

Adsorption of Molecules on Nitrogen-Doped Graphene: A First-Principles Study

Yoshitaka FUJIMOTO* and Susumu SAITO

Department of Physics, Tokyo Institute of Technology, Oh-Okayama, Meguro-ku, Tokyo 152-8551, Japan

E-mail: fujimoto@stat.phys.titech.ac.jp

(Received January 23, 2013)

We study the adsorption of NH_3 and H_2O molecules on pyridine-type nitrogen-doped graphene using a first-principles electronic-structure calculation. The adsorption energies of NH_3 and H_2O molecules on the pyridine-type defect are calculated and it is found that the adsorptions of NH_3 as well as H_2O molecules become energetically favorable. The pyridine-type defect in N-doped graphene is therefore expected to be highly reactive, and should be useful for reaction centers in chemical processes as well as for sensor applications.

KEYWORDS: Density-functional theory, Nitrogen-doped graphene, Molecular adsorption

1. Introduction

Graphene has attracted much attention from the viewpoint of fundamental physics and applicable systems in nanoelectronics since it possesses unique and excellent mechanical, electronic, and optical properties [1]. Especially, due to the extremely high carrier mobility, graphene is expected to be a good candidate for future nanoelectronics device materials [2].

Chemical functionalization should be an effective way to tune the electronic structures of carbon-based materials. Actually, the adsorption of NH_3 and H_2O on graphene as well as carbon nanotubes (CNTs) has been studied and it is expected to be useful for sensor applications [3, 4]. It is also well-known that substitutional doping is a practical way to modify electronic structures of graphene and CNTs, and therefore the molecular adsorption can be often enhanced by substitutional dopants. For example, nitrogen is a good dopant for carbon-based materials, and the adsorption of molecules on N-doped graphene and CNTs have been studied [5, 6, 7]. However, the knowledge as to the adsorption of molecules on N-doped graphene is still limited since it has been reported that there are several nitrogen-defect configurations in graphene [8, 9].

In this report, we study the adsorption of NH_3 and H_2O molecules upon nitrogen-doped graphene using a first-principles total-energy calculation within the framework of the density-functional theory. As the nitrogen defect in graphene to be studied, we consider the pyridine-type defect which consists of three nitrogen atoms around a single vacancy. The adsorption energies of NH_3 and H_2O molecules on N-doped graphene are calculated, and it is found that the adsorption of NH_3 and H_2O molecules



becomes energetically favorable.

2. Computational methods

The model system we study here consists of 4×4 unit cell in the direction parallel to the graphene sheet, and therefore the pyridine-type defective graphene sheet contains 28 C atoms and 3 N atoms. In Fig. 1(a), the optimized atomic structure of pyridine-type defective graphene is illustrated. Figures 1(b) and (c) show the optimized atomic geometries of NH_3 and H_2O adsorbed on the pyridine-type graphenes, respectively.

Our calculations are carried out using the first-principles total-energy methods within the density-functional theory [10, 11]. The interactions between the ions and the valence electrons are described by the norm-conserving Troullier-Martins pseudopotentials [12], and exchange-correlation effects are treated using the local density approximation (LDA) parameterized by Perdew and Zunger [13, 14]. The wave functions are expanded in a plane-wave basis and the kinetic-energy cutoff is taken to be 50 Ry [15]. The atomic positions are optimized until the Hellmann-Feynman force on each atom becomes less than 0.05 eV/\AA . Two-dimensional Brillouin-zone integration is performed with 36 k-point sampling.

3. Results and discussion

3.1 Energetics

To discuss the stabilities of NH_3 and H_2O molecules adsorbed on the pyridine-type N-doped graphene, we calculate the adsorption energy E_a defined as

$$E_a = E_{tot} - E_{sub} - E_{mol}, \quad (1)$$

where E_{tot} and E_{sub} are total energies of pyridine-type N-doped graphene with and without molecules, respectively, and E_{mol} is also total energy of the isolated molecule.

Table I shows the adsorption energies of NH_3 and H_2O molecules on N-doped graphene. We find that the NH_3 molecule is dissociated into H and NH_2 , and they bind with two N atoms in the pyridine-type defect (see Fig. 1(b)). We find that the adsorption of NH_3 molecule on the pyridine-type defect becomes energetically favorable. In Ref. [6], it has been reported that the adsorption of the NH_3 molecule on the substitutional N

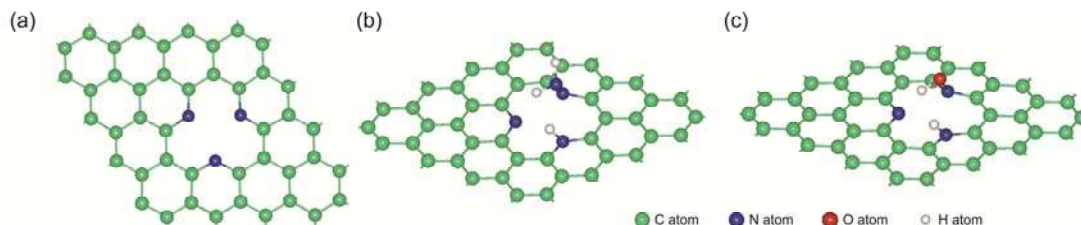


Fig. 1. (Color online) Optimized atomic geometries of N-doped graphenes: (a) the pyridine-type defect, (b) NH_3 adsorbed on the pyridine-type defect, and (c) H_2O adsorbed on the pyridine-type defect.

defective graphene, where one C atom is replaced by one N atom, is also favorable in energy. However, the adsorption energy in the case of pyridine-type defective graphene (-1.214 eV) is much lower than that in the case of the substitutional N defective graphene (-0.015 eV) [6].

Table I. Adsorption energies of NH₃ and H₂O molecules on pyridine-type graphene.

Adsorbed molecules	Adsorption energy (eV)
NH ₃	-1.214
H ₂ O	-0.769

For the adsorption of H₂O molecule, it is dissociated into H and OH, and they are also adsorbed on two N atoms in the pyridine-type defect (Fig. 1(c)). It is found that the adsorption of H₂O molecule also becomes energetically preferable, and its adsorption energy (-0.769 eV) is considerably lower than that for the adsorption on the substitutional N defect (-0.06 eV) [6]. The pyridine-type defect, thus, is found to be more reactive compared with the substitutional N defect. Moreover, the adsorption of NH₃ molecule is found to be preferred in energy rather than that of the H₂O molecule.

3.2 Geometry

We study the atomic geometries of NH₃ and H₂O molecules on N-doped graphene, as shown in Figs. 1(b) and (c), respectively. For the adsorption of NH₃ molecule, two bond angles of H-N-N bonds in the NH₂ adsorption site are 107.4° and 108.5° [Figs. 1(b)]. Two N-H bond lengths and N-N bond length in the NH₂ site are both 1.03 Å and 1.41 Å, respectively. Our calculated N-H bond length and the H-N-H bond angle of the isolated NH₃ molecule are 1.02 Å and 107.2°, respectively. For the adsorption of H₂O molecule, the lengths of O-H and N-O bonds are 1.02 Å and 1.41 Å, respectively, and the bond angle of H-O-N is 99.4°. The bond length of O-H and the bond angle of H-O-H in the isolated H₂O molecule are 0.98 Å and 104.3°, respectively. When NH₂ and OH are adsorbed at the N atoms in the pyridine-type defect, they keep similar configurations of isolated NH₃ and H₂O molecules, respectively. On the other hand, the N atom in the pyridine-type defect protrudes from the planar graphene sheet by the adsorption of NH₂ and OH.

4. Summary

We have studied the adsorption of NH₃ and H₂O molecules on the pyridine-type defective graphene using a first-principles density-functional calculation. The adsorption energies of NH₃ and H₂O molecules are calculated and the dissociative adsorptions of NH₃ and H₂O molecules on the pyridine-type defect are found to be favored energetically.

Acknowledgment

This work was supported by Global Center of Excellence Program by MEXT Japan

through the Nanoscience and Quantum Physics Project of the Tokyo Institute of Technology, and Elements Science and Technology Project of MEXT Japan. Computations were done at Institute for Solid State Physics, the University of Tokyo, on TSUBAME Grid Cluster at Tokyo Institute of Technology, and at Research Center for Computational Science, National Institute of Natural Sciences.

References

- [1] A. K. Geim and K. S. Novoselov: Nature Mater. **6** (2007) 183.
- [2] E. H. Hwang, S. Adam, and S. Das Sarma: Phys. Rev. Lett. **98** (2007) 186806.
- [3] B. Sanyal, O. Eriksson, U. Jansson, and H. Grennberg: Phys. Rev. B **79** (2009) 113409.
- [4] B. Huang, Z. Li, G. Zhou, S. Hao *et. al.*: J. Phys. Chem. C **112** (2008) 13442.
- [5] Y. Fujimoto and S. Saito: Physica E **43** (2011) 677.
- [6] J. Dai, J. Yuan, and P. Giannozzi: Appl. Phys. Lett. **95** (2009) 232105.
- [7] Y. Fujimoto and S. Saito: J. Phys.: Conf. Ser. **302** (2011) 012006.
- [8] D. Wei, Y. Liu, Y. Wang, H. Zhang, L. Huang, and G. Yu: Nano Lett. **9** (2009) 1752.
- [9] Y. Fujimoto and S. Saito: Phys. Rev. B **84** (2011) 245446.
- [10] P. Hohenberg and W. Kohn: Phys. Rev. **136** (1964) B864.
- [11] W. Kohn W and L. J. Sham: Phys. Rev. **140** (1965) A1133.
- [12] N. Troullier and J. L. Martins: Phys. Rev. B **43** (1991) 1993.
- [13] D. M. Ceperley and B. J. Alder: Phys. Rev. Lett. **45** (1980) 566.
- [14] J. P. Perdew and A. Zunger: Phys. Rev. B **23** (1981) 5048.
- [15] Computations have been performed using the Tokyo *Ab Initio* Program Package (TAPP) which was developed by a consortium initiated at the University of Tokyo: J. Yamauchi, M. Tsukada, S. Watanabe, and O. Sugino: Phys. Rev. B **54** (1996) 5586.