GDCh Highlights Angewandte International Edition Chemie

Boron Materials

International Edition: DOI: 10.1002/anie.201601463
German Edition: DOI: 10.1002/ange.201601463

Two-Dimensional, but not Flat: An All-Boron Graphene with a Corrugated Structure

Rian D. Dewhurst, Ralph Claessen, and Holger Braunschweig**

2D materials · elemental boron · graphene · materials science · scanning tunneling microscopy

The inability of boron to achieve a full octet of electrons through covalent bonding with its three electrons is at the heart of the element's fascinating chemistry and physics. Much has been written about the ability of boron to engage in molecular compounds with both classical and nonclassical bonding[1] by the formation of electron-precise (2c,2e) and/or multi-center (3c,2e) bonds. However, this phenomenon is also an issue in the solid-state science of boron, where its variable bonding abilities have led to confusion about its structure and phase diagram.[2] Unsurprisingly given boron's tendency towards multicenter bonding, all of these allotropes have three-dimensional structures, consisting of networks of fused icosahedra.

The incredible success of graphene in materials science (Figure 1 A)[3] has led to intense research efforts aimed at finding new 2D materials with unique properties.[4] Boron, having one electron fewer than carbon, was targeted early on in this process as a possible electron "hole" in a two-dimensional π-electron system,[5] for use in applications such as solar and fuel cells and as anode materials in lithium-ion batteries. This has led to numerous reports on the synthesis and study of boron-doped graphene and analogues (Figure 1 B)[6] as well as discrete, molecular models thereof (Figure 1 E).[7]

Taking this technique to its extreme—the complete replacement of carbon with boron—is expected to be an enormous practical challenge. Recent photoelectron spectroscopic investigations into the laser vaporization products of boron have led to a series of reports from the groups of Li, Wang, Li, Zhai, and Boldyrev.[8,9] This work described the generation of low-temperature-stable, planar boron networks of around 20–40 boron atoms,[8] as well as an all-boron fullerene.[9] These discoveries have shed light on the structural preferences of boron sheets, raising hopes for the synthesis of flat boron-only infinite networks able to rival graphene (Figure 1 A)[3] and other two-dimensional, one-atom-thick materials.[4]

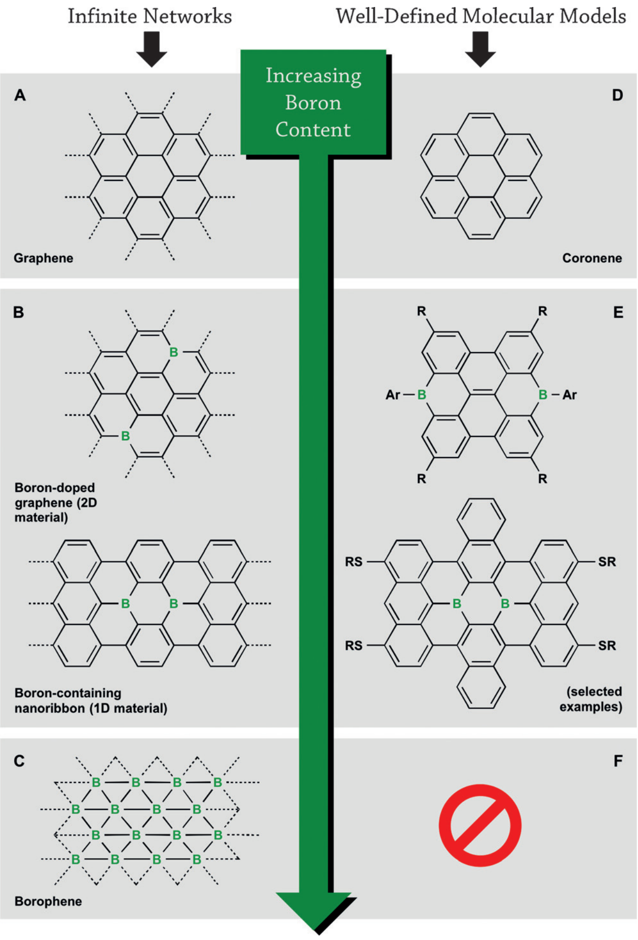

Figure 1. A–C) Selected 2D materials with increasing boron content and D, E) examples of their well-defined molecular counterparts.

In late 2015, the groups of Oganov, Hersam, and Guisinger reported the construction of a 2D, one-atom-thick sheet of boron atoms on a Ag(111) surface, a material they named "borophene" (Figures 1 C and 2).[10,11] In contrast to solid-state syntheses of other boron allotropes, the boron sheets were grown under ultrahigh vacuum conditions using

---

[*] Dr. R. D. Dewhurst, Prof. Dr. H. Braunschweig
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
E-mail: h.braunschweig@uni-wuerzburg.de
Homepage: http://www.braunschweiggroup.de/

Prof. Dr. R. Claessen
Physikalisches Institut and Röntgen Center for Complex Material Systems (RCCM), Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
E-mail: claessen@physik.uni-wuerzburg.de
Homepage: http://www.physik.uni-wuerzburg.de/EP4/team/claessen.php

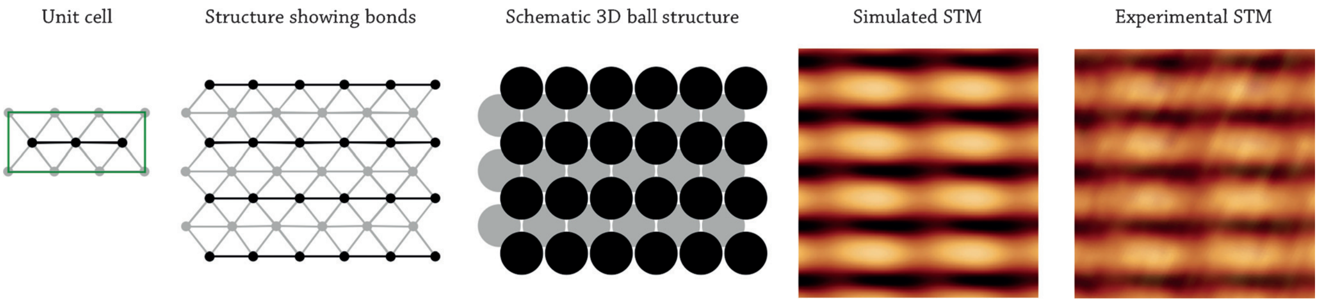

Figure 2. The ridged structure of the new borophene material on Ag(111), with simulated and experimental STM images of units of roughly the same size. Black: top-level boron atoms, gray: bottom-level boron atoms. Figures on the right reprinted with permission from Science Magazine/AAAS.

an electron beam evaporator, and characterized on the atomic scale by scanning tunneling microscopy (STM).

Considering the extensive theoretical predictions of the structures of 2D boron networks,[13] and the experimental evidence for planar molecular boron networks described above,[8] the structure of borophene on Ag(111) comes as something of a surprise. None of the previous work predicted the borophene structure that was found here, which consists of alternating ridges of boron atoms in a corrugated fashion parallel to the surface of the substrate (Figure 2). Each boron atom is bound to two other atoms along its ridge and four others on its two nearby ridges, leading to a rhombohedral repeating unit. This structure resulted in parallel lines in the experimental and simulated STM images (Figure 2) with repeating, aligned ovals of intensity, each corresponding to the six-boron-atom unit cell. It is important to note here that two subsequent Highlight articles[11] have described the structure as consisting of repeating B_6 hexagons capped by a single boron atom (i.e., poly(B_7)), in line with the prediction of Boustani.[12] In fact, the strong anisotropic corrugation as well as the oval-shaped STM structures, which are presumably due to substrate-induced B trimer formation, indicate a marked distortion of the B_7 structure owing to strong interactions with the underlying Ag surface.

Although the material clearly does not have a delocalized π-electron system like graphene, it is conductive in the direction of the ridges (but not across them), leading to its description as a highly anisotropic metal. This finding distinguishes borophene from the other known boron allotropes, which are in general semiconducting at ambient pressure and superconducting at high pressures.[14] It also singles borophene out from other 2D honeycomb metal networks, such as silicene, stannene, or bismuthene, which are insulating or even fall into the class of 2D topological insulators.[15] The mechanical properties of borophene are similarly anisotropic, with a Young's modulus of 398 GPa nm in the direction of the ridges and 170 GPa nm across the ridges. Notably, the former value rivals that of graphene itself.

Although the new borophene material has not yet been removed from its silver support or prepared on a larger scale, the initial report provides impetus for further work, both towards applications and a better understanding of its properties. It remains to be seen whether the ridged structure of borophene is an alternative to the previously observed planar structures,[8] or is merely a result of its attachment to the substrate. Whereas freestanding borophene may be difficult to realize, its growth on insulating substrates or even van der Waals type surfaces will assist the study of its conducting properties and potentially facilitate planar growth, respectively. Molecules with both planar[16] and butterfly-type[17] networks of boron atoms (the latter similar to that in borophene) are known in the literature; however, these consist of only a few boron atoms. The discovery of borophene may stimulate efforts into realizing larger 2D networks of boron atoms in discrete and stable molecular models, which are currently unknown and pose a formidable synthetic challenge (Figure 1F). Recent advances in the construction of boron–boron bonds may contribute to this goal.[18]

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 4866–4868
Angew. Chem. **2016**, *128*, 4948–4950

---

[1] a) R. B. King, *Chem. Rev.* **2001**, *101*, 1119–1152; b) V. I. Bregadze, *Chem. Rev.* **1992**, *92*, 209–223.
[2] T. Ogitsu, E. Schwegler, G. Galli, *Chem. Rev.* **2013**, *113*, 3425–3449.
[3] a) A. K. Geim, *Angew. Chem. Int. Ed.* **2011**, *50*, 6966–6985; *Angew. Chem.* **2011**, *123*, 7100–7122; b) K. S. Novoselov, *Angew. Chem. Int. Ed.* **2011**, *50*, 6986–7002; *Angew. Chem.* **2011**, *123*, 7123–7141.
[4] M. Xu, T. Liang, M. Shi, H. Chen, *Chem. Rev.* **2013**, *113*, 3766–3798.
[5] C. D. Entwistle, T. B. Marder, *Angew. Chem. Int. Ed.* **2002**, *41*, 2927–2931; *Angew. Chem.* **2002**, *114*, 3051–3056.
[6] See, for example: Z.-S. Wu, W. Ren, L. Xu, F. Li, H.-M. Cheng, *ACS Nano* **2011**, *5*, 5463–5471.
[7] See, for example: a) C. Dou, S. Saito, K. Matsuo, I. Hisaki, S. Yamaguchi, *Angew. Chem. Int. Ed.* **2012**, *51*, 12206–12210; *Angew. Chem.* **2012**, *124*, 12372–12376; b) V. M. Hertz, M. Bolte, H.-W. Lerner, M. Wagner, *Angew. Chem. Int. Ed.* **2015**, *54*, 8800–8804; *Angew. Chem.* **2015**, *127*, 8924–8928.
[8] A. P. Sergeeva, I. A. Popov, Z. A. Piazza, W.-L. Li, C. Romanescu, L.-S. Wang, A. I. Boldyrev, *Acc. Chem. Res.* **2014**, *47*, 1349, and references therein.
[9] H.-J. Zhai, Y.-F. Zhao, W.-L. Li, Q. Chen, H. Bai, H.-S. Hu, Z. A. Piazza, W.-J. Tian, H.-G. Lu, Y.-B. Wu, Y.-W. Mu, G.-F. Wei, Z.-P. Liu, J. Li, S.-D. Li, L.-S. Wang, *Nat. Chem.* **2014**, *6*, 727–731.
[10] A. J. Mannix, X.-F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, B. D. Myers, X. Liu, B. L. Fisher, U. Santiago, J. R. Guest, M. J. Yacaman, A. Ponce, A. R. Oganov, M. C. Hersam, N. P. Guisinger, *Science* **2015**, *350*, 1513–1516.

[11] a) H. Sachdev, *Science* **2015**, *350*, 1468 – 1469; b) M. Peplow, *Nature News*, DOI: 10.1038/nature.2015.19060.
[12] The confusion over the structure of borophene in the Highlight articles presumably stems from Figure 1 A in the original article, which depicts Boustani's proposed B_7 structural unit and not the observed structure.
[13] a) I. Boustani, *Phys. Rev. B* **1997**, *55*, 16426 – 16438; b) Y. Liu, E. S. Penev, B. I. Yakobson, *Angew. Chem. Int. Ed.* **2013**, *52*, 3156 – 3159; *Angew. Chem.* **2013**, *125*, 3238 – 3241; c) Z. Zhang, Y. Yang, G. Gao, B. I. Yakobson, *Angew. Chem. Int. Ed.* **2015**, *54*, 13022 – 13026; *Angew. Chem.* **2015**, *127*, 13214 – 13218; d) J. Yuan, L. W. Zhang, K. M. Liew, *RSC Adv.* **2015**, *5*, 74399 – 74407.
[14] M. I. Eremets, V. V. Struzhkin, H.-k. Mao, R. J. Hemley, *Science* **2001**, *293*, 272 – 274.
[15] a) P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet, G. Le Lay, *Phys. Rev. Lett.* **2012**, *108*, 155501; b) Y. Xu, B. Yan, H.-J. Zhang, J. Wang, G. Xu, P. Tang, W. Duan, S.-C. Zhang, *Phys. Rev. Lett.* **2013**, *111*, 136804; c) M. Wada, S. Murakami, F. Freimuth, G. Bihlmayer, *Phys. Rev. B* **2011**, *83*, 121310.
[16] S. Litters, E. Kaifer, M. Enders, J.-J. Himmel, *Nat. Chem.* **2013**, *5*, 1029 – 1034.
[17] J. A. J. Pardoe, N. C. Norman, P. L. Timms, S. Parsons, I. Mackie, C. R. Pulham, D. W. H. Rankin, *Angew. Chem. Int. Ed.* **2003**, *42*, 571 – 573; *Angew. Chem.* **2003**, *115*, 591 – 593.
[18] a) H. Braunschweig, R. D. Dewhurst, *Angew. Chem. Int. Ed.* **2013**, *52*, 3574 – 3583; *Angew. Chem.* **2013**, *125*, 3658 – 3667; b) H. Braunschweig, R. D. Dewhurst, S. Mozo, *ChemCatChem* **2015**, *7*, 1630 – 1638.

Received: February 10, 2016