Atomic structures and scanning tunnelling microscopy of nitrogen-doped carbon nanotubes

Yoshitaka Fujimoto1 and Susumu Saito1,2,3

1 Department of Physics, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan
2 Advanced Research Center for Quantum Physics and Nanoscience, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan
3 Materials Research Center for Element Strategy, Tokyo Institute of Technology, Yokohama, Kanagawa 226-8503, Japan
E-mail: fujimoto@stat.phys.titech.ac.jp

Abstract. We report on atomic structures, energetics, and scanning tunnelling microscopy images of nitrogen defects in carbon nanotubes (CNTs) based on first-principles density-functional study. As defect configurations in CNTs, not only the substitutional nitrogen defect but also the nitrogen-vacancy complex defects (pyridine-type defects) are considered. The substitutional nitrogen defect is found to be energetically the most stable defect. On the other hand, for the pyridine-type defects, the tetramerized and the trimerized configurations are found to be the possible configurations in energy. The scanning tunnelling microscopy (STM) images for defect configurations in N-doped CNTs are studied, and the various N defects in CNTs are expected to be identified by STM experiments.

1. Introduction
Carbon nanotubes (CNTs), which are composed of the quasi-one-dimensional cylinders, possess unique properties such as long mean free path and high current density [1,2]. Specifically, due to their high carrier mobility, CNTs are expected to be promising device materials to be used in nanoelectronics such as field effect transistors and sensors [3-13].

Substitutional doping with heteroatoms is known to be an effective way to tune the electronic properties of the CNTs. Nitrogen is one of promising dopants for carbon-based materials since it is a neighbouring element to carbon in periodic table. In the x-ray photoelectron spectroscopy observations, it has been suggested that there exist two major nitrogen-defect configurations in N-doped CNTs as well as N-doped graphene: One is the substitutional nitrogen defect where one carbon atom is replaced by one nitrogen atom. The other is the pyridine type where nitrogen atoms are located around the atomic vacancy [14-20]. Furthermore, it is reported that the transport properties of the substitutionally N-doped CNTs and graphene are much different from those of the pyridine-type defective ones: The substitutionally N-doped CNTs show n-type doping property, whereas the pyridine-type defective CNTs have p-type one [20-25].

Scanning tunnelling microscopy (STM) method is a powerful tool to observe the local electronic structures of the semiconductor and metal surfaces at atomic levels. The STM images of nitrogen-doped as well as boron-doped graphene have been examined theoretically and experimentally, and the theoretical and experimental STM images are confirmed to show good agreement with each other [24,26-28]. However, our knowledge as to the pyridine-type defects in N-doped CNTs is still limited.
In this work, we report on the atomic structures, energetics, and STM images of N-doped (10,0) CNTs using the first-principles density-functional study. From our results of the calculated formation energy, it is found that the substitutional N defects have the lowest formation energy, whereas the tetramerized and the trimerized configurations are energetically plausible configurations among the pyridine-type defects. The STM images of the substitutional N, the trimerized pyridine-type, and the tetramerized pyridine-type defects in CNTs are simulated. It is found that the STM images of those N defects are different considerably from one another.

2. Computational method

The supercell models used in this work consist of two unit cells for a zigzag (10,0) CNT having 80 C atoms. Figure 1 shows the optimized atomic structures of N-doped (10,0) CNTs. In Fig. 1(a), substitutional N-doped (10,0) CNT is depicted [C_{79}N]. For the pyridine-type defects in N-doped (10,0) CNTs, the monomeric [C_{78}N], the dimerized [C_{77}N_{2}], the trimerized [C_{76}N_{3}], and the tetramerized [C_{74}N_{4}] configurations are shown in Figs. 1(b)-(e), respectively.

Our calculations are carried out using the first-principles total-energy methods within the density-functional theory [29]. The interactions between the ions and the valence electrons are described by the norm-conserving Troullier-Martins pseudopotentials [30], and exchange-correlation effects are treated using the local density approximation (LDA) parameterized by Perdew and Zunger [31,32]. The wave functions are expanded in a plane-wave basis and the kinetic-energy cutoff is taken to be 50 Ry [33]. The atomic positions are optimized until the Hellmann-Feynman force on each atom becomes less than 0.05 eV Å. One-dimensional Brillouin-zone integration is performed with four k-point sampling.

The formation energy is defined as

\[ E_f = E_{tot} - m_c \mu_c - m_N \mu_N, \]

where \( E_{tot} \) is the total energy of the N-doped (10,0) CNT, and the chemical potentials \( \mu_c \) and \( \mu_N \) are the energies per carbon atom in pristine (10,0) CNT and nitrogen atom in N_{2} gas phase, respectively.

The STM images are obtained based on the Tersoff-Hamann approximation [34]. This method is known to be highly accurate for many systems despite its simplicity [35-37]. In this approximation, the tunnelling current \( I(r) \) is assumed to be proportional to the local density of states (LDOS) of the surface at the tip position integrated over a range of energy \( E \) restricted by the applied bias voltage \( V \):

\[ I(r) \sim \int_{E_F}^{E_F+eV} \rho(r, E) dE, \]

where \( E_F \) is the Fermi energy.

3. Results and discussion

![Figure 1. Optimized atomic structures for (10,0) carbon nanotubes with (a) substitutional nitrogen defect (C_{79}N), and (b) monomeric (C_{78}N), (c) dimerized (C_{77}N_{2}), (d) trimerized (C_{76}N_{3}), and (e) tetramerized (C_{74}N_{4}) pyridine-type defects.](image-url)
3.1. Energetics

We here examine the formation energies $E_f$ calculated by Eq. (1). Table 1 lists the formation energies for various N-defect configurations in N-doped (10,0) CNTs. The formation energy of the substitutionally N-doped (10,0) CNT is found to be the lowest, 0.41 eV ($C_{79}N$). This implies that the substitutional N defect is the most plausible configuration when the N atom is doped into the (10,0) CNTs. For N-doped (10,0) CNTs with a vacancy, the tetramerized pyridine-type defects are found to be the most stable structure ($E_f$=1.78 eV), while the formation energy of the trimerized defects is 2.16 eV. The formation energies of the tetramerized and the trimerized configurations are much lower than those of the monomeric and the dimerized ones, implying the existence of the tetramerized and the trimerized configurations. It has been reported that the atomic vacancies are often observed experimentally in CNTs and graphene [38,39]. The pyridine-type defects are energetically favorable than the substitutional N defects in the presence of the atomic vacancy in the CNTs and the graphene [20,24]. Furthermore, the formation energies of the N-doped CNTs with the pyridine-type defects decrease as the number of the N atoms around the monovacancy in the N-doped (10,0) CNTs increases (see Figs. 1(b)-(d)). Therefore, the trimerized and the tetramerized pyridine-type defects would be plausible configurations if there exist the pyridine-type defects in the (10,0) CNT.

We here discuss the difference in energetics between the N-dope (10,0) CNTs and N-doped graphene. Interestingly, the formation energy of the substitutionally N-doped (10,0) CNT ($C_{79}N$) is higher than that of the substitutionally N-doped graphene, where the formation energy of the substitutionally N-doped graphene is reported to be 0.32 eV [24]. For the pyridine-type defects in the N-doped (10,0) CNTs, the formation energy of the N-doped (10,0) CNT with the tetramerized pyridine-type defect ($C_{79}N_4$) is lower than that with the trimerized one ($C_{79}N_3$). On the other hand, for the N-doped graphene, the formation energy of the N-doped graphene with the tetramerized pyridine-type defects is slightly higher than that with the trimerized one [24]. Thus, it showed be concluded that the behaviour of the formation energies for the N-doped (10,0) CNTs is considerably different from that for the N-doped graphene.

| Nitrogen-defect configuration | Formation energy (eV) |
|------------------------------|-----------------------|
| $C_{79}N$                    | 0.41                  |
| $C_{79}N$                    | 3.79                  |
| $C_{79}N_2$                  | 2.91                  |
| $C_{79}N_3$                  | 2.16                  |
| $C_{79}N_4$                  | 1.78                  |

3.2. Scanning tunnelling microscopy images

Figure 2(a) shows the STM image of the substitutional N defect in N-doped (10,0) CNTs. The STM image around the N atom in the substitutionally N-doped CNT is different from that at the C atoms since the STM image of the substitutional N defects mainly reflects the donor states below the conduction band [5]. This behaviour is also seen in the graphene and the hexagonal boron-nitride layers [26,40-47]. Therefore, the N atom in the substitutionally N-doped CNT could be identified in the STM images. Figures 2(b) and 2(c) also illustrate the STM images of the trimerized and the tetramerized pyridine-type defective (10,0) CNTs, respectively. It is found that the N atoms in the pyridine-type defects would appear to be individual regions in the STM images, which depends on the number of the N atoms in the pyridine-type defects [see Figs. 2(b) and 2(c)]. These STM images are similar to those of the N-doped graphene [24]. Thus, the STM images of the N-doped (10,0) CNTs with the substitutional N, the trimerized pyridine-type, and the tetramerized pyridine-type defects must
be distinguished from one another and those three types of N-defect configurations would be observable by the STM measurements.

4. Conclusions

We have reported the atomic structures, energetics, and STM images of N-doped (10,0) CNTs using the first-principles density-functional study. From the results of the formation energy calculations, the substitutional N defect is found to be the most stable configuration. On the other hand, the tetramerized as well as the trimerized pyridine-type defects are the plausible configurations among the pyridine-type defects in the (10,0) CNTs. The STM images of (10,0) CNTs with the substitutional N, the trimerized pyridine-type, and the tetramerized pyridine-type defects are examined, and are found to be considerably different from one another. Therefore, those N defects in the N-doped (10,0) CNTs could be identified by using the STM methods.

Figure 2. Simulated STM images of N-doped (10,0) CNTs with (a) substitutional nitrogen, (b) trimerized pyridine-type, and (c) tetramerized pyridine-type defects. The STM images are generated at applied bias voltage of -0.5 eV. The yellow balls denote the positions of N atoms in N-doped (10,0) CNTs.

Acknowledgments

This work was partly supported by MEXT Elements Strategy Initiative to Form Core Research Center through Tokodai Institute for Element Strategy, JSPS KAKENHI Grant Numbers JP19H01823 and JP17K05053. Computations were partly done at Institute for Solid State Physics, the University of Tokyo and at Global Scientific Information and Computing Center of the Tokyo Institute of Technology, and the Center for Computational Materials Science, Institute for Materials Research, Tohoku University for the use of MASAMUNE-IMR.

References

[1] Iijima S 1991 Nature 354 56.
[2] Dürkop T, Getty SA, Cobas E and Fuhrer MS 2004 Nano Lett. 4 35.
[3] Kong J et al. 2000 Science 287 622.
[4] Schlappbach L and Züttel A 2001 Nature (London) 414 353.
[5] Fujimoto Y and Saito S 2011 J. Phys.: Conf. Ser. 302 012006.
[6] Li E and Marzari N 2011 ACS Nano 5 9726.
[7] Teerapanich P, Myint M, Joseph C, Hornyak G, Dutta J 2013 IEEE Trans. Nanotechnol. 12, 255.
[8] Fujimoto Y and Saito S 2014 J. Appl. Phys. 115 153701.
[9] Fujimoto Y and Saito S 2016 Chem. Phys. 478 55.
[10] Nikolina A et al. 2016 ACS Sens. 1 591.
[11] Yu L, Shearer C, and Shapter J 2016 Chem. Rev. 116 13413.
[12] Fujimoto Y 2018 New Polymer Nanocomposites for Environmental Remediation ed C Hussain and A Mishra (Amsterdam: Elsevier) Chapter 9 pp 207-222.
[13] Fujimoto Y and Saito S 2019 Jpn. J. Appl. Phys. 58 015005.
[14] Czerw R et al. 2001 Nano Lett. 1 457.
[15] Ayala P et al. 2007 J. Phys. Chem. C 111 2879.
[16] Fang WC 2008 Nanotechnol. 19 165705.
[17] Wei D, Liu Y, Wang Y, Zhang H, Huang L, and Yu G 2009 Nano Lett. 9 1752.
[18] Lin YC, Lin CY, and Chiu PW 2010 Appl. Phys. Lett. 96 133110.
[19] Sus T, Pichler T and Ayala P 2015 Beilstein J Nanotechnol. 6 177.
[20] Fujimoto Y and Saito S 2011 Physica E 43 677.
[21] Fujimoto Y and Hirose K 2003 Phys. Rev. B 67 195315.
[22] Fujimoto Y, Asari Y, Kondo H, Nara J, and Ohno T 2005 Phys. Rev. B 72 113407.
[23] Min YS et al. 2008 Appl. Phys. Lett. 93 043113.
[24] Fujimoto Y and Saito S 2011 Phys. Rev. B 84 245446.
[25] Yokoyama K et al. 2016 Carbon 142 518.
[26] Shao L et al. 2013 Nano Lett. 13 518.
[27] Fujimoto Y and Saito S 2015 Surf. Sci. 634 S7.
[28] Fujimoto Y and Saito S 2017 Springer Proc. Phys. 186 107.
[29] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133.
[30] Troullier N and Martins JL 1991 Phys. Rev. B 43 1993.
[31] Perdew JP and Zunger A 1981 Phys. Rev. B 23 5048.
[32] Computations have been performed using Tokyo Ab-initio Program Package (TAPP) which is developed by a consortium initiated at University of Tokyo: Yamauchi J, Tsukada M, Watanabe S, and Sugino O, 1996 Phys. Rev. B 54 5586.
[33] Ceperley DM and Alder B J 1980 Phys. Rev. Lett. 45 566.
[34] Tersoff J and Hamann DR 1985 Phys. Rev. B 31 805.
[35] Okada H, Fujimoto Y, Endo K, Hirose K, and Mori Y 2001 Phys. Rev. B 63 195324.
[36] Fujimoto Y, Okada H, Endo K, Ono T, Tsukamoto S, and Hirose K 2001 Mater. Trans. 42 2247.
[37] Fujimoto Y, Okada H, Inagaki K, Goto H, Endo K, and Hirose K 2003 Jpn. J. Appl. Phys. 42 5267.
[38] Hashimoto A, Suenaga K, Gloter A, Urita K, Iijima S 2004 Nature (London) 430 870.
[39] Amorim R, Fazzio A, Antonelli A, Novaes F, daSilva A 2007 Nano Lett. 7 2459.
[40] Terrones M et al. 2002 Appl. Phys. A 74 355.
[41] Fujimoto Y and Saito S 2015 J. Ceram. Soc. Jpn. 123 576.
[42] Ćirić-Marjanović G, Pašti I, and Mentus S 2015 Prog. Mater. Sci. 69 61.
[43] Fujimoto Y and Saito S 2016 Phys. Rev. B 93 045402.
[44] Fujimoto Y and Saito S 2016 Phys. Rev. B 94 245427.
[45] Haga T, Fujimoto Y, and Saito S 2019 Phys. Rev. B 100 125403.
[46] Haga T, Fujimoto Y, and Saito S 2019 Jpn. J. Appl. Phys. 58 SIIB03.
[47] Fujimoto Y and Saito S 2016 J. Ceram. Soc. Jpn. 124 584.