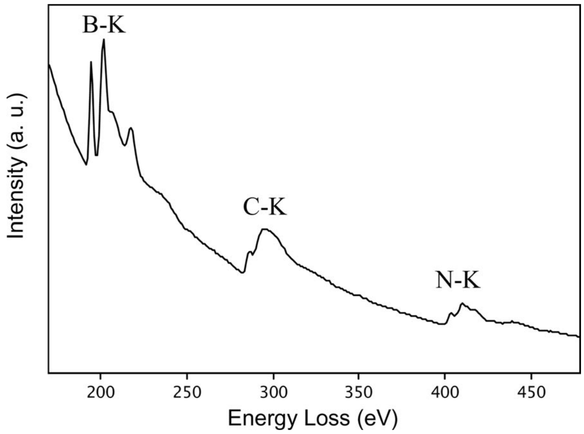


Figure 9. EEL spectrum showing the K-edges of boron, carbon and nitrogen of BCN. Adapted from ref.[19]

TEM and FESEM images of BCN show a flaky morphology with ripples and entanglement, similar to that of graphene. High-resolution TEM images show that the majority of the flakes consist of 2 or 3 layers with an interplanar distance of 3.43 Å. AFM images and the corresponding height profiles in Figure 10a and b exhibit flakes with thicknesses of 0.65 and 1.1 nm, which correspond to two and three layers, respectively. AFM analysis of over 100 BCN flakes has shown that they generally comprise two to three layers, with an occasional presence of single layers.

Few-layer BCN exhibits interesting gas adsorption properties. The BET surface area of the BCN sample was calculated to be 2911 m^2/g, by using the N_2 adsorption–desorption isotherms shown in Figure 11. The obtained surface area of BCN is higher than that for any composition of the $B_xC_yN_z$ materials reported so far. This high-surface-area BCN exhibits a remarkably high CO_2 uptake of 100 wt.-% at 195 K and 1 atm [inset (i) in Figure 11]. However, at room temperature and 40 bar, the CO_2 uptake is 44 wt.-%. Materials with high H_2 uptake are important for clean-energy alternatives. H_2 adsorption on BCN at 77 K and 1 atm is found to be 2.6 wt.-% [see inset (ii) in Figure 11]. H_2 uptake on BCN remains the same even after increasing the gas pressure. The BCN sample also adsorbs methanol vapour (about 26 wt.-% at room temperature and atmospheric pressure).

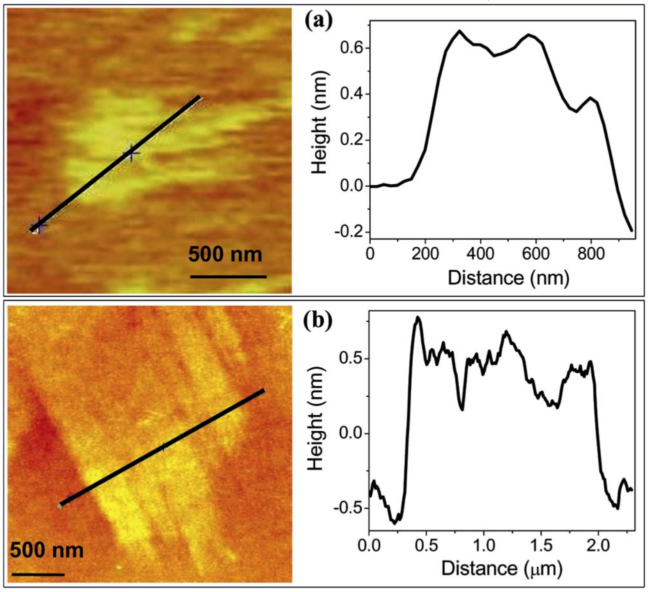


Figure 10. AFM images and their corresponding height profiles for (a) two-layered and (b) three-layered BCN. Adapted from ref.[19]

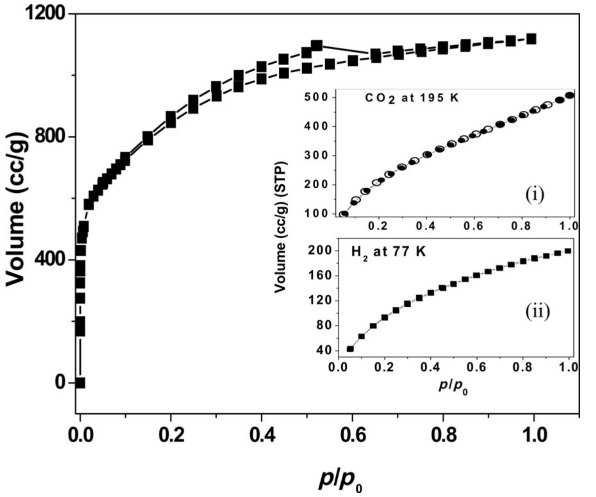


Figure 11. Nitrogen adsorption–desorption isotherms of few-layer BCN. Insets (i) and (ii) show the CO_2 and H_2 adsorption–desorption isotherms of the BCN sample at 195 K and 77 K, respectively and at 1 atm. Adapted from ref.[19]

The magnetic properties of BCN with 2–3 layers were compared with those of graphene. The temperature-dependent magnetic properties of few-layer BCN at 500 Oe show a divergence between field-cooled (FC) and zero-field-cooled (ZFC) data below 300 K. The divergence disappears at higher fields. Such a divergence between FC and ZFC at lower fields is somewhat similar to that seen in magnetically frustrated systems or phase-separated oxides. The Curie–Weiss temperature is –350 K, which indicates antiferromagnetic interactions. However, the material shows weak ferromagnetic hysteresis at 300 K. The presence of both ferromagnetic and antiferromagnetic interactions in BCN is similar to those in graphene,[50] and such magnetism could arise from the contribution of edge effects and defects.

Conclusions

It is noteworthy that we have been able to prepare graphene analogues of WS_2, MoS_2, BN and BCN using bottom-up chemical methods. These are rare examples of inorganic graphene analogues, which constitute a new family of two-dimensional nanostructures. All these layered materials have been characterized unambiguously by using a plethora of techniques to establish the formation of single- and bi- or few-layer material. Inorganic graphenes are expected to exhibit unique properties. For example, few-layer BCN exhibits high surface areas as well as high CO_2 uptake. Few-layer BN shows a systematic increase in the surface area with decreasing thickness of the layer. The interesting gas adsorption properties of these materials arise because of their graphene-like morphology. Few-layer BN can be used to prepare novel polymer composites. Few-layer MoS_2 could be useful in solid-state lubrication. Clearly, there is much to be explored with this new class of two-dimensional inorganic nanomaterials.

Acknowledgments

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