

Carboxylation of Boron- and Nitrogen-Doped Graphene and Carbon nanotubes

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ABSTRACT

We study the mechanism of covalent functionalization of boron (B) and nitrogen (N) doped graphene and carbon nanotubes by carboxyl (COOH) groups. Our calculations are carried out using an *ab initio* density functional pseudopotential computational method combined with the generalized gradient approximation for the exchange-correlation functional. The binding energies and equilibrium structures of carboxylated B/N-doped graphene sheets and carbon nanotubes are examined in cases of graphene and nanotubes containing no surface defects, containing Stone-Wales defects, and containing vacancies. We find that B-doping increases and N-doping decreases the binding energy of COOH groups to defect-free and defective graphene and carbon nanotubes. This result is consistent with previous observations that carbon nanotubes and graphene act as electron acceptors with respect to COOH groups.

Keywords: density functional theory, graphene, carbon nanotubes, functionalization, B-doping, N-doping, carboxyl groups, surface defects.

1 INTRODUCTION

The properties of carbon materials can be modified through chemical functionalization and doping. Covalent functionalization of graphene and carbon nanotubes provides a framework for the development of carbon-based molecular electronics. The functionalization of graphene sheets and carbon nanotubes has a significant effect on their conductance and transport properties [1]. This process can also be used to bind small metal particles and nanoclusters to the surface of carbon nanostructures [2]. One of the frequently used approaches to chemical functionalization of graphene and nanotubes is carboxylation, which is usually carried out by treating carbon materials with oxidizing inorganic acids [3,4]. The attachment of molecules and functional groups to the surface of graphene and carbon nanotubes preferentially occurs at the surface defect sites introduced by acid treatment [5-7]. The most common types of stable point defects observed in carbon nanostructures are Stone-Wales (SW) defects and vacancies [8,9]. The functionalization of defect sites significantly changes the electronic and structural characteristics of defective graphene and carbon nanotubes [7,10,11].

The electrochemical activity of carbon materials can be increased by the addition of impurity atoms. It has

been demonstrated that the chemical, mechanical, and electric transport properties of carbon nanostructures can be tailored by introducing a suitable dopant [12]. The doping of graphene sheets and carbon nanotube sidewalls could increase the reactivity of these structures and improve the chemistry necessary for anchoring molecules and chemical groups on their surfaces. The boron and nitrogen doping of graphitic carbon materials has been recently investigated experimentally and theoretically [13,14]. However, the effect of B and N doping on chemical functionalization of graphene and carbon nanotubes so far has not been studied in detail.

In this paper, we investigate the mechanism of chemical functionalization of B/N-doped graphene and carbon nanotubes by COOH groups, using first principles density functional computational methods. The goal of our study is to analyze the structural and electronic properties of carboxylated graphene and carbon nanotubes in the presence of boron and nitrogen impurity atoms combined with the other types of point surface defects, e.g. SW defects and vacancies.

2 COMPUTATIONAL METHODS

Our computational method was based on density functional theory (DFT) [15] combined with the pseudopotential approach. The calculations were conducted in the framework of the periodic supercell method using the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) electronic structure code [16,17]. The SIESTA code employs localized orbital basis sets to represent the valence electronic wave functions [16,17]. The exchange-correlation energy was evaluated in our calculations using the generalized-gradient approximation (GGA) in the form introduced by Perdew, Burke, and Ernzerhof [18]. We used norm-conserving Troullier-Martins nonlocal pseudo-potentials [19] in the Kleinman-Bylander form [20]. All our calculations were conducted using the double zeta plus polarization (DZP) basis set for the atomic orbitals [21]. The energy cut-off, which corresponds to the grid spacing, was chosen to be 200 Ry for graphene and 150 Ry for carbon nanotubes. Spin polarization effects were explicitly included in the computational formalism.

The initial atomic structures of graphene and carbon nanotubes were obtained by minimizing the total energy of undoped carbon structures within the supercell geometry. The equilibrium configurations of the B/N-doped and defective graphene sheets and carbon nanotubes were obtained by introducing dopant atoms and point

surface defects into the carbon nanostructure and re-optimizing the geometry of the system within the supercell. The binding energies and equilibrium distances for the COOH groups attached to the surface of defect-free, defective, and B/N-doped graphene and carbon nanotubes were calculated by adding the COOH group to the system and relaxing the positions of all atoms within the previously optimized supercells under the condition of the fixed supercell volume. The structural optimization was performed using the conjugate gradient algorithm. After the structural optimization, the residual forces acting on any atom within the supercell were smaller than 0.03 eV/Å. In order to eliminate the basis set superposition error associated with the differences in the size of the localized SIESTA basis sets for the COOH group, graphene, and carbon nanotubes, the values of the binding energy were computed using the counterpoise method [22,23]. The net charge transfer between the COOH groups and the carbon structures was calculated using the Mulliken population analysis.

3 RESULTS AND DISCUSSION

3.1 Carboxylated Graphene

First, we investigated the structural properties of carboxylated undoped, B-doped, and N-doped graphene sheets containing no surface defects, containing a SW defect and containing a vacancy. The lowest-energy configurations of the COOH groups attached to the surface of B-doped graphene sheets are shown in Fig. 1. Our calculations indicate that surface carboxylation induces substantial electronic and structural changes in the B/N-doped graphene. In the B-doped graphene sheets, the B-C bond lengths increase, while the angles between the interatomic bonds decrease. This result can be explained by the fact that the COOH group pulls out the boron atom from the surface of graphene, inducing a significant change in the geometry of the carbon structure. The B-COOH bond is positioned nearly perpendicular to the graphene surface. The geometry of the carboxylated B-doped defective graphene sheet suggests the formation of a relatively strong covalent bond between the COOH group and the boron atom located at the defect site.

The calculated binding energies of the COOH groups attached to the undoped and B/N-doped graphene, E_b , the equilibrium graphene-COOH distances, d_{\min} , and the amount of transferred Mulliken charge between the COOH group and the graphene surface, Q_{trans} , are summarized in Table 1. We found that the graphene sheets doped with the boron atoms were more energetically favorable for carboxylation. The values of the binding energies in Table 1 show that N-doping decreases and the B-doping increases the strength of chemical bonding between the COOH groups and graphene. The binding energy between the COOH group and undoped graphene is estimated to be 0.82 eV. Introducing a SW defect and a

vacancy to the surface of graphene increases the binding energy to 1.65 eV and 3.57 eV, respectively. These binding energies are close to the values obtained in our previous real-space DFT calculations, which predicted the binding energies of 0.94 eV, 1.88 eV, and 3.41 eV for carboxylated undoped graphene clusters with no surface defects, with a SW defect, and with a vacancy, respectively [7]. The values in Table 1 show that for graphene containing a SW defect B-doping increases the binding energy of the COOH group by 28%, while N-doping decreases this energy by 24%.

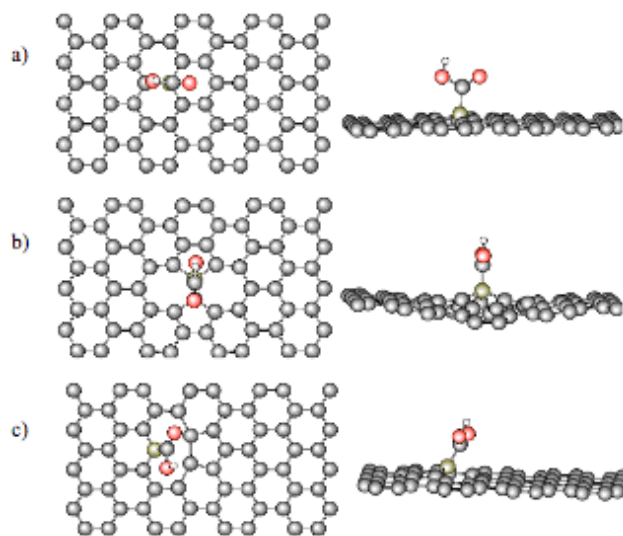


Figure 1. The optimized structures of carboxylated B-doped graphene sheets with (a) no defects, (b) a SW defect, and (c) a vacancy.

The amount of transferred charge between the COOH group and the graphene sheet was estimated from the Mulliken population analysis. We found that for the carboxylated undoped and B-doped graphene, a small portion of the electronic charge is transferred from the COOH group to the surface of graphene. The result for the undoped graphene is consistent with our previous real-space DFT study of carboxylated graphene clusters [7]. In contrast, we found that for the carboxylated N-doped graphene, a small portion of the electronic charge is transferred from the surface of graphene to the COOH group.

3.2 Carboxylated Carbon nanotubes

Next, we investigated the properties of carboxylated undoped, B-doped, and N-doped defect-free and defective carbon nanotubes. We selected the (5,5) and (8,0) single-walled carbon nanotubes for this study. The lowest-energy structures of the COOH groups attached to the surface of B-doped (5,5) and (8,0) carbon nanotubes are shown in Fig. 2. Our calculations demonstrate that, similarly to the case of carboxylated graphene, the B-C bond lengths increase and the angles between the

interatomic bonds decrease in the carboxylated B-doped carbon nanotubes. The decrease of the B-C bond angles indicates the buckling of the carbon nanotube surface near the attachment site of the COOH group. The geometry of the carboxylated B-doped carbon nanotubes suggests the formation of a covalent bond between the COOH groups and the surfaces of the B-doped nanotubes.

Graphene	d_{\min} (Å)	E_b (eV)	Q_{trans} (e)
No defects			
Undoped	1.6	0.82	0.094
B-doped	1.71	1.22	0.05
N-doped	1.61	0.24	-0.008
SW defect			
Undoped	1.55	1.65	0.112
B-doped	1.64	2.12	0.08
N-doped	1.55	1.25	-0.002
Vacancy			
Undoped	1.5	3.57	0.145
B-doped	1.63	3.86	0.038
N-doped	1.42	2.59	-0.208

Table 1: Equilibrium bond lengths, d_{\min} , binding energies, E_b , and the amount of the transferred charge, Q_{trans} , for the COOH group attached to defect-free and defective undoped, B-doped, and N-doped graphene.

Table 2 presents the calculated binding energies, E_b , of the COOH groups attached to the undoped and B/N-doped (5,5) and (8,0) carbon nanotubes, the equilibrium nanotube-COOH distances, d_{\min} , and the amount of transferred Mulliken charge between the COOH group and the nanotube surface, Q_{trans} . In agreement with our results for carboxylated graphene, we found that B-doping increases and N-doping decreases the strength of chemical bonding between the COOH groups and carbon nanotubes. The binding energy between the COOH group and the undoped carbon nanotubes containing SW defects is estimated to be about 1.7 – 2.1 eV. The presence of a vacancy on the surface of the carbon nanotube increases this energy to ~ 3.4 eV. The binding energies of the COOH groups to the defective carbon nanotubes are close to our results for graphene. For the carbon nanotubes with SW defects, N-doping decreases the binding energy to approximately 0.6 – 0.8 eV, while B-doping increases this

energy to about 2.3 – 2.5 eV. In the case of carbon nanotubes containing vacancies, N-doping decreases and B-doping increases the binding energy of the COOH group to 2.4 – 2.5 eV and 3.8 – 3.9 eV, respectively. The Mulliken population analysis shows that, similarly to the case of carboxylated graphene, a small portion of the electronic charge is transferred from the COOH group to the surface of the undoped and B-doped carbon nanotubes, while for the N-doped carbon nanotubes the charge is transferred from the surface of nanotube to the COOH group. This result is consistent with our previous observations that undoped carbon nanotubes and graphene act as electron acceptors with respect to COOH groups [7].

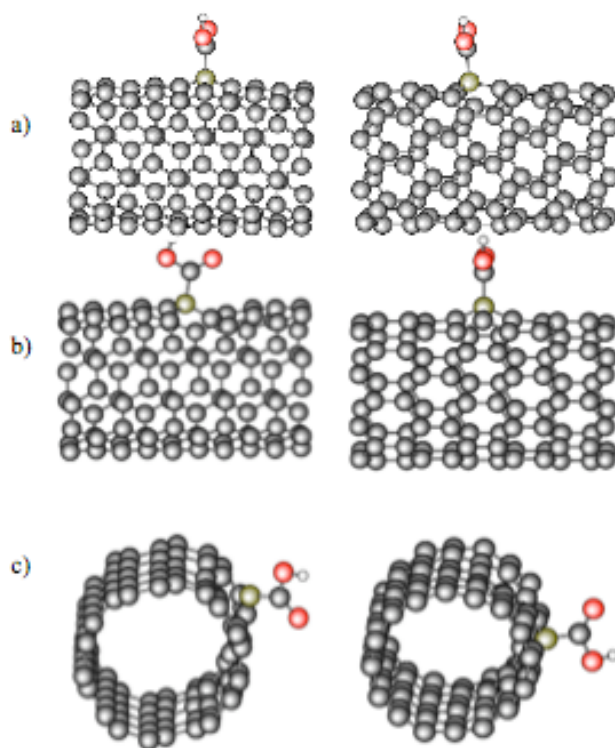


Figure 2. The optimized structures of carboxylated B-doped (5,5) (left) and (8,0) (right) single-walled carbon nanotubes with (a) no defects, (b) a SW defect, and (c) a vacancy.

4 CONCLUSIONS

We have studied the mechanism of covalent functionalization of boron (B) and nitrogen (N) doped graphene and carbon nanotubes by carboxyl (COOH) groups. Our calculations were performed in the framework of density functional theory combined with the pseudopotential approximation and the generalized gradient approximation for the exchange-correlation functional. The binding energies, equilibrium geometries, and the amounts of transferred electronic charge were calculated in cases of carboxylated B/N-doped graphene sheets and carbon nanotubes with no defects, Stone-Wales defects, and

vacancies. The results of our calculations indicate that B-doping increases and N-doping decreases the binding energy of the COOH group to defect-free and defective graphene and carbon nanotubes. This suggests that impurity doping may significantly affect the chemical reactivity of graphene sheets and carbon nanotube sidewalls.

Surface defects	B/N doping	d_{\min} (Å)	E_b (eV)	Q_{trans} (e)
(5,5) carbon nanotube				
SW defect	Undoped	1.52	2.15	0.126
	B-doped	1.65	2.47	0.024
	N-doped	1.55	0.64	-0.02
Vacancy	Undoped	1.47	3.41	0.204
	B-doped	1.61	3.8	0.066
	N-doped	1.39	2.35	-0.296
(8,0) carbon nanotube				
SW defect	Undoped	1.55	1.71	0.124
	B-doped	1.65	2.3	0.092
	N-doped	1.53	0.82	-0.016
Vacancy	Undoped	1.47	3.38	0.176
	B-doped	1.61	3.9	0.092
	N-doped	1.38	2.48	-0.211

Table 2: Equilibrium bond lengths, d_{\min} , binding energies, E_b , and the amount of the transferred charge, Q_{trans} , for the COOH group attached to defective undoped, B-doped, and N-doped (5,5) and (8,0) single-walled carbon nanotubes.

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