Atomically controlled substitutional boron-doping of graphene nanoribbons

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Boron is a unique element in terms of electron deficiency and Lewis acidity. Incorporation of boron atoms into an aromatic carbon framework offers a wide variety of functionality. However, the intrinsic instability of organoboron compounds against moisture and oxygen has delayed the development. Here, we present boron-doped graphene nanoribbons (B-GNRs) of widths of \( N = 7, 14 \) and \( 21 \) by on-surface chemical reactions with an employed organoboron precursor. The location of the boron dopant is well defined in the centre of the B-GNR, corresponding to 4.8 atom\%, as programmed. The chemical reactivity of B-GNRs is probed by the adsorption of nitric oxide (NO), which is most effectively trapped by the boron sites, demonstrating the Lewis acid character. Structural properties and the chemical nature of the NO-reacted B-GNR are determined by a combination of scanning tunnelling microscopy, high-resolution atomic force microscopy with a CO tip, and density functional and classical computations.

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Boron is a unique element in terms of electron deficiency and Lewis acidity, yet it has a comparable size to carbon. Incorporation of boron atoms into an aromatic carbon framework like carbon nanotubes\(^1\) and graphene\(^2\) offers a wide variety of functionality in, for example, chemical sensing\(^3,4\), nanoelectronics\(^5,6\), photocatalysis\(^7\) and battery electrodes\(^8\). So far, the syntheses have been demonstrated by both the chemical vapour deposition method with co- or mono-depositing of small molecules, like \(\text{B}_2\text{H}_6\), \(\text{BCl}_3\), and \(\text{PhB(OH)}_2\) (refs 7–11), and by the reactive microwave plasma method with \(\text{B(CH}_3)_3\) (ref. 12). However, besides the formation of Stone–Wales defects\(^10\), the coordination environment of the boron sites in the graphiteh carbons, namely the doping site and density of boron, cannot be precisely controlled in these methods. This limitation can be overcome by a recently developed on-surface chemical reaction\(^13,14\). In fact, nitrogen atoms have been doped into the edges of graphene nanoribbons (GNRs) by employing nitrogen-doped precursor molecules\(^15,16\). In contrast, the intrinsic instability of organoboron compounds against moisture and oxygen has delayed the development of boron-doped nanocarbon chemistry\(^17,18\) and has led to the unavailability of boron-doped precursor molecules. However, our recent chemical synthesis of polycyclic aromatic hydrocarbons with boron atoms proved the stability of this materials class\(^19\). The use of such an organoboron precursor can pave the way for boron doping into GNRs. We now present a well-structured boron-doped-GNR (B-GNR) in terms of valency, position and doping ratio and study its chemical structure and property by high-resolution atomic force microscopy (AFM) and scanning tunneling microscopy (STM).

**Results**

**Synthesis of boron-doped graphene nanoribbons.** Figure 1a shows the chemical structure of the precursor molecule, in which two pristine anthracene units and one 9,10-dibora-9,10-dihydroanthracene moiety are covalently bonded while two bromine atoms are located at both termini. By annealing the molecules on a Au surface at 180 °C, the bromine atoms are removed by surface catalytic dehalogenation. Consequently, the precursor molecules are linearly polymerized. At an elevated temperature of up to 400 °C, the surface-assisted cyclodehydrogenation results in the formation of an aromatic graphene nanoribbon\(^20\). Employing this reaction, boron atoms can be doped as \(\text{BC}_3\) Lewis acidic sites at the centre row in the armchair-edge GNR (B-GNR) with a width of seven carbon atoms (\(N = 7\)). The interval between the boron sites is fixed with a doping density of 4.8 atom%.

In experiments, the precursor molecules were deposited on a clean Au(111) surface in ultra-high vacuum and were subsequently annealed at 180 °C (Fig. 1b). At 4.8 K the molecules mainly stay along the valley of the herringbone structure on Au(111). We performed tip-induced lateral manipulation to check the presence of the polymer chain. After scanning the tip at a constant height along the line indicated with an arrow in Fig. 1b, several molecular units moved together, indicating successful polymerization (Fig. 1c). The successive anthracene units have opposite tilts to the Au substrate owing to the repulsion between hydrogen atoms in the adjacent anthracene moieties. After annealing at 400 °C, such corrugated structures disappeared. Instead, stripe-shaped flat nanoribbons appeared (Fig. 1d).

The observed STM contrast is inverted by the polarity of the applied tip bias voltage (-3 and 3 V), indicating the perturbation of the electronic structure by the doped boron atoms as an electron-accepting unit (Fig. 1c,e, Supplementary Fig. 1). Pink crosses indicate the same atomic site in B-GNR. By setting close to zero bias voltage (-2 mV), the electronic states near the Fermi level of B-GNR are resolved (Fig. 1g). We also observed two different contrasts at the armchair type edge, where the ratio of...
one dark- and two bright-contrasts suggests that the dark-contrast edge relates to the boron-doped anthracene. The hydrogen atoms at the armchair edge can be desorbed by the tunnelling current at a large negative tip bias (\(-3.5\) V and 100 pA, Supplementary Fig. 2) as indicated with an arrow. The simulated STM topographies (right panel in Fig. 1e–g) are in good agreement with the experimental results (left panel), so that the chemical structure can be unambiguously assigned as shown in Fig. 1h.

Electronic structure of boron-doped graphene nanoribbons. To measure the electronic structure of B-GNR, \(dI/dV\) spectra were taken with a clean Au tip above four different sites of B-GNR and, for reference, above one Au(111) site (Fig. 2a). The conductance is related to the local density of states at the tip position. At the Au(111) site, the effect of Shockley surface states locates around \(-0.5\) eV below the Fermi energy. The contribution, originating from the surface state, is even visible on B-GNR as modulations of the \(dI/dV\) spectrum down to \(-1.0\) eV, and rather stronger than on the non-doped GNR\(^{21–23}\). This may relate to the stronger coupling to the substrate due to the presence of boron atoms. More interestingly, in contrast to the pristine GNR\(^{22}\), the presence of these boron atoms downshifts the interface state. Nevertheless, the valence band edge locates around \(-0.8\) eV below the Fermi energy, with clear peaks at \(1.6\) eV corresponding to the conduction band edge. Consequently, the band gap of the B-GNR is \(2.4\) eV, which is comparable to the non-doped GNR on Au(111) (ref. 22). Previous theoretical studies indicate that the position of doped boron strongly affects the modulation of the electronic structure and so that the minimum (maximum) effect is expected with a doping at the centre (edge)\(^7\). In this system, boron atoms locate exactly at the centre of \(N=7\) B-GNR and, thus, no significant electron–hole asymmetry is present (full suppression of backscattering), leaving intact the overall electronic structure (this is seen also in our calculated electronic structure, Supplementary Fig. 3). Yet, in a detailed inspection, the presence of boron atom in the GNR can be observed. The inversions of the conductance between the doping and non-doping sites occur twice between 1.4 and \(2.0\) eV and between \(-1.0\) and \(-0.4\) eV both at the edge and centre. This is consistent with the scanning tunnelling spectroscopy (STS) images taken within the energy levels at constant heights (Fig. 2b), and also the location of the boron features in the calculated projected density of states.

**Figure 2 | \(dI/dV\) curve on B-GNR.** (a) Differential conductance (\(dI/dV\)) spectra taken at four different sites of \(N=7\) B-GNR and one Au(111) site with a clean Au tip. The spectra were numerically calculated from the measured bias dependent curves of the tunnelling current. The bias voltage is only here redefined with respect to the tip grounding instead of the sample grounding. (b) Constant height \(dI/dV\) maps measured with a lock-in amplifier (root mean square amplitude = 14 mV and frequency = 521 Hz) at the different bias voltages. Pink crosses indicate at the centre of the same \(C_4B_2\) site.

**Figure 3 | Fused B-GNR.** (a) STM overview of fused B-GNR. Scale bar, 10 nm. (b) Frequency shift \(\Delta f\) map of \(N = 7\) B-GNR and (c) the corresponding Laplace filtered image for a better view of bonds. (d) and the simulated AFM image. (e,f) \(\Delta f\) maps of fused \(N = 14\) B-GNR with different structures. (g) \(\Delta f\) map of fused \(N = 21\) B-GNR. Measurement parameters: \(A = 38\) pm and \(V = 0\) V.
periodic aromatic carbons are clearly revealed, in which every three anthracene units have a defect-like feature, with darker contrast (more negative frequency shift). To enhance the observed bond visually, a Laplace filter27 was applied in the contrast (more negative frequency shift) observed and predicted in simulations (see also calculated the AFM image in Fig. 3d and Supplementary Fig. 5). In the absence of this topographic distortion, the difference in local charge density and resulting electrostatic interactions is not enough to produce a clear contrast change. The B–C bond (longer than the C–C bond) also deforms the honeycomb structure19, while the distortion of the carbon ring in the AFM image relates to the effect of tilting CO tip27.

On the basis of these observations, we state that the on-surface chemical reaction was accomplished as demonstrated in Fig. 1a. Some defects, presumably relating to the on-surface dissociation of B–C bonds in the first annealing process, are also observed (Supplementary Figs 6 and 7). We further analysed B-GNRs with wider widths (Supplementary Fig. 8). For N=14 B-GNRs, two different fused configurations with the out-of-phase (Fig. 3e) and the shifted phase (Fig. 3f) were observed. Since the configuration is determined by the relative position in the fusing process, the shifted phase N=14 B-GNR has a mirror configuration, thus, in total three configurations. In such a process, the C–C link seems to be caused by a zipping up process of the C–C bond, thus, in total three configurations. In such a process, the C–C link seems to be caused by a zipping up process of the C–C bond, thus, in total three configurations.
only static control. The tunable response presented here offers great potential in many technologies, particularly where dynamic control would be a disruptive development. Besides this application, the fabrication of boron-doped nanoribbons could allow for the design of mobility gaps and novel types of graphene transistors.\(^2\)\(^3\)\(^4\)\(^5\). In the \(N = 7\) B-GNR, the boron locates exactly at the centre of the ribbon, so that the backscattering is fully suppressed. Yet, in the fused B-GNRs, the symmetry can vary. Further, the asymmetry can be increased by co-depositing boron-doped and non-doped precursor molecules. To fabricate such devices, transferring on-surface synthesized B-GNRs is a critical issue, yet we believe that the recently developed thin film etching technique can solve this.\(^6\)\(^7\)\(^8\).

Methods

Experimental measurement. All experiments were performed with an Omicron STM/AFM with a qPlus configuration, operating at 4.8 K in ultrahigh vacuum. A clean Au(111) surface was in situ prepared by repeated cycles of standard sputtering and annealing. The tungsten tip of a tuning fork sensor constructed by contacting to the sample surface. The resonance frequency of the tungsten tip was sharpened by a focused ion beam milling technique and was then in situ coated with Au atoms by contacting to the sample surface. The resonance frequency of the sensor was measured at 123 K with a Rigaku X-ray diffractometer with Au atoms by contacting to the sample surface. The resonance frequency of the sensor was measured at 123 K with a Rigaku X-ray diffractometer. The intensity data were collected at 123 K with a Rigaku X-ray diffractometer. The intensity data was collected at 123 K with a Rigaku X-ray diffractometer. The intensity data was collected at 123 K with a Rigaku X-ray diffractometer. The intensity data was collected at 123 K with a Rigaku X-ray diffractometer.

Synthesis of precursor molecule. The precursor \(1, 9,10\)-bis(10-bromanthracen-9-yl)-9,10-dihydro-9,10-diboraanthracene, was obtained from compounds \(2\) and \(3\) through the synthetic route shown in Supplementary Fig. 11a. Although some derivatives of the precursor \(1\) with extra bulky substituents have been reported,\(^9\) the precursor \(1\) has not been characterized because of its low solubility in common organic solvents. We successfully characterized the isolated precursor \(1\) by the NMR analyses in tetrachloroethane at 100 °C and by X-ray crystal structure analysis using chlorobenzene as solvent. The crystalline sample of the precursor \(1\) can be stored at ambient conditions as a result of the steric protection of the boron atoms by the anthracene groups. Compounds \(2\) and \(3\) were prepared according to literature procedures. The compound \(2\) is a NO molecule, were carefully checked within this methodology, and excellent agreement was achieved with experiments. Systematic k-point convergence was checked for all systems and a \(5 \times 1 \times 1\) mesh was found to be sufficient for the large GNR-Au systems. All reference calculations for adsorption energies, charge densities and projected density of states were performed with 4-anthracene GNR on gold, which had a lattice mismatch of only 1.4% (accommodated in the ribbon). When adding boron (B-GNR), this mismatch reduced to 0.3% as the ribbon expanded slightly (Supplementary Fig. 4). To have a comparable absorption of B–B sites as in experiments, particularly for the STM simulations, we also performed calculations on isolated 3-anthracene GNRs (for this size the mismatch with the Au surface would be over 10% unless an unfeasibly large unit cell is used). The simulated STM images were very similar, and hence were used for the image comparison in Fig. 1 for simplicity.

Calculated AFM image. Recently, several mechanical AFM models have been proposed,\(^6\)\(^7\)\(^8\)\(^9\), where the approach of a CO-functionalized AFM tip over a substrate can be simulated. To obtain an accurate 3D force map, the key idea is that during approach they allow the CO molecule to tilt under influence of the forces it experiences. This tilting proved to be key to understand the sharp contrast observed in atomic bonds. Here we used the model developed by Hapala et al.\(^6\) and extended it by adding electrostatic interactions on top of the van der Waals interactions. The B-GNR structure was taken from the DFT simulations of B-GNR on Au and the charges were extracted from the DFT calculations via Bader analysis.\(^6\). The mechanical AFM model relies on empirical Lennard–Jones parameters, which were taken from the Chemistry at HARvard Molecular Mechanics (CHARMM) force field\(^6\)\(^7\)\(^8\)\(^9\), with additional boron parameters.\(^6\)\(^7\)\(^8\)\(^9\). All other parameters are the same as mentioned by Hapala et al. and the simulated AFM scan is performed at a resolution of 0.025 Å (in all directions), with a force tolerance criterion of \(4 \times 10^{-6}\) eV Å\(^{-1}\). The 3D force field is subsequently converted into a frequency shift image,\(^6\)\(^7\)\(^8\)\(^9\), using the experimental parameters (\(f = 24.76\) kHz, \(A = 53\) pm and \(k = 1.800\) N m\(^{-1}\)). In Fig. 3d the simulated AFM image for the approximate same height as in the experiments is shown (the height in the bottom left corner of the figure denotes the distance of the carbon of the CO-molecule to the plane going through the carbons of the B-GNR).

References

1. Iijima, S. Helical microtubules of graphitic carbon. Nature 354, 56–58 (1991).
2. Novoselov, K. S. et al. Electric field effect in atomically thin carbon films. Science 306, 666–669 (2004).
3. Zhang, Y., Zhang, D. & Liu, C. Novel chemical sensor for cyanides: boron-doped carbon nanotubes. J. Phys. Chem. B 110, 4671–4674 (2006).
4. Yuan, J. & Giannaris, J. Gas adsorption on graphene doped with B, N, Al, and S: a theoretical study. Appl. Phys. Lett. 95, 232105 (2009).
5. Bieß, B., Blase, X., Triozon, F. & Roche, S. Anomalous doping effects on charge transport in graphene nanoribbons. Phys. Rev. Lett. 102, 096803 (2009).
6. Terrones, H., Lv, R., Terrones, M. & Dresselhaus, M. S. The role of defects and doping in 2D graphene sheets and 1D nanoribbons. Rep. Prog. Phys. 75, 062501 (2012).
7. Xing, M., Fang, W., Yang, X., Tian, B. & Zhang, J. Highly-dispersed boron-doped graphene nanoribbons with enhanced conductivity and photocatalysis. Chem. Commun. 50, 6637–6640 (2014).
8. Wu, Z.-S., Ren, W., Xu, L. & Cheng, H.-M. Doped graphene sheets as anode materials with superhigh rate and large capacity for lithium ion batteries. ACS Nano 5, 5463–5471 (2011).
9. Panchakarla, L. S. et al. Synthesis, structure, and properties of boron- and nitrogen-doped graphene. Adv. Mater. 21, 4726–7430 (2009).
10. Zhao, L. et al. Local atomic and electronic structure of boron chemical doping in monolayer graphene. Nano Lett. 13, 4659–4665 (2013).
11. Wang, H. et al. Synthesis of boron-doped graphene monolayers using the sole solid feedstock by chemical vapor deposition. Small 9, 1316–1320 (2013).
12. Tang, Y.-B. et al. Tunable band gaps and p-type transport properties of boron-doped graphenes by controllable ion doping using reactive microwave plasma. ACS Nano 6, 1970–1978 (2012).
13. Ruffieux, P. et al. Nano-architectures by covalent assembly of molecular building blocks. Nat. Nanotechnol. 2, 687–691 (2007).
14. Cai, J. et al. Atomically precise bottom-up fabrication of graphene nanoribbons. Nature 466, 470–473 (2010).
15. Brodmer, C. et al. Aligning the band gap of graphene nanoribbons by monomer doping. Angew. Chem. Int. Ed. 52, 4422–4425 (2013).
16. Cai, J. et al. Graphene nanoribbon heterojunctions. Nat. Nanotechnol. 9, 896–900 (2014).
17. Jakle, F. Advances in the synthesis of organoboron polymers for optical, electronic, and sensory applications. Chem. Rev. 110, 3985–4022 (2010).
18. Aranea, J. F., Neue, B. & Pierr, W. E. Enforced planarity: a strategy for stable boron-containing π-conjugated materials. Angew. Chem. Int. Ed. 51, 9977–9979 (2012).
19. Dou, C., Saito, S., Matsuo, K., Hisaki, I. & Yamaguchi, S. A boron-containing PAH as a substructure of boron-doped graphene. Angew. Chem. Int. Ed. 51, 12206–12210 (2012).
20. Treier, M. et al. Surface-assisted cyclodehydrogenation provides a synthetic route towards easily processable and chemically tailored nanographenes. Nat. Chem. 3, 61–67 (2011).