Graphene Analogues of BN: Novel Synthesis and Properties

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ABSTRACT Enthused by the fascinating properties of graphene, we have prepared graphene analogues of BN by a chemical method with a control on the number of layers. The method involves the reaction of boric acid with urea, wherein the relative proportions of the two have been varied over a wide range. Synthesis with a high proportion of urea yields a product with a majority of 1−4 layers. The surface area of BN increases progressively with the decreasing number of layers, and the high surface area BN exhibits high CO_2 adsorption, but negligible H_2 adsorption. Few-layer BN has been solubilized by interaction with Lewis bases. We have used first-principles simulations to determine structure, phonon dispersion, and elastic properties of BN with planar honeycomb lattice-based *n*-layer forms. We find that the mechanical stability of BN with respect to out-of-plane deformation is quite different from that of graphene, as evident in the dispersion of their flexural modes. BN is softer than graphene and exhibits signatures of long-range ionic interactions in its optical phonons. Finally, structures with different stacking sequences of BN have comparable energies, suggesting relative abundance of slip faults, stacking faults, and structural inhomogeneities in multilayer BN.

KEYWORDS: BN · graphene · gas adsorption · phonons · mechanical stability · elastic modulus

Boron nitride (BN) is a wide band gap ceramic with remarkable properties. It forms nanotubes just as carbon, and there has been extensive work of the synthesis and characterization of BN nanotubes in the past few years.[1−5] It is of considerable interest to synthesize and characterize graphene analogues of BN which are likely to have interesting properties and potential applications. It is possible to peel off BN layers from a bulk BN crystal by micromechanical cleavage,[6] while few-layer BN can be made by sonication[7,8] of BN particles or by using a high-energy electron beam.[9,10] There is, however, no report of the controlled chemical synthesis of graphene analogues of BN possessing a desired number of layers. Such a method would be useful for large-scale production of the material which can be used for preparing composites and in other applications. We have sought to explore such a synthesis of few-layer BN that permits the generation of materials with the desired number of layers. In this purpose, we have employed the reaction of boric acid with urea at high temperatures,[11−13] wherein we have varied the relative proportions of the two reagents. This simple method has enabled us to prepare graphene analogues of BN of varying thicknesses, exhibiting novel properties.

RESULTS AND DISCUSSION

In order to prepare few-layer BN, we prepared a mixture of boric acid and urea in the molar ratio of 1:*x* with $x = 6$, 12, 24, 48, and 72 and heated the mixture at 900 °C in a nitrogen atmosphere. We have examined the reaction products by X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), and atomic force microscopy (AFM). The XRD patterns of the products exhibit the characteristic (002) reflection of hexagonal BN ($d = 3.51$ Å), whose width increases with the increasing proportion of urea in the starting reaction mixture. Therefore, the *d* spacing corresponding to the (002) plane increased slightly when the boric acid to urea ratio was 1:48, indicating lower sheet-to-sheet registry in the sample. Raman spectra of all the samples show a band centered at 1373 cm^{-1} due to the E_{2g} tangential mode.[14] Fourier transform infrared (FTIR) spectra show peaks at 1384 and 800 cm^{-1} corresponding to in-plane B−N transverse optical mode and out-of-plane B−N−B bending mode, respectively, along with the N−H stretching band due to the amino groups on the surface.[15,16] The formation of BN in the procedure employed by us is given by the following reactions.

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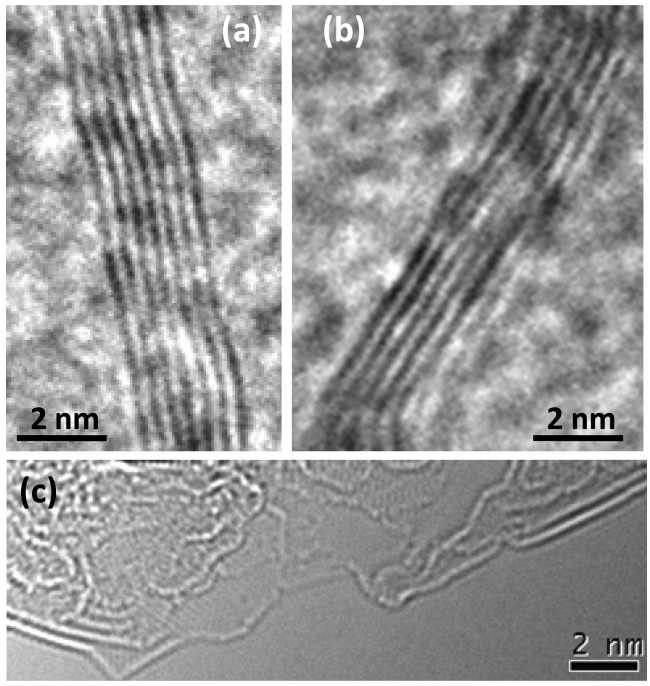

Figure 1. TEM images of few-layer BN prepared with (a) 1:12, (b) 1:24, and (c) 1:48 boric acid/urea mixture.

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

$$NH_2CONH_2 \xrightarrow{\Delta} NH_3 + HNCO$$

$$B_2O_3 + 2NH_3 \xrightarrow{\Delta} 2BN + 3H_2O$$

TEM investigations reveal the presence of single- as well as few-layer BN in the products. Electron energy loss spectroscopy (EELS) carried out on the microscope shows K-edge absorptions of B and N at 188 and 401 eV, respectively. Both the core edges exhibit π^* and σ^* peaks, characteristic of sp^2-hybridized BN.[7] EELS measurements also reveal the composition of the product to be stoichiometric. In Figure 1, we show representative high-resolution TEM images of a few of the samples synthesized with different boric acid to urea ratios. The interlayer spacing in all of the cases is ~3.5 Å, corresponding to the (002) planes of *h*-BN. In bulk BN, this distance is 3.3 Å. The images in Figure 1a,b correspond to samples prepared with boric acid to urea ratios of 1:12 and 1:24, showing the presence of eight and six layers of BN, respectively. The image in Figure 1c, obtained from the sample prepared with 1:48 boric acid/urea ratio, shows the presence of single layers along with two layers. This image also shows evidence for curves and bends in the layers representing a possible intermediate stage in the formation of nanotube by rolling. The hexagonal atomic arrangement of the BN crystal can be seen from the high-resolution TEM image in Figure 2a with the incident electron beam along the

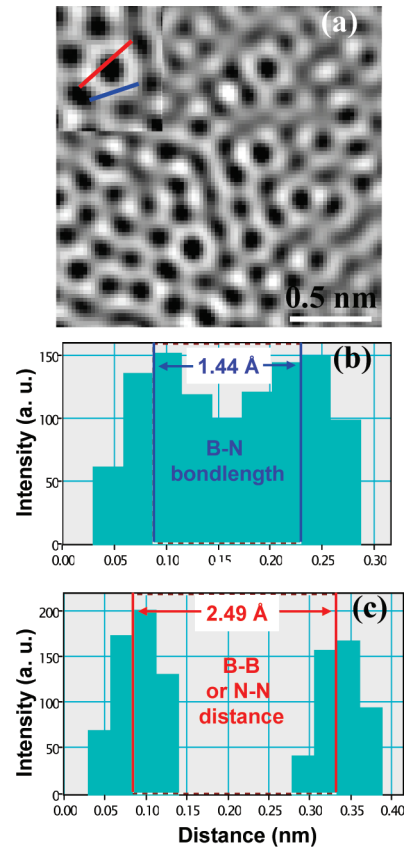

Figure 2. (a) High-resolution TEM image of few-layer BN prepared with 1:48 boric acid/urea mixture. Inset shows a typical hexagonal atomic arrangement, magnified from the mainframe. Intensity line profile of the bright and dark spots along the (b) blue line and (c) red line in the inset of panel a.

⟨001⟩ direction. The distance between two neighboring bright dots in the hexagon is 1.44 Å (Figure 2b), which corresponds to the known length of the B−N bond. The distance between the alternating dots in the hexagon is 2.49 Å (Figure 2c), corresponding to the (100) lattice constant of *h*-BN. This distance describes the separation between nearest N or B atoms.[8−10] Thus, TEM studies of the products of urea/boric acid reaction reveal the formation of graphene analogues of BN, the layer thickness decreasing with increasing urea concentration in the reaction mixture. The observation of a single-layer BN with a high proportion of urea in the reaction mixture is significant.

More reliable information on the number of layers in the BN samples was obtained by the AFM examination of the products, as shown in Figure 3. The average sheet areas varied between 0.1 μm × 0.1 μm and 1 μm × 1 μm depending on the starting reactant ratio. Figure 3a shows a micrometer size BN flake obtained with a boric acid/urea ratio of 1:12. The step-like increase in the height profile from 3 to 5 nm along the white line shown in the image represents an increase in the number of layers from 8 to 14 layers. The AFM image in Figure 3b of a BN flake (150 × 200 nm^2) obtained with a reactant ratio of 1:24 exhibits a step-like

increase in height from 0.4 to 0.8 nm corresponding to single and bilayers. Figure 3c shows an AFM image and corresponding height profile of a single-layer BN obtained from the sample prepared with a boric acid/urea ratio of 1:48. AFM images with larger scanning area show multiple BN flakes with a thickness in the 0.5−0.9 nm range. In Figure 4, we show the histograms of layer thickness obtained from an analysis of the AFM images. We clearly see that, with the increasing proportion of the urea in the starting reaction mixture, the number of BN layers decreases. While the number of layers is between 8 and 14 for the sample with the reactant ratio of 1:12, we obtain ~1−4 layers of BN with a boric acid/urea ratio of 1:48 (see Figure 4a−c). In Figure 4d, we show the variation of the average number of layers with the reactant ratio. Further increase in urea content in the reaction mixture had little effect on the number of BN layers in the product.

We have determined the BET surface areas of the few-layer BN samples by employing N_2 adsorption−desorption isotherms (Figure 5). The surface area increases with the increasing proportion of urea in the reaction mixture. We consider this to reflect the decrease in the number of layers, rather than the variation of the area of the BN flakes. Thus, the high value of surface area of 927 m^2/g when the boric acid/urea ratio is 1:48 cannot be accounted for on the basis of the area of the flakes. The variation of the surface area with the proportion of urea is shown in inset (a) of Figure 5. This inset also shows that the width of the (002) reflection increases with the proportion of urea. To the best of our knowledge, such high surface area BN samples are not reported hitherto. 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 inset (b) of Figure 5. This sample, however, adsorbs only ~0.5 wt % of H_2 at 77 K and 1 atm.

As-prepared BN layers are insoluble in both polar and nonpolar solvents. For possible applications of few-layer BN in composites and elsewhere, it is necessary to functionalize the samples. We have accomplished this by making use of the inherent electron deficiency of boron to form Lewis acid−Lewis base adducts, by interacting few-layer BN with Lewis bases.[17] Thus, adducts with trioctylamine (TOA) and trioctylphosphine (TOP) are soluble in nonpolar solvents such as toluene, heptane, and benzene. This behavior is different from the dispersion of BN in polar solvents such as dimethylformamide. Figure 6 shows photographs of clear solutions of functionalized BN in toluene.

We now present the results of our theoretical studies of few-layer BN. The structural parameters of bulk (hexagonal) BN determined from our calculations agree with the experimental values within typical errors of LDA. We have considered the variation in stacking sequences of bulk (*e.g.*, AB, AA, AB′, where B′ is B rotated by 180°). The lowest energy structure has AB stacking

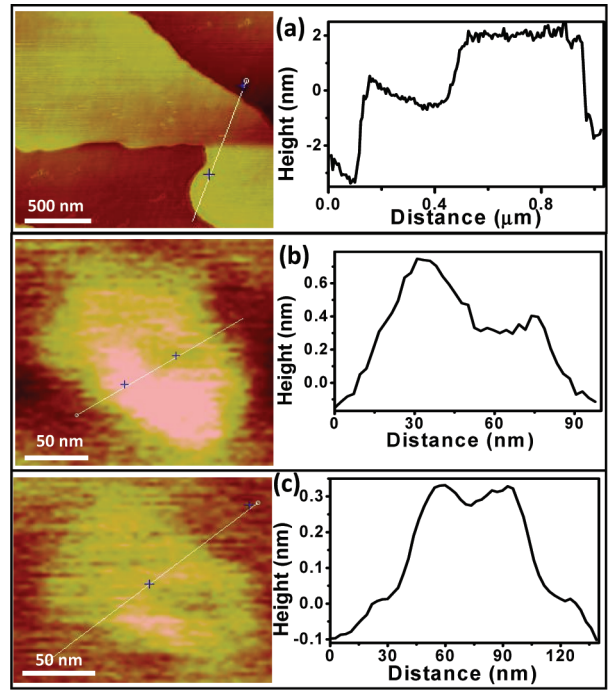

Figure 3. AFM images and corresponding height profiles of few-layer BN prepared with different boric acid/urea molar ratios of (a) 1:12, (b) 1:24, and (c) 1:48.

in which B and N atoms of the consecutive layers are on top. The next two higher energy structures correspond to the AB′ and AA stacking, which are the configurations with twist and slip faults, respectively. They are 2 and 4 meV/BN higher in energy than the ground state structure. While the estimated B−N bond lengths in these structures are the same, the interplanar distance increases by about 2%. These results show that (a) it should be easy to form stacking faults in BN and (b) the interplanar distance consequently can be inhomogeneous, as revealed by high-resolution TEM images of the few-layer BN samples. Cohesive energies of few-layer BN sheets converge close to bulk values for $n > 4$ (see Figure 7), indicating that the few-layer BN sheets are quite stable. Interestingly, we find that the interplanar distance in few-layer BN is larger than that of the bulk BN. This is counterintuitive but is in agreement with experiment (see Table 1). The origin of this probably lies in the fact that the stability of BN is controlled by long-range Coulomb interactions and not just the local coordination or weak interplanar bonds.

The bulk modulus of monolayer BN is determined using

$$B = A\frac{d^2E}{dA^2}\Big|_{A_{min}} \quad (1)$$

where A is the area of the unit cell and A_{min} is the unit cell areas of the equilibrium structure. We find the bulk modulus of BN is 160 Pa · m, as compared to 202 Pa · m of graphene, clearly showing the relative softness of BN. This is also reflected in the slopes of branches of acous-

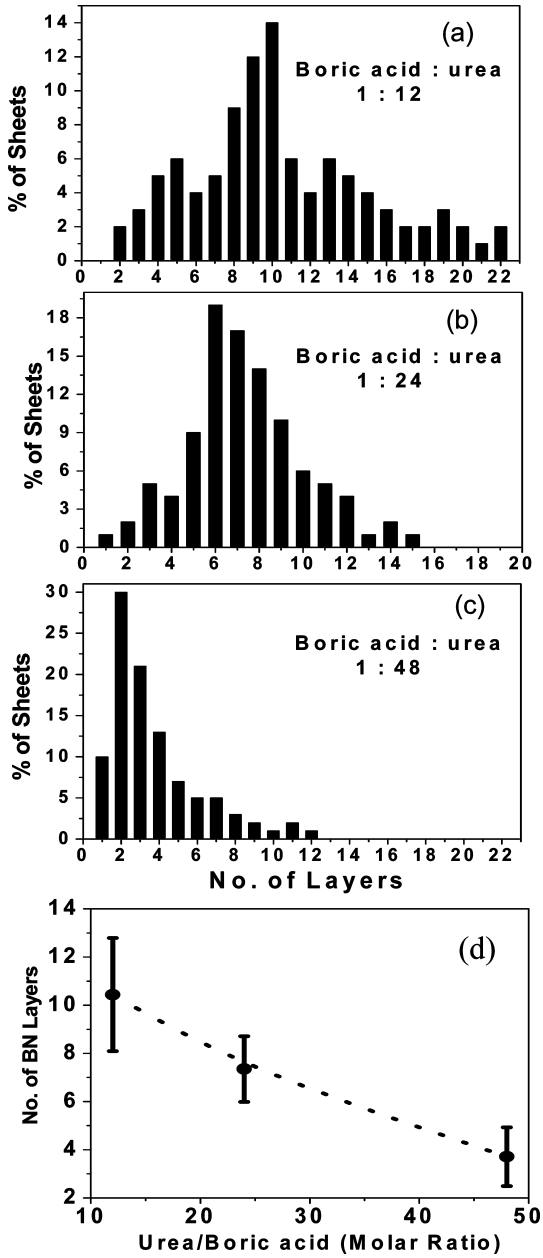

Figure 4. Bar diagrams derived from an analysis of AFM images, showing the layer distribution of few-layer BN prepared with different boric acid/urea molar ratios of (a) 1:12, (b) 1:24, and (c) 1:48. (d) Variation of the average layer thickness *vs* urea/boric acid ratio.

tic phonons in their phonon dispersion (see Figure 8a). It is evident from the phonon dispersion that flexural modes (acoustic modes with out-of-plane polarization) are significantly softer in BN (310 cm^{-1} at K-point) than those in graphene (527 cm^{-1} at K-point). More importantly, the branch of flexural modes in BN is isolated (decoupled) from the rest, clearly revealing greater tendency of BN to form ripples and deform out-of-plane than of graphene. Optic modes of BN, analogous to the doubly degenerate G-band of graphene, are split due to long-range interactions (LO-TO splitting) by 135 cm^{-1}. As one evolves from the monolayer to bilayer BN, another branch of phonons similar to the flexural

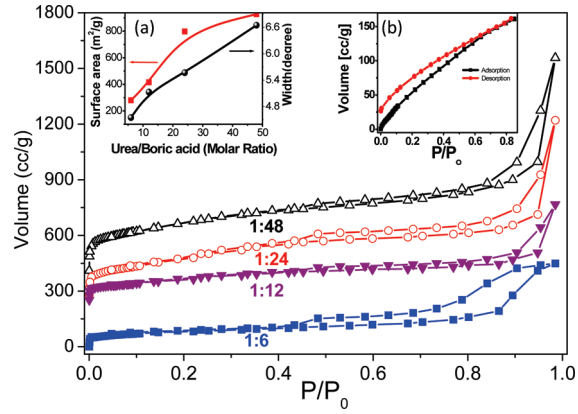

Figure 5. Nitrogen adsorption−desorption isotherms of few-layer BN prepared with different boric acid/urea ratios. Plots for boric acid/urea ratios of 1:12, 1:24, and 1:48 have been moved vertically upward by 150, 270, and 400 units, for a clear representation. Inset (a) shows the variation of the BET surface area *vs* urea/boric acid precursor ratio. Also, it shows the variation of the width of (002) diffraction, obtained from powder XRD patterns (not shown here) with urea/boric acid precursor ratio. Inset (b) shows the CO_2 adsorption−desorption isotherms at 195 K and 1 atm for the BN sample with boric acid/urea ratio of 1:48.

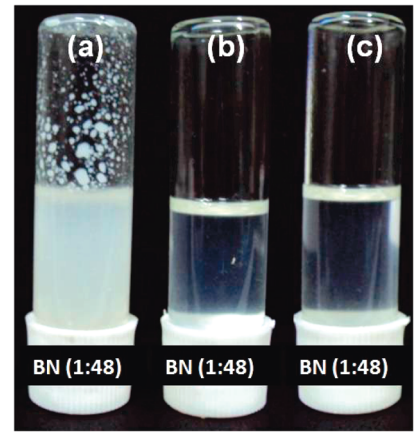

Figure 6. Photographs of the solutions of (a) as-prepared few-layer BN along with BN functionalized with (b) TOP and (c) TOA in toluene. The BN sample was prepared with a boric acid/urea ratio of 1:48.

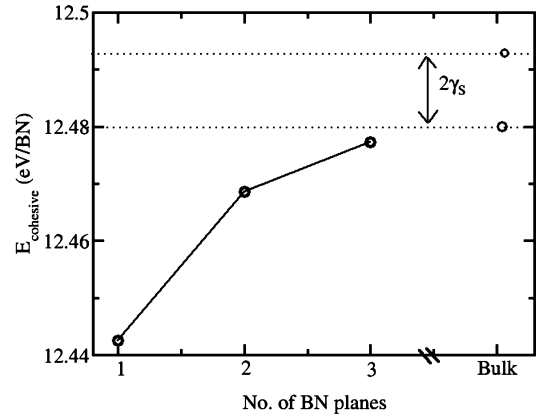

Figure 7. Stability of *n*-layer BN, as reflected in cohesive energy as a function of number *n*; at large *n*, it converges to the cohesive energy of the bulk and two surfaces (*i.e.*, a thick slab); γ_S is the surface energy of BN.

TABLE 1. Lattice Parameters (*a*, Å) and Interlayer Distances (*d*, Å) in BN Structures

	experiment[a,b,c]		theory	
BN structures	*a* (Å)	*d* (Å)	*a* (Å)	*d* (Å)
bulk	2.5	3.3	2.48	3.2
two or few layers	2.5	3.5	2.48	3.3

[a]From ref 8. [b]From ref 19. [c]Our experimental results.

modes arises, through starting at a nonzero frequency (74 cm^{-1} ~ 9 meV) at Γ point, indicative of the shear strength of bilayer BN (Figure 8b). The branch of optic phonons shows a dependence on the stacking sequence, confirming our earlier comment that the stability is controlled by the long-range interactions. Other phonons of bilayer BN are essentially the same as those in monolayer BN.

We considered various sites of adsorption of H_2 molecule on a BN sheet, (a) with different atomic sites (B and N), and (b) with the center of a pore of the honeycomb structure with varied orientations of H_2 molecule in the initial structure, and relaxed the structures fully to determine the adsorption energy. Our calculations show a weaker H_2 adsorption on BN layers compared to graphene in accord with our experimental results.

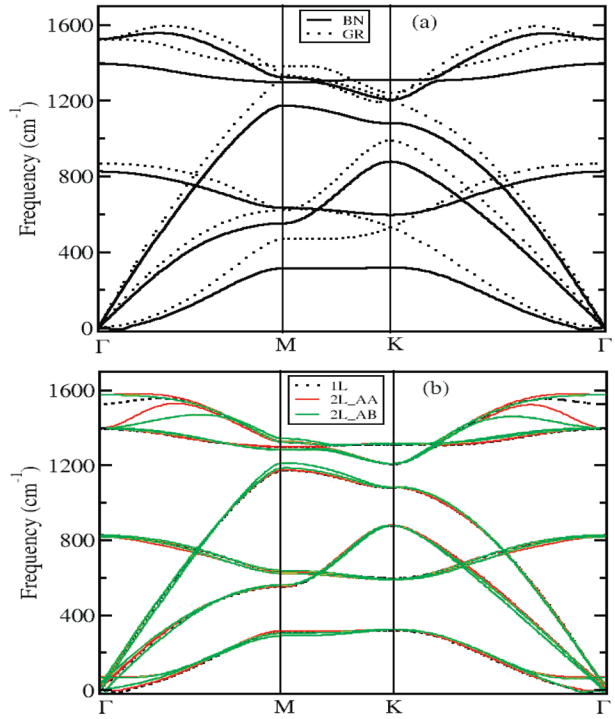

Figure 8. Phonon spectra of (a) monolayer BN, compared with graphene (dotted line) and (b) two-layer BN (2 L) with AA and AB stacking sequences, compared with that of monolayer BN (1 L).

CONCLUSIONS

In conclusion, single- and few-layer graphene analogues of BN flakes could be prepared successfully by reacting boric acid with different proportions of urea at 900 °C. The number of BN layers decreases with the increase in urea content in the reaction mixture, allowing a control on the number of BN layers. We believe that this is the first report of a bottom-up chemical synthesis of few-layer BN, enabling large-scale production. The surface area of the BN layers increases with the decrease in layer thickness as expected, the sample with lowest layer thickness exhibiting a surface area of 927 m^2/g and high CO_2 uptake. Few-layer BN can be functionalized and solubilized by employing Lewis bases.

From first-principles simulations, we show that it is energetically easy for few-layer BN to (a) form stacking faults that involve slips and twists of adjacent planes resulting in inhomogeneity in the interplanar distances and (b) deform through forming ripples. It has a smaller buckling strength and elastic stiffness than graphene. Long-range Coulomb interactions are found to be important to the stability of the different structures of BN. Our calculations demonstrate only weak interaction of hydrogen with BN sheets. Graphene analogues of BN may find several interesting applications. They can be used to form composites with polymers, with desirable applications.

METHODS

Boric acid (SD Fine-Chemicals Limited)/urea (SD Fine-Chemicals Limited) mixtures with different molar ratios (1:6, 1:12, 1:24, 1:48, and 1:72) were dissolved in ~40 mL of Millipore water and heated at 65 °C, until the evaporation of water was complete. The dried mixtures were heated at 900 °C for 5 h in a N_2 atmosphere, yielding white products. Powder XRD patterns of the products were recorded with a Bruker-D8 X-ray diffractometer using Cu Kα radiation. Raman spectra were recorded employing a LabRAM HR with a 633 nm line from a HeNe laser. FTIR spectra were recorded using a Bruker IFS 66v/S spectrometer. AFM measurements were performed using a NanoMan instrument using tapping mode. A dilute dispersion of BN flakes in acetone was dropped on a SiO_2 substrate and was used for AFM measurements. QUANTACHROME QUADRASORB-1C surface area analyzer was used for gas adsorption studies. Brunauer−Emmett−Teller (BET) surface areas were obtained from a nitrogen adsorption−desorption isotherm at 77 K. To functionalize the few-layer BN, 1 mg of BN was mixed with 3 mL of toluene followed by addition of 0.3 mL of trioctylamine (Aldrich) or trioctylphosphine (Aldrich). The mixture was then sonicated for ~15 min to obtain a clear and stable solution of BN.

TEM studies were carried with a FEI TITAN (cube) 80-300 and a JEOL JEM 3010 instrument operating at 300 kV. Atomic arrangement of hexagonal BN in Figure 2 (no reconstruction) was obtained from the FEI TITAN[3] 80−300 kV aberration corrected transmission electron microscope with a negative spherical aberration coefficient (C_s) of ~−30 μm and a positive defocus about +8 nm, where atomic potentials appear with bright contrast in a dark background.[18] This bright atom imaging mode is an essential condition for imaging light atoms.

We use plane wave self-consistent field (PWSCF)[20] implementation of density functional theory (DFT) with a local density approximation (LDA)[21] to exchange correlation energy of electrons and ultrasoft pseudopotentials[22] to represent interaction between ionic cores and valence electrons. Use of a generalized gradient approximation (GGA) to density functional gave unrealistic estimates of interplanar distances.[23] Kohn−Sham

wave functions were represented with a plane wave basis with an energy cutoff of 40 Ry and charge density cutoff of 480 Ry. Integration over Brillouin zone (BZ) was sampled with a uniform with a 10 × 10 × 1 mesh of k-points. For *n*-layer BN, different stacking sequences (AA, AB) were considered in the identification of stable structures. Dynamical matrices on a mesh of wavevectors in BZ were computed using DFT linear response, and phonon dispersion was determined using Fourier interpolation. To study hydrogen adsorption on BN and graphene, 3 × 3 super cell in the *ab* plane was used with periodic boundary condition and a vacuum of 16 Å in the third direction. Different configurations and coverages of H_2 molecules were simulated to estimate energies and related properties of adsorption.

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REFERENCES AND NOTES

1. Chopra, N. G.; Luyken, R J.; Cherrey, K. C.; Crespi, V. H.; Cohen, M. L.; Louie, S. G.; Zettl, A. Boron Nitride Nanotubes. *Science* **1995**, *269*, 966–967.
2. Rao, C. N. R.; Nath, M. Inorganic Nanotubes. *Dalton Trans.* **2003**, 1–24.
3. Tenne, R.; Rao, C. N. R. Inorganic Nanotubes. *Philos. Trans. R. Soc. London, Ser. A* **2004**, *362*, 2099–2125.
4. Zhi, C. Y.; Bando, Y.; Tang, C. C.; Huang, Q.; Golberg, D. Boron Nitride Nanotubes: Functionalization and Composites. *J. Mater. Chem.* **2008**, *18*, 3900–3908.
5. Rao, C. N. R.; Govindaraj, A. Synthesis of Inorganic Nanotubes. *Adv. Mater.* **2009**, *21*, 4208–4233.
6. Pacile, D.; Meyer, J. C.; Girit, C. O.; Zettl, A. The Two-Dimensional Phase of Boron Nitride: Few-Atomic-Layer Sheets and Suspended Membranes. *Appl. Phys. Lett.* **2008**, *92*, 133107.
7. Han, W. Q.; Wu, L. J.; Zhu, Y. M.; Watanabe, K.; Takiguchi, T. Structure of Chemically Derived Mono- and Few-Atomic-Layer Boron Nitride Sheets. *Appl. Phys. Lett.* **2008**, *93*, 223103.
8. Zhi, C.; Bando, Y.; Tang, C.; Kuwahara, H.; Golberg, D. Large-Scale Fabrication of Boron Nitride Nanosheets and Their Utilization in Polymeric Composites with Improved Thermal and Mechanical Properties. *Adv. Mater.* **2009**, *21*, 2889–2893.
9. Meyer, J. C.; Chuvilin, A.; Algara-Siller, G.; Biskupek, J.; Kaiser, U. Selective Sputtering and Atomic Resolution Imaging of Atomically Thin Boron Nitride Membranes. *Nano Lett.* **2009**, *9*, 2683–2689.
10. Jin, C.; Lin, F.; Suenaga, K.; Iijima, S. Fabrication of a Freestanding Boron Nitride Single Layer and Its Defect Assignments. *Phys. Rev. Lett.* **2009**, *102*, 195505.
11. Gomathi, A.; Sundaresan, A.; Rao, C. N. R. Nanoparticles of Superconducting γ-Mo_2N and δ-MoN. *J. Solid State Chem.* **2007**, *180*, 291–295.
12. Gomathi, A.; Harika, M. R.; Rao, C. N. R. Urea Route To Coat Inorganic Nanowires, Carbon Fibers and Nanotubes by Boron Nitride. *Mater. Sci. Eng.* **2008**, *476*, 29–33.
13. Gomathi, A.; Reshma, S.; Rao, C. N. R. A Simple Urea-Based Route to Ternary Metal Oxynitride Nanoparticles. *J. Solid State Chem.* **2009**, *182*, 72–76.
14. Saha, S.; Muthu, D. V. S.; Goldberg, D.; Tang, C.; Zhi, C.; Bando, Y.; Sood, A. K. Comparative High Pressure Raman Study of Boron Nitride Nanotubes and Hexagonal Boron Nitride. *Chem. Phys. Lett.* **2006**, *421*, 86–90.
15. Zhi, C.; Bando, Y.; Tang, C.; Golberg, D. Immobilization of Proteins on Boron Nitride Nanotubes. *J. Am. Chem. Soc.* **2005**, *127*, 17144–17145.
16. Gu, Y. L.; Zheng, M. T.; Liu, Y. L.; Xu, Z. L. Low-Temperature Synthesis and Growth of Hexagonal Boron-Nitride in a Lithium Bromide Melt. *J. Am. Ceram. Soc.* **2007**, *90*, 1589–1591.
17. Pal, S.; Vivekchand, S. R. C.; Govindaraj, A.; Rao, C. N. R. Functionalization and Solubilization of BN Nanotubes by Interaction with Lewis Bases. *J. Mater. Chem.* **2007**, *17*, 450–452.
18. Jia, C. L.; Lentzen, M.; Urban, K. Atomic-Resolution Imaging of Oxygen in Perovskite Ceramics. *Science* **2003**, *299*, 870–873.
19. Paine, R. T.; Narula, C. K. Synthetic Routes to Boron Nitride. *Chem. Rev.* **1990**, *90*, 73–91.
20. Baroni, S.; Corso, A. D.; Gironcoli, S. D.; Gianozzi, P. http://www.pwscf.org
21. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
22. Vanderbilt, D. Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism. *Phys. Rev. B* **1990**, *41*, 7892–7895.
23. Saha, S. K.; Chandrakanth, R. C.; Krishnamurthy, H. R.; Waghmare, U. V. Mechanisms of Molecular Doping of Graphene: A First-Principles Study. *Phys. Rev. B* **2009**, *80*, 155414.