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ARTICLE

Chemical Nature of Boron and Nitrogen Dopant Atoms in Graphene Strongly Influences its Electronic Properties

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Boron and nitrogen doped graphenes are highly promising materials for electrochemical applications, such as energy storage, generation and sensing. The doped graphenes can be prepared by a broad variety of chemical approaches. The substitution of a carbon atom should induce n-type in the case of nitrogen and p-type in the case of boron behavior in doped graphene, however, the real situation is more complex. Electrochemical experiments show that boron-doped graphene prepared by hydroboration reaction exhibits similar properties as the nitrogen doped graphene; according theory, the electrochemical behavior of B and N doped graphenes should be opposite. Here we analyze the electronic structure of N/B-doped graphene (at ~5% coverage) by theoretical calculations. We consider graphene doped by both substitution and addition reactions. Density of states (DOS) plots show that graphene doped by substitution of the carbon atom by N/B behaves as expected, i.e., n/p-doped material. N-doped graphene has also lower value of the workfunction (3.10 eV) with respect to that of the pristine graphene (4.31 eV), whereas the workfunction of B-doped graphene is increased to the value of 5.57 eV. On the other hand, the workfunctions of graphene doped by addition of $-NH_2$ (4.77 eV) and $-BH_2$ (4.54 eV) groups are both slightly increased and therefore the chemical nature of dopant is less distinguishable. This shows that n- and p- type doping depends significantly on the synthesis method used, as it leads to different types of doping, and, in turn, different electronic and electrochemical properties of doped graphene, as observed in electrocatalytic experiments. This study has tremendous impact on the design of doped graphene systems from synthetic chemistry point of view.

Introduction

Doping of graphene with boron and nitrogen atoms is technologically important due to tailoring the band-gap of the resulting materials, which broadens practical applications of graphene-based materials in electronic and electrochemical devices.[1-7] Compared to a carbon atom, nitrogen has one additional electron and thus can be expected to act as n-type of dopant when substituted into graphene lattice. Boron, which has one electron less than carbon, would analogically behave as p-type dopant. Therefore, one could expect contrasting electronic and electrochemical properties of the B- and N-doped graphenes, if the doping is carried out by substitution of carbon atom in graphene. Indeed, there are many theoretical studies showing that this should be the case.[8-10] However, from experimentalist point of view, the situation is more complex. The substitution of carbon atom with boron is challenging procedure for the chemical synthesis.[11] When employing wet chemistry, addition reactions - such as hydroboration - are used for doping the graphene with boron (Scheme 1). If hydroboration reaction is used, the end product contains solely $-BH_2$ groups added to the graphene sheets.[12] Similarly, N

doping may be carried out at different conditions, causing N to be included in the aromatic system,[13] added as non-lattice ("external") nitrogen,[14] or added as $-NH_2$ group (hydroamination reaction).[5] Based on abovementioned arguments, one would expect that N-doping of graphene should inject an electron to its structure, and, thus, lead in cathodic electrocatalysis of doped graphene, whereas B-doping should lead into the electrocatalysis in anodic region. However, it was experimentally found that graphenes doped with boron using hydroboration reaction show similar properties as nitrogen doped graphenes.[15, 16] Notice that previous theoretical studies focused only on graphene with substituted carbon atoms and do not provide explanation of the experimental observations.[15, 16] Here we provide theoretical base and explanation for such behavior. Using theoretical density functional theory (DFT) calculations we compare electronic properties of graphene doped with $-BH_2$ as well as $-NH_2$ groups, and we further compare them to the electronic properties of graphene doped by boron and nitrogen substitutionally (Scheme 2). We show that the effect of doping on the electronic structure depends on the character of doping (substitution or addition) so much as on the chemical nature of doping element.

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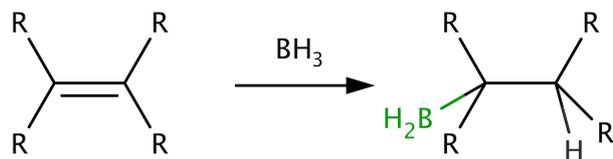
Scheme 1. Hydroboration reaction on C=C bond is an addition of –BH$_2$ group and hydrogen. In similar manner, hydroamination reaction can be carried out (with NH$_3$ giving –NH$_2$ group addition).
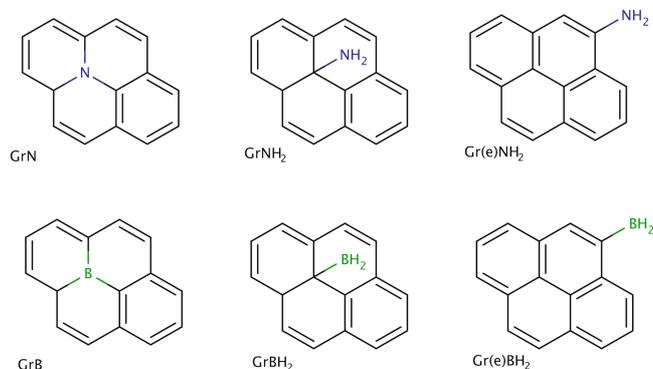
Scheme 2. Models of graphene doped by nitrogen and boron by substitution of C atom in the graphene lattice (left panel) and by addition of amine and boron groups on surface (middle panel) and edge (right panel) by hydroboration and hydroamination reactions.

Results and discussion

We first inspected thermodynamic stabilities of inspected dopants in order to assess, which doping mode is thermodynamically preferred. Assuming that the initial reactants are pristine graphene and ammonia NH$_3$ or diborane B$_2$H$_6$, the energy differences with respect to the corresponding reference states are in all cases positive (Table 1), which indicates that the doping process is endothermic. Similar behavior was also observed for Diels-Alder reactions on graphene.[17]

It is worth noting that the substitutional doping is preferred over the additive mode of doping for both boron and nitrogen from thermodynamic point of view. The reason for preferred substitutional doping of graphene lies in the high value of "deformation energy" associated with the transition of sp^2 in plane carbon to sp^3 out of plane carbon, which is also accompanied by partial loss of aromaticity. NH$_2$ pulls neighboring carbon atom by 0.45 Å above the graphene sheet (Figure 1). Resulting length of the N-C bond is 1.52 Å. This geometry of adsorbed NH$_2$ is in agreement with the result given by Junkermeier et al.[18] The BH$_2$ adsorbs on the bridge position above the bond connecting two neighboring carbon atoms; the length of the B-C bond 1.73 Å (Figure 1). These two carbon atoms are pushed 0.25 Å above the graphene plane. It should be noted that textbook schemes of hydroboration (Scheme 1) show BH$_2$ bonded directly to the carbon atom. Our calculations reveal that the adsorption at the position on top of the carbon atom is strongly disfavored in the case of graphene, as the respective adsorption energy is by 63.1 kcal/mol higher that the adsorption energy in the bridge position.

The substitutional doping, on the other hand, retains the local coordination of graphene. The substitutional doping is

energetically preferred, however, the energy differences between both modes of doping are rather small (11 and 15 kcal/mol for N and B, respectively). In turn, the particular synthetic method of preparation of doped graphene and used synthetic method mechanism together with a presence of other defects and impurities shall be a decisive factor controlling the preferred mode of graphene functionalization.
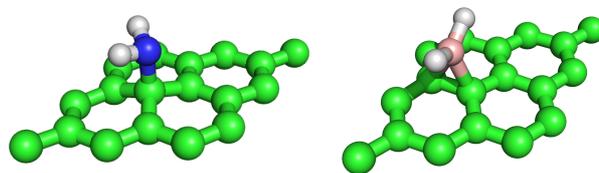
Figure 1. Left panel shows the geometry of NH$_2$ adsorbed on graphene (GrNH$_2$) and the right panel BH$_2$ adsorbed onto the bridge site (in the middle of a bond connecting two neighboring carbon atoms) of graphene (GrBH$_2$).

For the sake of completeness, we calculated also the adsorption energies on the zigzag edge of graphene. The steps and edges in particular on multi-layer graphene create high-energy sites, in which the adsorption is preferred.[19] The adsorption energies on the edge are −129.6, and −128.2 kcal/mol for NH$_2$ and BH$_2$, respectively. These values greatly surpass the values of adsorption energies of NH$_2$ and BH$_2$ on the graphene surface (−1.1 and −26.7 kcal/mol, respectively) and indicate that these species can create strong covalent bonds with edge or defect sites on graphene. Thus, the number of other defects in graphene such as vacancies and the quality of graphene samples in general can be important factors as well, in particular in the cases when the concentration of dopants is low and high-energy sites are filled dominantly. Concerning the low adsorption of NH$_2$ group, it should be noted that the interaction energy of NH$_2$ to graphene is comparable to the interaction energy of BH$_2$, however, NH$_2$ induces larger deformation of graphene and the associated deformation energy (27.9 kcal/mol) counterbalances the favorable interaction energy. In turn, the adsorption energy of NH$_2$ is considerably lower than the adsorption energy of BH$_2$.

Table 1. The total energies (in kcal/mol) of considered doped graphenes calculated by PBE functional. Graphene and NH$_3$ molecule, or graphene and half of B$_2$H$_6$ molecule are considered as the reference.

Compound	E (kcal/mol)
GrN + C + 3/2 H$_2$	47.7
GrB + C + 3/2 H$_2$	37.8
GrNH$_2$ + ½ H$_2$	58.8
GrBH$_2$ + ½ H$_2$	52.7

We further investigated the electronic properties of the studied materials. Workfunction (W$_f$) is a material property, which corresponds to the energy required to remove an electron from the material. The calculated W$_f$ of graphene by both GGA (PBE) and hybrid (PBE0) functionals (Table 2) fit into an interval of graphene W$_f$ (4.2-4.5 eV) calculated by various theoretical methods.[20, 21] The workfunction calculated by the hybrid PBE0 functional is closer to the experimental values of the graphene W$_f$ ranging from 4.57 to 5.16 eV.[22, 23]

Table 2. Workfunctions (W_f in eV) of graphene with various dopants (see Scheme 2 for labelling) calculated by PBE and PBE0 functionals.

Compound	PBE	PBE0
graphene	4.20	4.31
GrN	3.24	3.10
GrB	5.25	5.57
GrNH$_2$	4.24	4.77
GrBH$_2$	4.17	4.54

W_f of N-doped graphene, which contains the N atoms substituting the C atoms with a ratio C17:N1, is by 1.21 eV lower than W_f of graphene. It indicates that N-doped graphene (GrN) can release electrons easier than graphene. This agrees with the idea that N atoms work as n-type (electron-donating) dopants by increasing the number of electrons in a system.[5] Naturally, the B-doped graphene (GrB, with stoichiometry C17:B1) displays the opposite behavior, i.e. higher W_f with respect to graphene by 1.26 eV. In turn, the B-atoms serve as p-type (electron-accepting) dopants.[11] It should be noted that both functionals show the same trends, however, the differences are more pronounced when the hybrid PBE0 functional is used.

These findings are also in line with the observed shifts in the density of states (DOS) of the respective materials (Figure 2 and S1). The Dirac point of graphene is downshifted in N-doped graphene (GrN) and upshifted in B-doped (GrB) graphene with respect of the Fermi level. The hybrid PBE0 functional retains the significant features of the DOS of substitutionally doped graphene, but increases the magnitude of shifts of the Dirac point. For the additive doping, the defect peaks appear close to the Fermi level, disrupting characteristic band-structure of graphene. Interestingly, the gap opens at the Fermi level upon adsorption of NH$_2$ molecule (GrNH$_2$). The opening of the gap corroborates the experimental results showing that it is possible to open the gap in bilayer graphene with NH$_2$-functionalized self-assembled monolayers.[24] In this case, the effect of the hybrid functional is even more pronounced, because the PBE yields the size of this gap of 0.18 eV, whereas the PBE0 functional gives significant gap of 1.27 eV. It is well known that local functionals (LDA and GGA) underestimate the gaps for small gap systems, or strongly correlated insulators.[25] In this context, it is worth mentioning also controversial prediction of half-metallic behavior of graphene nanoribbons upon the application of the electric field, which may be caused by underestimated HOMO-LUMO gap of the nanoribbon in calculations using the local functional.[26, 27] The deficiencies of local functionals are well recognized in structures involving atoms with localized d-states, strong correlations, or non-local dispersive bonding, but these results show that they influence the results also in seemingly simple graphene-based systems.

The work functions of graphene doped by addition of NH$_2$ (GrNH$_2$) and BH$_2$ (GrBH$_2$) groups differ from the properties of B/N-doped graphenes. The attachment of NH$_2$ and BH$_2$ groups to the graphene surface leads (in our case represented by 18 C atoms in the unit cell) to smaller changes in W_f of the respective materials, which also display opposite behavior with respect of the substitutional doping. The attachment of NH2 group enhances W_f by 0.46 eV while the BH$_2$ group decreases W_f by 0.23 eV (Table 2). The densities of states (Figure 3 and S2) indicate that addition of NH$_2$ and BH$_2$ groups decomposes

characteristic band structure of graphene around the Fermi level. This effect can be attributed to the breaking of the symmetry, because dopants pull neighboring carbon atoms out of the graphene sheet (Figure 1).
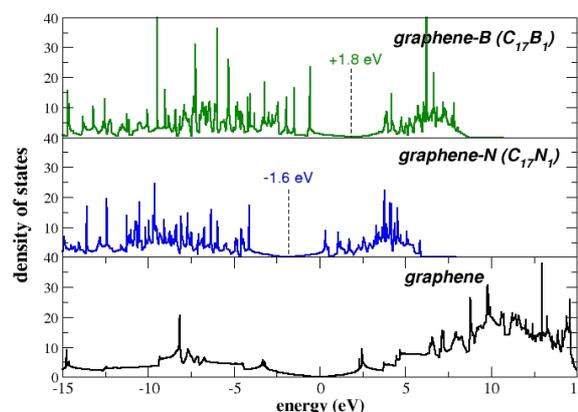
Figure 2. Density of states of B- and N-doped graphene (GrB and GrN) calculated with the PBE0 functional.
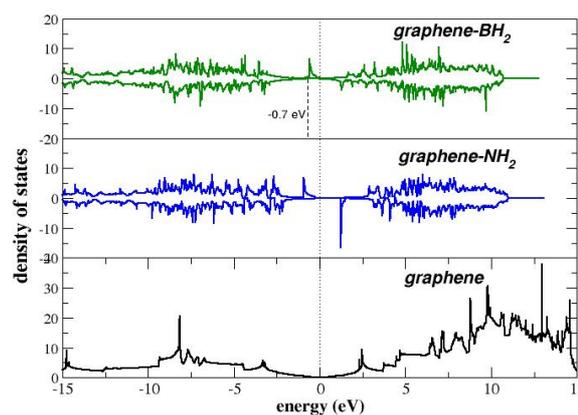
Figure 3. Density of states of GrBH$_2$ and GrNH$_2$ calculated with the PBE0 functional.

Computational details

DFT calculations of doped graphene were performed using the projector-augmented wave method in the Vienna Ab initio Simulation Package (VASP) suite.[28, 29] The energy cutoff for the plane-wave expansion was set to 400 eV. The graphene sheet was modeled using a 3×3 supercell (18 carbon atoms) with a calculated C-C bond length of 1.44 Å. The periodically repeated sheets were separated by 18 Å of vacuum. Substitutional doping was modeled by replacing one of carbon atoms with boron or nitrogen atom. NH$_2$ and BH$_2$ species were placed above one of carbon atoms, and the atomic forces were fully relaxed using conjugate gradient algorithm. It should be noted that NH$_2$ stayed above carbon atom, whereas BH$_2$ slid

into the 'bridge' position (above bond connection two neighboring carbon atoms, Figure 1).

The workfunction W_f was calculated as $W_f = E(\mathrm{vac}) - E_f$, where $E(\mathrm{vac})$ is the local potential in vacuum, calculated using large slab having 26 Å of vacuum between repeating graphene layers, and E_f is the Fermi energy. The density of states was calculated using tetrahedron smearing with Blöchl corrections and employing two exchange-correlation functionals: 1) generalized gradient method in the Perdew-Burke-Ernzerhof (PBE)[30] formulation, and 2) hybrid functional PBE0.[31] Hybrid functional involves a portion of the exact Hartree-Fock exchange and reduces some of shortcomings of classical DFT functionals such as self-interaction error.[32, 33] Hybrid functional also improves the tendency of (semi-)local functionals to underestimate band gaps in solids,[25] or HOMO-LUMO gaps in molecules.

Thermodynamic stability of inspected dopants was calculated by comparing the total energy of respective doped supercell (Scheme 2) with respect to the sum of the total energies of initial reactants. We assumed that the initial reactants are pristine graphene and ammonia NH_3 or (formally one half of) diborane B_2H_6 and that the products are substitutionally doped graphene (by the N or B atoms, i.e. GrN and GrB depicted in Scheme 2), carbon and hydrogen, or graphene with added ammine or borane groups (GrNH$_2$ and GrBH$_2$, Scheme 2) and hydrogen. The reference energies for the pure states of carbon and hydrogen were chosen as one half the energy of graphene primitive cell and one half of the energy of hydrogen molecule.

Conclusions

Our data show that the chemical nature of doping process significantly influences the final electronic properties of the doped material. The substituonally-doped materials show increase and decrease in W_f as expected for classical p- and n-types of dopants, respectively. On the other hand, the ad-doped materials display smaller (but significant) changes in W_f, which have the same trend for doping by BH$_2$ and NH$_2$. It means that addition of NH$_2$ leads to increase in W_f as does the addition of BH$_2$. One may also expect changes in electronic transport properties, as the ad-doping introduces sp^3 carbon atoms in the sp^2 honey-comb graphene lattice. In turn, various methods of preparation of doped graphenes may provide materials with different properties. This may explain some controversial experimental observations[11, 15, 16] and, on the other hand, open new ways how to design and control electronic properties of doped graphenes.

Acknowledgements

Notes and references

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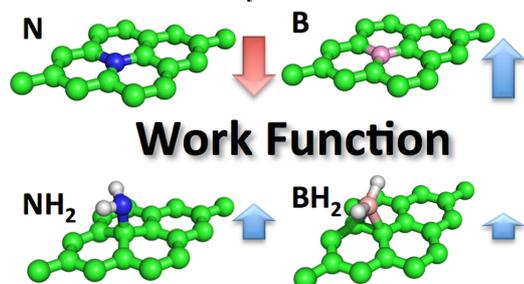
The electronic properties of the N- and B-doped graphenes depend, besides the doping element, on the nature of doping.