In recent times, atomically thin alloys of boron, nitrogen, and carbon have generated significant excitement as a composition-tunable two-dimensional (2D) material that demonstrates rich physics as well as application potentials. The possibility of tunably incorporating oxygen, a group VI element, into the honeycomb sp²-type 2D-BNC lattice is an intriguing idea from both fundamental and applied perspectives. We present the first report on an atomically thin quaternary alloy of boron, nitrogen, carbon, and oxygen (2D-BNCO). Our experiments suggest, and density functional theory (DFT) calculations corroborate, stable configurations of a honeycomb 2D-BNCO lattice. We observe micrometer-scale 2D-BNCO domains within a graphene-rich 2D-BNC matrix, and are able to control the area coverage and relative composition of these domains by varying the oxygen content in the growth setup. Macroscopic samples comprising 2D-BNCO domains in a graphene-rich 2D-BNC matrix show graphene-like gate-modulated electronic transport with mobility exceeding 500 cm² V⁻¹ s⁻¹, and Arrhenius-like activated temperature dependence. Spin-polarized DFT calculations for nanoscale 2D-BNCO patches predict magnetic ground states originating from the B atoms closest to the O atoms and sizable (0.6 eV < Eₕ < 0.8 eV) band gaps in their density of states. These results suggest that 2D-BNCO with novel electronic and magnetic properties have great potential for nanoelectronics and spintronic applications in an atomically thin platform.

INTRODUCTION

Alloy formation is a powerful technology, one that has enabled a variety of semiconductors to be used in an array of tunable optics and electronics (1, 2). In recent times, atomically thin two-dimensional (2D) semiconductors have become extremely important for both fundamental science and technology owing to their unique electronic, optical, and mechanical properties (3–9). Hence, the possibility of alloy formation in 2D materials is a topic of significant interest because composition-tunable 2D materials are expected to show a rich variety of tunable electronic, optical, and magnetic properties in an atomically thin layer. So far, the most promising approach for developing composition-tunable 2D materials has been chemical vapor deposition (CVD) synthesis of hybrid domains of boron, nitrogen, and carbon in an atomically thin plane (10–16). This B–N–C system allows the substitution of C atoms of graphene by B, N, and/or hexagonal BN (h-BN), and enables the growth of atomically thin alloys with band gaps ranging from 0 eV (graphene) to 5.2 eV (h-BN).

In all relevant reports, the possible role of oxygen, whose presence in small quantities is inevitable in CVD chambers, has not received any attention (11, 17–19). Oxygen has been proposed to cause C species oxidation and, hence, etching of carbon (19). In the context of BNC growth, this is significant, because in a recent report, Liu et al. have shown that any etched edge of graphene can, in principle, be a template for 2D heteroepitaxial growth (that is, growth from a 1D edge) of h-BN species (13). Because oxygen is always present during the synthesis of graphene, either as an adsorbed impurity on Cu substrates (18) or in the surrounding gaseous environment, the question arises whether simultaneous growth of BN species in graphene can be influenced by controlling the oxygen content in the CVD chamber. Moreover, Krivanek et al. have shown, using annular dark-field electron microscopy, that oxygen can enter the BNC honeycomb lattice by forming in-plane covalent bonds with B and C (20). It is rather remarkable that oxygen, a group VI element, can enter the hexagonal sp²-type lattice of graphene and h-BN. Hence, it is also a matter of immense fundamental interest whether oxygen can be controllably introduced into the BNC system and whether an atomically thin quaternary material, that is, BNCO, can be stably synthesized with tunable composition. Here, we show that B, N, C, and O atoms can indeed form a single-atomic-layer, graphene-like honeycomb lattice (which we call 2D-BNCO), resulting in the first demonstration of a purely 2D quaternary alloy.

RESULTS AND DISCUSSION

BNCO samples were fabricated on Cu foils in a low-pressure CVD system (see Materials and Methods) with CH₄ as the carbon source and powdered NH₄BH₄ as the common source for B and N. To analyze the effect of oxygen content, we synthesized a set of eight samples by introducing Ar/O₂ (O₂ mole fraction of 10⁻³) into the CVD chamber.
and varying its flow rate. These samples, synthesized using flow rates of 0, 2, 4...14 standard cm$^3$/min (sccm), were correspondingly labeled BNCO-0, BNCO-2...BNCO-14. For samples synthesized using flow rates between 0 and 8 sccm, we found reproducible results and systematic correlations between various investigated material properties. Beyond a flow rate of 8 sccm, the system became unstable, with fluctuating and irreproducible results, most possibly due to the uncontrolled oxidation of the samples. Figure 1A shows a transmission electron microscopy (TEM) image of a typical sample, which was found to be mostly monolayer and bilayer in nature. Figure 1B shows typical selected-area electron diffraction (SAED) patterns from various locations, revealing the ubiquitous sixfold honeycomb symmetry of the crystal lattice. Analysis of SAED results suggests the presence of monolayer, possible Bernal-stacked bilayer, and some turbostratic bilayer regions, as exemplified in the four diffraction patterns shown. SAED analysis of monolayer samples reveals a nearest-neighbor lattice separation of 0.21 nm. From these, we conclude that the samples are atomically thin (mostly mono- or bilayered), with a graphene-like honeycomb lattice structure.

Although the structure appears to be highly homogeneous in the TEM images, closer inspection of the samples using scanning electron microscopy (SEM) provides a clear indication of the presence of two distinct phases, characterized by contrast between brighter and darker regions, as seen in the two samples shown in Fig. 1 (C and D), which were synthesized under different growth conditions (see the Supplementary Materials). For convenience, we term the brighter regions “domains,” because they are compositionally different from the surrounding matrix and have several interesting properties. First, the sharp visual contrast between the domains and the surrounding regions (matrix) is only visible when the SEM images are collected from samples on Cu substrates. Upon being transferred to insulating surfaces such as SiO$_2$, the contrast difference completely vanishes. This observation, along with the homogeneous nature of the TEM image in Fig. 1A and similar SAED diffraction patterns obtained everywhere in the samples, suggests that the two regions, the “bright” domains and the “dark” matrix, have differing electrical conductivities but are structurally similar.

Second, when sufficiently isolated from each other, the domains appear to have very well defined shapes, mostly six-sided and with sharp, angular edges as seen in Fig. 1D. Liu et al. demonstrated the growth of h-BN domains from the graphene edges in a two-step process (13). In our “single-step” process, we observed domain geometry and sizes that look strikingly similar to those of Liu et al., although as shown later, in our case, the chemical composition of the domains is different. We believe that introduction of oxygen during the synthesis process collapses the two-step process of Liu et al. into a single step either by slowing down or terminating the growth, or by etching away carbon-rich regions and introducing a richer combination of 2D-BNCO in their place.

Third, the relative coverage of these domains over the entire millimeter-scale sample could be systematically controlled between 0

---

**Fig. 1.** Atomically thin 2D-BNCO sheets. (A) A bright-field TEM image of a typical BNCO sample transferred onto a lacey carbon-coated TEM grid. (B) Typical SAED pattern from various locations demonstrating honeycomb-like lattice structure in monolayer or rotated bilayer forms. (C and D) SEM images of a BNCO sample as grown on Cu substrate. The samples shown here were grown with different oxygen flow rates in the CVD chamber. See the Supplementary Materials, section S1, for details of sample synthesis. (E) Percent surface coverage of domains and graphitic areas as extracted from the analysis of SEM images, as a function of O$_2$ flow rate into the chamber. (F) Typical XPS survey scan from BNCO-12 sample. The B1s and N1s peaks (regions marked by arrows) are only visible in high-resolution detailed scans (see the Supplementary Materials, section S4). (G) Relative occurrence of oxygen atoms as a function of the fractional coverage of the samples by domains, providing direct evidence of the presence of oxygen in the domain areas.
and 60% by changing the oxygen content during CVD growth (see the Supplementary Materials for measurement details). Figure 1E shows the percentage coverage of domains as progressively more oxygen is introduced into the CVD chamber. Starting from a near-complete absence of the domains at 0 sccm Ar/O₂, there is a clear overall increase in the surface coverage of the domains, although the dependence is nonmonotonic.

Figure 1F shows an x-ray photoelectron spectroscopy (XPS) survey scan performed on a typical sample (BNCO-12). Peaks corresponding to C1s and O1s are immediately visible in the survey, whereas weak peaks corresponding to B1s and N1s are found only in high-resolution scans of the regions indicated with red arrows (see the Supplementary Materials). In all samples between 0 and 8 sccm, the B1s peaks were too weak for any quantitative analysis, and the presence of B was confirmed through analysis of the N peak and Raman spectroscopy. Because the XPS beam size is much larger (400 μm) than the domains, it was not possible to obtain XPS for individual domains (that is, the XPS survey scan contains contributions from both domain and matrix regions). Hence, the question arises: What fraction of each observed element originates from the domains? To address this question, in Fig. 1G, the relative concentrations of oxygen atoms and carbon atoms are plotted against fractional domain coverage (for the set of samples that were examined in this study). We see a clear correlation between the domain coverage and the relative concentration of oxygen atoms, and especially at higher surface coverage of domains, the relation is nearly linear. This correlation implies that the XPS-observed oxygen is present predominantly in the domains. Detailed peak analysis (see the Supplementary Materials) shows that the oxygen atoms are bonded with B, N, and C atoms, and we next present some of the salient features of the chemical bonding of the oxygen and other atoms in the system.

Figure 2 (A and B) shows examples of typical high-resolution XPS scans of the O1s and C1s spectra, each fitted to several identifiable peaks representing known chemical shifts. In the O1s spectrum, the most significant contribution came from a peak at 532 eV identified with O–Cu bonds (21). A red-shifted O–N peak at 530.7 eV (22) and a blue-shifted O–B (23) peak were also identified in all samples. A very

---

**Fig. 2. Chemical composition and structure of the 2D-BNCO samples through XPS studies.** (A) Typical high-resolution O1s XPS spectrum. The oxygen atoms were mostly found to attach with N-, B-, and C-based moieties that could include B and N (see text). Direct bond formation with Cu (the growth substrate) was almost negligible in all samples. a.u., arbitrary unit. (B) Typical high-resolution C1s spectrum, which could be resolved into a number of peaks associated with known bonds –sp² (graphene-like) carbon, as well as bonds with B, N, and O entities. (C and D) Specific bonds whose relative occurrences were found to (C) grow or (D) decrease/remain negligible as the oxygen flow rate was increased during CVD growth of samples. Specifically, some of the flow rate dependences seen in (C) appear to have a reasonable similarity to the flow rate dependence of domain area coverage as shown in Fig. 1E, implying that these bonds were instrumental in the formation of these domains. Similarly, the bonds that decreased or remained negligibly low as seen in (D) could be less associated with the 2D-BNCO domains.
small contribution to the overall oxygen content comes from the Cu surface oxide (24), as indicated by the nearly negligible size of the O–Cu peak. The above observations imply that the O atoms are primarily attached to the B, N, and C atoms in the sample and not to the substrate. The C1s spectrum can be decomposed into several known peaks as seen in Fig. 2B. In addition to a peak due to the graphitic C–C bonds and a defect-induced peak (25–27), the C atoms were found to be attached to oxygen (11, 25), to nitrogen (28), and, in small parts, to boron (29). Together with the TEM structure analysis, the XPS results suggest that B, N, C, and O atoms are chemically bonded with each other in a honeycomb lattice with lattice spacing similar to graphene or h-BN. To obtain a better understanding of whether these bonds lie within the domain or matrix regions of our samples, the percentages of each bond type (for example, O–C, O–B, O–N, or O–Cu) for a given element (for example, O) were obtained as a function of O2 flow rate during synthesis. Figure 2C shows the variation of all bonds whose relative occurrence increased with increasing oxygen flow (implying their growing dominance in the domain regions), and Fig. 2D shows the relative concentrations of bonds whose occurrence decreased (implying their possible presence in the matrix region) or remained insignificantly low (implying insignificant presence in either domain or matrix) with the same. The most striking similarity was found between the manner in which (i) the percentage of total oxygen bonds attached to C atoms (O–C, obtained from the O1s spectrum), and (ii) the percentage of C bonds that were attached to O atoms (C–O, obtained from the C1s spectrum) varied with the increasing percentage coverage of the domain regions in the samples (Fig. 1E). Although less conspicuous, there is a corresponding correlation between the growth of bonds between nitrogen and carbon (that is, both N–C, obtained from the N1s spectrum as shown in the Supplementary Materials, and C–N, obtained from the C1s spectrum) as a function of domain size. Analysis of the N1s and O1s peaks show that the relative number of bonds that participated in the N–B (in h-BN form), N–O, and B–O bonds changed nonmonotonically as the oxygen content in the CVD chamber was increased. There was an overall increase in B–N bonds and decrease in N–O bonds, which implied that the presence of O in the chamber facilitated the relative growth of h-BN while sacrificing the less-preferred N–O bonds. Other N moieties such as amine groups decreased as a function of oxygen inclusion into the chamber, whereas there was a remarkable suppression of C–B bonds over the entire range of samples synthesized, indicating that C–B is not a preferred bonding configuration for this alloy system. As a result of the above analysis, we are able to conclude that as more oxygen was introduced into the CVD chamber, (i) the percentage coverage of the domains increased, (ii) the percentage of O atoms in the samples increased whereas the percentage of C atoms decreased, and (iii) the formation of domain regions is favored by the presence of O–C, N–C, and B–N bonds.

Having inspected the chemical bonding in the domains, we now investigate a few morphological characteristics of these 2D materials. Figure 3 (A and B) shows SEM and atomic force microscopy (AFM)
investigate three representative nano patch configurations of 2D-BNCO properties, we have used ab initio density functional theory (DFT) to patchwork of nanoscale domains of B, N, C, and O atoms bonded to form roughly at 1580 and 2700 cm\(^{-1}\), respectively, implying that both regions contained graphitic (\(\sim\)sp\(^2\) C=C) carbon. A detailed line shape analysis of the G' bands confirms that the thinner region is monolayer in nature (the G' band was fitted to a single Lorentzian), whereas the thicker layer is bilayer (the G' band was fitted to a sum of four Lorentzians) (30), which is consistent with both TEM and AFM measurements. Further information could be obtained by deconvolving the spectral shape between 1300 and 1400 cm\(^{-1}\) (Fig. 3D). A graphitic defect-induced D band occurs near 1350 cm\(^{-1}\) in the monolayer region, whereas contributions from the vibrational modes of B–C bonds (31) (relatively weaker) and h-BN (12, 15) are identified in the bilayer region. In general, it was found that the second layers were richer in h-BN content. To establish this, we obtained Raman spectral maps of a sample area that encompasses a two-layer region, as shown in the digital optical image in Fig. 3E, where a second layer is seen to have grown over the first (darker green). Figure 3F shows a map of the G band (1580 cm\(^{-1}\)) intensity, measured with a \(\approx\)350-nm spatial resolution, which illustrates the non-uniform distribution of graphitic carbon in the sample. Figure 3G shows a map of the h-BN (1367 cm\(^{-1}\)) intensity, which correlates strongly with the second layer. A second region of the sample, indicated by arrows, was also found to be h-BN rich (and less populated by graphitic carbon, as seen in Fig. 3F). Note that the contrast seen in the Raman spectral maps is not reproduced in the optical image of Fig. 3E. These investigations reveal that the various bonding configurations obtained via XPS measurements, some are arranged in graphene-like carbon bonds, a small quantity of B–C bonds, and h-BN bonds.

An interesting observation is the behavior of h-BN-rich regions as the oxygen content of the CVD chamber was increased. Figure 3H shows the fraction of the randomly selected regions that show h-BN peaks, as well as the fraction of regions that do not, as a function of increasing oxygen content in the system. An overall increase in the fractional occurrence of h-BN regions in the samples is seen as a function of increasing oxygen, which implies that the presence of oxygen promotes the formation of h-BN domains within 2D-BNCO layers, in agreement with our XPS analysis results.

The observations reported in this study suggest that the four constituent elements of 2D-BNCO are present in a number of different bonding configurations. At the macroscale, the samples can be viewed as a patchwork of nanoscale domains of B, N, C, and O atoms bonded together in a honeycomb lattice with energetically stable configurations. To gain further insight into their possible structural and electronic properties, we have used ab initio density functional theory (DFT) to investigate three representative nano patch configurations of 2D-BNCO with an increasing number of O atoms around an h-BN hexagon embedded in the graphene matrix, as shown in Fig. 4A (a to c). The technical details and the metastable structures found in the DFT calculations are discussed in the Supplementary Materials. The stability of these patches was verified in the DFT calculations by confirming the return of intentionally out-of-plane displaced atoms back into the plane. In particular, the atomic arrangements of Fig. 4A (c) have no B–C bonds, and hence, the rather low percentage of B–C bonds seen in our XPS measurements could imply that patches of samples such as the one seen in Fig. 4A (c) may be prevalent in the system. The remaining bonding configurations are consistent with all the experimental (TEM, XPS, and Raman) observations, implying that energetically stable in-plane oxygen inclusion into the BNCO system may be possible through B–O–C bonds at the periphery of h-BN domains.

The DFT calculations reveal extremely interesting local structural and magnetic properties of these patches. In agreement with our experimental finding, all three nano patches are planar in the sense that the hexagonal bonding is preserved. As shown in the side views in Fig. 4B, the pair of B atoms, closest to the O atoms, are slightly displaced out of plane (by 0.26 to 0.67 Å). This result highlights the fact that the O atoms can indeed be stably introduced into the plane of a graphene-like honeycomb lattice at the cost of a small out-of-plane distortion of the B–O bonds. Furthermore, spin-polarized DFT calculations reveal another rather surprising result: The differential spin density (\(\Delta \rho = \rho_{\uparrow} - \rho_{\downarrow}\)) is localized on the B atoms, which are bonded to the O atoms (and which exhibit the largest out-of-plane displacement), implying that these B atoms carry non-zero magnetic moments. The possible magnetization of a 2D system composed of nonmagnetic elements and without the addition of any defects is an extremely intriguing result. Here, the localized magnetic moments originate from the fact that the BO\(_2\) motif has an odd number of electrons. As seen from the spin-selective density of state (DOS) plots in Fig. 4C, all nano patches exhibit sizable band gaps exceeding 0.5 eV. The projected DOS (PDOS) analysis of all three structures shows that the states near the valence and conduction band edges are mainly composed of \(p_z\) orbitals, with B \(p_z\) orbitals dominating over \(p_x, p_y\) orbitals of C, N, and O. The DFT predictions for bond lengths, magnetic moments, and electronic band gaps are tabulated in Fig. 4D. The possible magnetic nature of these 2D sheets along with their semiconducting behavior (see the Supplementary Materials) gives rise to the intriguing possibility that controlled structures of 2D-BNCO sheets may be atomically thin diluted magnetic semiconductors, which are key spintronic materials (32). Furthermore, these DFT-predicted ground states are more stable than the possibly nonmagnetic metastable states (see the Supplementary Materials) by nearly 200 meV, implying that they may be magnetic even at room temperature (~25 meV).

In conclusion, we have synthesized and characterized atomically thin layers of 2D-BNCO, a quaternary system that allows for the incorporation of oxygen into a graphene-like honeycomb lattice. Under suitable conditions, isolated 2D-BNCO domains grow within a graphene-rich 2D-BNC matrix with well-defined shapes and sharp edges, which suggests that these domains grow hetero-epitaxially from the 1D edges of graphene-rich monolayer 2D-BNC in a manner similar to how 2D h-BN can grow from 1D etched edges of graphene (13). We believe that oxygen plays an important role in partially etching or limiting the monolayer graphene-rich 2D-BNC edge growth, providing active 1D edges where 2D-BNCO can continue to grow. It also appears that oxygen promotes the increased presence of h-BN rings in the 2D-BNCO crystal. Detailed investigation of synthesis as a function of growth durations,
preferably under in situ probes, could potentially provide a clear picture regarding the exact nature of 2D-BNCO domain growth. The possibility that oxygen, a group VI element, can be controllably introduced into an sp²-type hexagonal lattice with only small out-of-plane distortions is by itself a fundamentally exciting discovery. In addition, our DFT results predict that in their most stable configurations, the boron atoms closest to oxygen atoms have non-zero differential spin density, rendering 2D-BNCO nano patches with sizable magnetic moments. Magnetism in carbon-based materials (33, 34) is of great importance, because such materials are expected to provide lightweight and low-cost alternatives to conventional magnets. In this context, the possibility of magnetic 2D-BNCO sheets, which are also semiconducting with variable band gap values, could have exciting potential for fundamental investigations and applications in spin-based electronics. Furthermore, because oxygen is a critical ingredient in many important classes of materials such as superconductors, electroceramics, magneto-resistors, and solid-state catalysts, inclusion of oxygen into the 2D-BNC lattice could potentially lead to new classes of 2D materials. We believe that this is a big step toward designing next-generation atomically thin functional alloys that may find applications in a number of technologies.

**MATERIALS AND METHODS**

Conventional CVD chambers operating under low pressure always contain oxygen as an ambient element. Although this oxygen rarely enters the graphitic lattice during pure graphene synthesis, it has been suggested that the presence of nitrogen can promote oxygen inclusion in the graphene lattice. In our study, we utilized these conditions to introduce oxygen into the BNCO framework. The resulting 2D-BNCO nano patches exhibit unique electronic and magnetic properties, which we explore in detail below.
into the lattice (35). In our synthesis method, carbon was sourced from CH₄ boron, and nitrogen from NH₃BH₃ (2, 3), whereas oxygen was supplied from an Ar/O₂ mixture (0.1%). Large-area atomically thin BNCO sheets were grown directly on copper at temperatures of 1015 °C using a custom-built CVD setup (see the Supplementary Materials for an image of the growth setup). A set of eight samples with varying O₂ flow rates were grown for this study. Samples BNCO-0 to BNCO-14 correspond to oxygen flow rates of 0, 2, 4, to 14 sccm. All other growth parameters listed below were kept the same for all samples. Cleaned copper foils were placed in a quartz tube inside a furnace, which was subsequently pumped down to base pressures about 1 Pa (10 mtorr). Hydrogen (H₂) was introduced as carrying gas at a controlled flow rate of 4 sccm. Boron and nitrogen were introduced by placing 60 mg of ammonia borane (NH₃BH₃) in an alumina boat in the outside chamber (see fig. S1), and this chamber was not heated during the growth in contrast to other published reports where NH₃BH₃ was always heated (see fig. S1), and this chamber was not heated during the growth in low pressure conditions (lower than 650 mtorr). The source for carbon was methane (CH₄), with a controlled flow rate of 30 min growth time in low pressure conditions.

3. K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. K. Khotkevich, S. V. Morozov, A. K. Geim, Two-dimensional atomic crystals. Proc. Natl. Acad. Sci. U.S.A. 102, 10451–10453 (2005).

4. J. N. Coleman, M. Lotya, A.-O. Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Greiveson, K. Theuwissen, D. W. Mc Comb, P. D. Nellist, V. Nicolosi, Two-dimensional nanosheets produced by liquid exfoliation of layered materials. Science 331, 568–571 (2011).

5. B. Radišavliev, A. Radenovic, J. Brivio, V. Giacometti, A. Kisk, Single-layer MoS₂ transistors. Nat. Nano. 6, 147–150 (2011).

6. J. A. Schuller, S. Karavelli, T. Schiros, K. He, S. Yang, I. Kymissis, J. Shan, R. Zia, Orientation of luminescent excimers in layered nanomaterials. Nat. Nano. 8, 271–276 (2013).

7. C. Chiritescu, D. G. Cahill, N. Nguyen, D. Johnson, A. Bodapati, P. Keblishki, P. Zschack, Ultralow thermal conductivity in disordered, layered WSe₂ crystals. Science 315, 351–353 (2007).

8. D.-M. Tang, X. Wei, M.-S. Wang, N. Kawamoto, Y. Bando, C. Zhi, M. Mitome, A. Zak, R. Tenne, D. Golberg, Revealing the anomalous tensile properties of W₂Se₇ nanotubes by in situ transmission electron microscopy. Nano Lett. 13, 1034–1040 (2013).

9. H. Wang, Y. Liang, M. Gong, Y. Li, W. Chang, T. Mefford, J. Zhou, J. Wang, T. Regier, F. Wei, H. Dai, An ultrafast nickel–iron battery from strongly coupled inorganic nanoparticle/nanocarbon hybrid materials. Nat. Commun. 3, 917 (2012).

10. L. C Li, L. Song, C. J. J. Darijwala, D. Wu, Y. L. A. Sivivastava, Z. F. Wang, K. Storr, B. Salicic, F. Liu, P. M. Ajayan, Atomic layers of hybridized boron nitride and graphene domains. Nat. Mater. 9, 430–435 (2010).

11. T.-W. Lin, C.-Y. Su, X.-Q. Zhang, W. Zhang, Y.-H. Lee, C.-W. Chu, H-Y. Lin, M.-T. Chang, F.-R. Chen, L.-J. Li, Converting graphene oxide monolayers into boron carbide nanosheets by substitutional doping. Small. 8, 1384–1391 (2012).

12. Y. Gong, G. Shi, Z. Zhang, W. Zhou, J. Jung, W. Gao, L. Ma, Y. Yang, S. Yang, G. You, R. Vajtai, Q. Xu, A. H. MacDonald, B. I. Yakobson, J. Lou, Z. Liu, P. M. Ajayan, Direct chemical conversion of graphene to boron- and nitrogen-containing atomic layers. Nat. Commun. 5, 3193 (2014).

13. L. Liu, J. Park, D. A. Siegel, K. F. McCarty, K. W. Clark, W. Deng, L. Basile, J. C. Idrobo, A.-P. Li, G. Gu, Heteroepitaxial growth of two-dimensional hexagonal boron nitride templated by graphene edges. Science 343, 163–167 (2014).

14. H. Gao, L. Song, W. Guo, L. Huang, D. Yang, F. Wang, Y. Zuo, X. Fan, Z. Liu, W. Gao, R. Vajtai, K. Hackenberg, P. M. Ajayan, A simple method to synthesize continuous large area nitrogen-doped graphene. Carbon 50, 4476–4482 (2012).

15. Z. Liu, L. Ma, G. Shi, W. Zhou, Y. GONG, S. Lei, X. Yang, J. ZHU, Y. Ju, K. P. Hackenberg, A. Babakhani, J.-C. Idrobo, R. Vajtai, J. Lou, P.M. Ajayan, In-plane heterostructures of graphene and hexagonal boron nitride with controlled domain sizes. Nat. Nano. 8, 119–124 (2013).

16. B. Muchiarla, A. Pathak, Z. Liu, S. Song, T. Jayasekera, S. Kar, R. Vajtai, B. Salicic, P. M. Ajayan, S. Talapatra, N. Ali, Tunable electronics in large-area atomic layers of boron-nitrogen-carbon. Nano Lett. 13, 3476–3481 (2013).

17. W.-D. Dou, Q. Yang, C.-S. Lee, The effects of oxygen on controlling the number of carbon layers in the chemical vapor deposition of graphene on a nickel substrate. Nanotechnology 24, 185603–185611 (2013).

18. Y. Hao, M. S. Bharathi, L. Wang, Y. Liu, H. Chen, S. Nie, X. Wang, H. Chou, T. Ban, F. Fallahazar, H. Ramanarayan, C. W. Magnuson, E. Tutuc, B. I. Yakobson, K. F. McCarty, Y.-W. Zhang, P. Kim, J. Hone, L. Colombo, R. S. Ruoff, The role of surface oxygen in the growth of large single-crystal graphene on copper. Science 342, 6159 (2013).

19. E. Starodub, N. C. Bartlett, K. F. McCarty, Oxidation of graphene on metals. J. Phys. Chem. C 114, 5134–5140 (2010).

20. O. L. Krivanek, M. F. Chisholm, V. Nicolosi, J. T. Pennycook, G. J. Corbin, N. Delbey, M. F. Muffett, C. S. Own, Z. S. Szügyi, M. P. Oxley, S. T. Panteleides, S. J. Pennycook, Atom-by-atomic structural and chemical analysis by annular dark-field electron microscopy. Nature 464, 571–574 (2010).

21. G. Zhang, S. Sunb, D. Yanga, J.-P. Dodeletb, E. Sachera, The surface analytical characterization of carbon fibers functionalized by H₂SO₄/HNO₃ treatment. Carbon 44, 4482–4487 (2006).

22. J. Yang, X. Yan, J. Chen, H. Ma, D. Sun, Q. Xue, Comparison between metal ion and polyelectrolyte functionalization for electrophoretic deposition of graphene nanosheet films. RSC Adv. 2, 9665–9670 (2012).

23. B. Schmid, S. Uhlrich, J. Yeb, M. Stüber, XPS investigations of thick, oxygen-containing carbon boron nitride coatings. Solid State Sci. 12, 1903–1906 (2010).

24. J. A. Anderson, L. G. Fierro, Bulk and surface properties of copper-containing oxides of the general formula LaZr₁ₓCuₓO₃. J. Solid State Chem. 108, 305–313 (1992).

25. X. Feng, N. Dementiev, W. Feng, R. Vidica, E. Borquez, Detection of low concentration oxygen containing functional groups on activated carbon fiber surfaces through fluorescent labeling. Carbon 44, 1203–1209 (2006).

26. H. Estrade-Szwarckopf, XPS photoemission in carbaceous materials: A “defect” peak beside the graphitic asymmetric peak. Carbon 42, 1713–1721 (2004).

27. X. An, T. Simmons, R. Shah, C. Wolfe, K. M. Lewis, W. Nash, S. K. Nayak, S. Talapatra, S. Kar, Stable aqueous dispersions of noncovalently functionalized graphene from graphite and their multifunctional high-performance applications. Nano Lett. 10, 4295–4301 (2010).
28. Y. S. Gu, Y. P. Zhang, Z. J. Duan, X. R. Chang, Z. Z. Tian, D. X. Shi, L. P. Ma, X. F. Zhang, L. Yuan, Crystalline $\beta$-C$_3$N$_4$ films deposited on metallic substrates by microwave plasma chemical vapor deposition. Mater. Sci. Eng. A 271, 206–212 (1999).
29. M. O. Watanabe, S. Itoh, K. Mizushima, T. Sasaki, Bonding characterization of BC$_2$N thin films. Appl. Phys. Lett. 68, 2962–2964 (1996).
30. M. S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus, R. Saito, Perspectives on carbon nanotubes and graphene Raman spectroscopy. Nano Lett. 10, 751–758 (2010).
31. X.-F. Zhou, J. Sun, Q.-R. Qian, X. Guo, Z. Liu, Y. Tian, H.-T. Wang, A tetragonal phase of superhard BC$_2$N. J. Appl. Phys. 105, 093521–093524 (2009).
32. More than just room temperature. Editorial. Nat. Mater. 9, 951 (2010).
33. J. Červenka, M. I. Katsnelson, C. F. J. Flipse, Room-temperature ferromagnetism in graphite driven by two-dimensional networks of point defects. Nat. Phys. 5, 840–844 (2009).
34. Y. Zhang, S. Talapatra, S. Kar, R. Vajtai, S. K. Nayak, P. M. Ajayan, First principle studies of defect induced magnetism in carbon. Phys. Rev. Lett. 99, 107201 (2007).
35. Y. Wang, Y. Shao, D. W. Matson, J. Li, Y. Lin, Nitrogen-doped graphene and its application in electrochemical biosensing. ACS Nano 4, 1790–1798 (2010).
36. G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comp. Mat. Sci. 6, 15–50 (1996).
37. G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758–1775 (1999).
38. J. P. Perdew, K. Burke, M. Ernzerhof, generalized gradient approximation made simple. [Phys. Rev. Lett. 77, 3865 (1996)]. Phys. Rev. Lett. 78, 1396 (1997).

Funding: We acknowledge financial support from ARL/DARPA (U.S. Army Research Laboratory/Advanced Research Projects Agency) contract number ARMY/W911NF-11-2-0080 for the experimental aspects of this work. S.K. also acknowledges partial financial support from NSF-ECCS-1351424 (for. F.L.), NSF ECCS 1202376 (for M.F., J.L., and cost of publication), as well as U.S. Army Grant, W911NF-10-2-0098, sub-award 15-215456-03-00 (for A.V.). N.K., X.J., and S.K.N. would like to thank the Interconnect Focus Center (MARCO program), State of New York, the NSF Petascale Simulations and Analysis (PetaApps) program (grant no. 0749140), and an anonymous gift from Rensselaer for the support. Computing resources of the Computational Center for Nanotechnology Innovations at Rensselaer, partly funded by the State of New York, have been used for this work. This work is a partial contribution of the National Institute of Standards and Technology, an agency of the U.S. government. Hence, it is not subject to copyright in the United States. Author contributions: B.O. and S.K. designed the study, developed the methodology, performed the analysis, and wrote the manuscript. B.O., A.d.L.B., E.P., A.N.C., F.L., A.V., O.Y., M.A., M.J.F., J.L., Y.Z., and N.K. collected the data. X.J., N.K., and S.K.N. performed DFT calculations. N.K.D., M.D., S.S. and S.K. provided direction and guidance and participated in writing and reviewing the manuscript. Competing interests: The authors declare that they have no competing interests.

Submitted 24 January 2015
Accepted 14 May 2015
Published 31 July 2015
10.1126/sciadv.1500094

Citation: B. Ozturk, A. de-Luna-Bugallo, E. Panaitescu, A. N. Chiaramonti, F. Liu, A. Vargas, X. Jiang, N. Kharche, O. Yavuzcetin, M. Alnaji, M. J. Ford, J. Lok, Y. Zhao, N. King, N. K. Dhar, M. Dubey, S. K. Nayak, S. Sridhar, S. Kar, Atomically thin layers of B–N–C–O with tunable composition. Sci. Adv. 1, e1500094 (2015).