Investigation of adsorbed small-molecule on boron nitride nanotube (BNNT) based on first-principles calculations

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***Abstract*—Based on the first-principles calculations, we have investigated the structure and electronic property of adsorbed small-molecules on boron nitride nanotubes (BNNTs). It is found that the sites of LUMO and HOMO would be changed after BNNTs absorbed the different small molecules. The energy gap of BNNTs decreases with increasing the distance between small molecule and BNNT. The adsorption effect of BNNT will be optimal as the distance between the small molecule and BNNT is from 1 to 1.5 Å. The potential application of BNNT as highly sensitive gas sensor for N-based small molecules has also been discussed.**

Keywords—first-principles calculations, boron nitride nanotubes, adsorption effect, small molecule

I. INTRODUCTION

Since carbon nanotubes (CNTs) were discovered in 1991, plenty of nanomaterials, such as zero-dimensional nanoparticles, one-dimensional nanowires or nanotubes (NTs), have attracted intensive attentions due to their unique applications in microscopic physics and nanoscale devices [1-3]. Similar to CNTs, boron nitride nanotubes (BNNTs) is a semiconductor material with a stable wide band gap (3.5-5.5 eV), superb mechanical strength, high thermal conductivity, and ultra-violet light emission [4-6]. Generally, BNNTs are a polar material due to the slight positive charges of boron (B) atoms and the slight negative charges of nitrogen (N) atoms [7], which provide the solid basis for the future applications in nano-electronic devices such as sensor and hydrogen storage media.

Sensors with high sensitivity and selectivity act as the role for real-time detections of a variety of industrial processes and environment. Currently, plenty of low dimensional materials, such as graphene, layered MoS_2, and nanotubes, have been proposed as potential candidates of gas sensors [8-10]. The nanotubes are generally porous due to their high reactivity exterior surface, which makes them sensitive to small molecular [11]. As being important low-dimensional materials with wide band gaps, boron nitride nanotubes (BNNTs) have also received considerable interests. Despite the adsorption behavior of pure or doped BNNTs has been reported [12, 13], the basic understandings of the sensors, especially the structure and electronic properties of adsorbed small molecule on BNNTs, had been left insufficient until recently. Here, based on the first-principles calculations we investigate the structure and electronic properties of BNNTs with absorbed small molecules, and then effect of physisorbed small molecules.

II. THEORETICAL MODEL

Figure 1 displays a BNNT device structure for gas sensors. The first-principles calculations are performed within the framework of density function theory (DFT) by using GGA-PW91 to an energy convergence of $5 \times 10^{-6}\, eV/atom$ and max forces less than $0.01\, eV/Å$ [14-17]. Ultrasoft pseudopotentials, periodical boundary conditions, and a cutoff energy of 450 eV are employed. The Brillouin zone integration is performed by using the Monkhorst-Pack scheme with $1 \times 1 \times 1$ k-points. To avoid the interaction among BNNTs, the nanotube distance of 20 Å are set during the calculation in tetragonal supercells. The zigzag (5,5), (6,6), (7,7) and (8,8) BNNTs are used as the simulated structure, respectively, and the BNNT supercell consists of five unit cells. Figure 2 shows the structure with different small molecules on zigzag (5, 5) BNNTs, as an example for first-principles calculations.

Once the total energies of BNNTs structure and BNNTs with the absorbed small molecules were obtained, the

adsorption energy of a small molecule on the nanotube can be calculated as [18]

$$E_{ad} = E_{BNNT/gas} - E_{BNNT} - E_{gas}, \quad (1)$$

here $E_{BNNT/gas}$, E_{BNNT}, and E_{gas} denote the total energies of BNNTs with a gas molecule attached, the pristine BNNT, and the gas molecule, respectively.

Then, the charge transfer induced by the absorbed small molecules can be obtained as [19]

$$\Delta Q = Q_{BNNT/gas} + Q_{BNNT}, \quad (2)$$

here $Q_{BNNT/gas}$ and Q_{BNNT} denote the total charge of BNNTs with the absorbed small molecules and the pristine sample, respectively. Otherwise, the charge transfer generally can be obtained by using the Mulliken populations of BNNT with the absorbed small molecules and the pristine BNNT, based on the first-principles calculation.

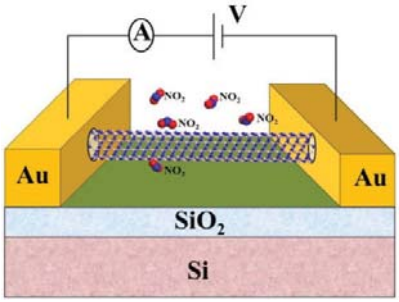

Fig. 1 BNNTs device structure for gas sensors

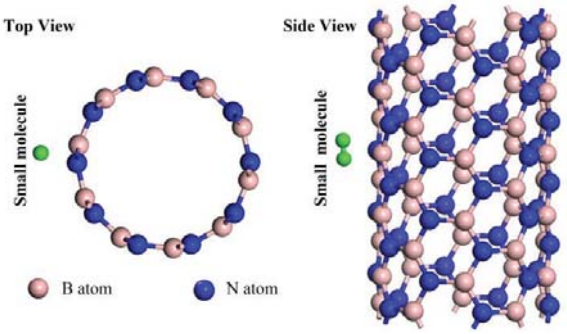

Fig. 2 Top and side views of the lowest energy structures with different small molecules on zigzag (5, 5) BNNTs for first-principles calculations.

III. Results and Discussion

In order to understand the adsorption effect of BNNTs, we first examine the structure and electronic properties of the BNNTs with the absorbed small molecules and the pristine sample based on the first-principles calculations. Figure 3 shows the calculated densities of states (DOS) with different small molecules adsorbed on zigzag (5, 5) BNNTs. As compared with the pristine sample with the larger energy gap (c.a. 4.680 eV), the energy gaps of BNNTs with different small molecules have been remarkably decreased. Figure 4 shows the site of LUMO and HOMO for pristine zigzag (5, 5) BNNT and different zigzag (5, 5) BNNT/gas. It is found that the LUMO and HOMO has been changed after BNNTs absorbed the different small molecules.

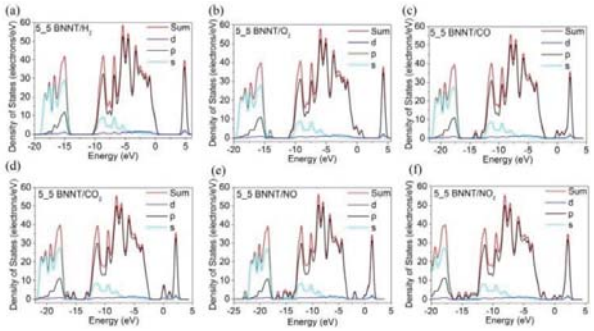

Fig. 3 The calculated densities of states (DOS) with different small molecules adsorbed on zigzag (5, 5) BNNTs.

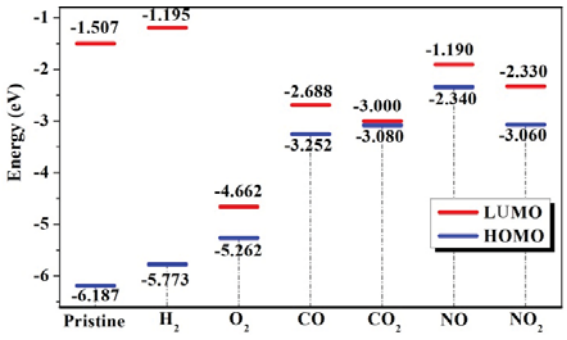

Fig. 4 LUMO and HOMO of zigzag(5, 5) BNNT for pristine and with adsorbed small molecule. LUMO is the lowest unoccupied molecular orbital, and HOMO is highest occupied molecular orbital.

Based on the first-principles calculations, and using the Eq. (1) and Eq. (2), we have calculated the adsorption energy, charge transport from BNNT to gas molecules for pristine and BNNT/gas for zigzag (5,5), (6,6), (7,7) and (8,8) BNNTs, as summarized in Table I and Table II, respectively. It is found that, as compared with other small molecules, such as H_2, O_2, CO, CO_2, BNNT with different zigzag can provide high sensitivity for N-based small molecules, especially NO_2. Otherwise, the elementary molecule (such as H_2, O_2) adsorbs weakly on BNNT with lower adsorption energies. Actually, the adsorption energy $|E_a|$ in BNNTs is higher than that in other two dimensional materials (such as, graphene, MoS_2) [8, 9], which suggests that the BNNT will be a potential gas sensor. What's more, the calculated results also demonstrate that the interaction with N-based molecules is stronger (such as, $E_{ad} = 1.451\ eV$ for NO_2 absorbed on zigzag (6, 6)), which implies that BNNT can provide high sensitivity for N-based small molecules. This result is similar to other low dimensional materials [9, 18]. The adsorption energies of CO and CO_2 on BNNT are also lower, which suggests that BNNT is not suitable to CO and CO_2 molecules as gas sensors.

Then we discuss the charge transfer characteristics from BNNT to small molecules ΔQ (eV) for zigzag (5,5), (6,6), (7,7) and (8,8) BNNTs, respectively. In Table II, H_2 and CO_2, molecules are found to donate charge to the BNNTs, while O_2, CO, NO and NO_2 molecules accept charge.

Otherwise, the results show that the stronger charge transfer corresponds to higher adsorption energy, such as NO, NO_2.

TABLE I. THE ADSORPTION ENERGY FROM BNNT TO GAS MOLECULES FOR ZIGZAG(5, 5), (6, 6), (7, 7) AND (8, 8) BNNTS, RESPECTIVELY

Gas	H_2	O_2	CO	CO_2	NO	NO_2
zigzag (5, 5)	0.148	0.023	0.157	0.546	0.447	1.377
zigzag (6, 6)	0.251	0.174	0.077	0.196	0.319	1.451
zigzag (7, 7)	0.066	0.120	0.426	0.341	0.488	1.415
zigzag (8, 8)	0.074	0.064	0.204	0.356	0.497	1.040

TABLE II. CHARGE TRANSFER FROM BNNT TO SMALL MOLECULES ΔQ(EV) FOR ZIGZAG (5,5), (6,6), (7,7) AND (8,8) BNNTS, RESPECTIVELY.

Gas	H_2	O_2	CO	CO_2	NO	NO_2
zigzag (5, 5)	0.011	-0.199	-0.252	-0.163	-0.159	-0.195
zigzag (6, 6)	0.078	-0.086	-0.337	-0.080	-0.289	-0.438
zigzag (7, 7)	0.058	-0.270	-0.360	0.238	-0.251	-0.474
zigzag (8, 8)	0.076	-0.081	-0.370	0.061	-0.392	-0.456

To better understand the physisorbed small molecules, the distance of between NO_2 and BNNT dependence of the energy gap, adsorption energy and charge transfer of zigzag (5, 5) BNNT/NO_2 have been discussed in details in Fig. 5 and Fig. 6, respectively. In Fig. 5, it is found that the energy gap will decrease with the increase of the distance between the small molecule and BNNT. Otherwise, the adsorption effect of BNNTs will be optimal as the distance between the small molecule and BNNT is between 1 and 1.5 Å.

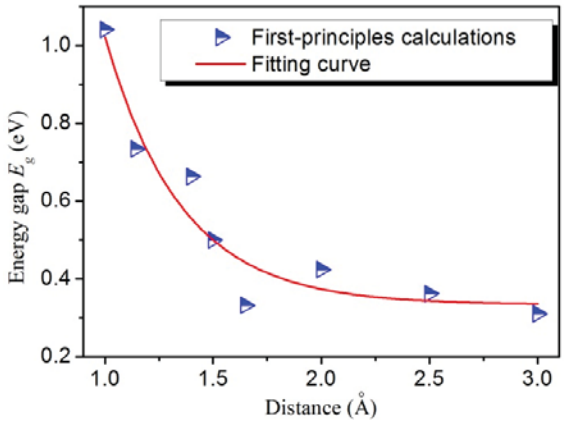

Fig. 5 The distance of between NO2 and BNNT dependence of the energy gap of zigzag (5, 5) BNNT/NO_2.

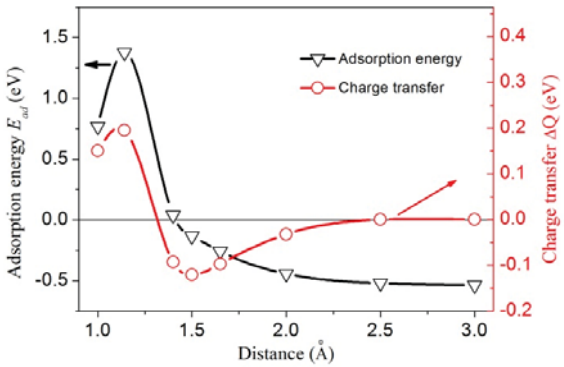

Fig. 6 The distance of between NO_2 and BNNT dependence of adsorption energy and charge transfer of zigzag (5, 5) BNNT/NO_2, respectively.

Finally, we want to discuss the adsorption energy and temperature dependence of recovery time. To estimate the effect of absorption, the recovery time is usually employed to describe the property of the gas sensor. Based on the conventional transition state theory, the recovery time can be expressed as [20, 21]

$$\tau = \frac{1}{v_0} exp\left(-\frac{E_{ad}}{k_B T}\right), \quad (3)$$

where v_0 is the attempt frequency, E_{ad} is the adsorption energy, k_B is the Boltzmann's constant and T is the temperature.

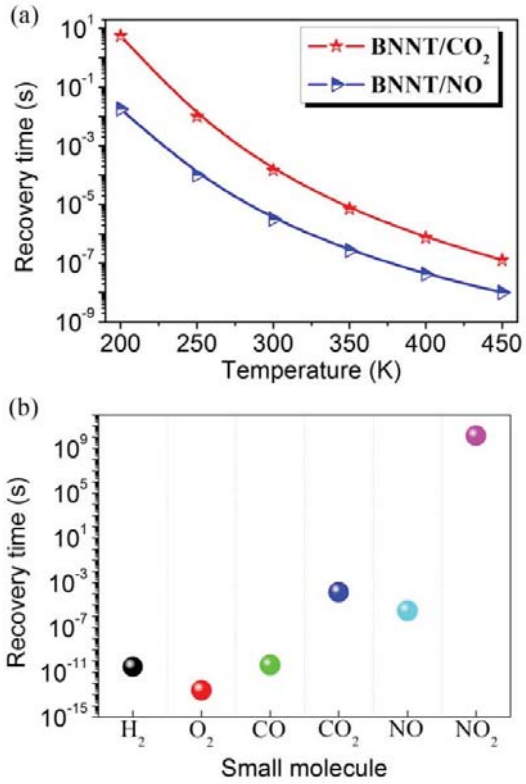

Fig. 7 Recovery time for CO_2 and NO adsorbed on BNNT at different temperature (a), and for different molecules adsorbed on BNNT at room temperature (b).

Figure 7 shows the temperature dependence of recovery time for CO_2 and NO adsorbed on BNNT and for different molecules adsorbed on BNNT at room temperature. It is found in Fig. 7(a) that the recovery time decreases with the increase of the temperature. This result shows that increasing the temperature can decrease the interaction between BNNTs and small molecules, and then decrease the adsorption effect. Fig. 7(b) shows the recovery time for different molecules adsorbed on BNNT at room temperature. One can see that, for the small molecules with larger adsorption energy (such as CO_2 and NO_2), the recovery time is higher, thus it is difficult to desorb from a BNNT to recover the initial state.

IV. Conclusion

In terms of first-principles calculations, the structure and electronic properties of the adsorbed small molecules on boron nitride nanotube (BNNT) have been investigated in details. The potential application of BNNT as highly sensitive gas sensor for N-based small molecules has been demonstrated, but not suitable to CO and CO_2 molecules as gas sensor. The adsorption effect of BNNTs will be optimal as the distance between the small molecule and BNNT is between 1 and 1.5 Å. Otherwise, our calculations show that the recovery time will enhance with the adsorption energy $|E_{ad}|$, while decrease with the increase of temperature.

Acknowledgment

This work was supported in part by the Opening Project of Key Laboratory of Microelectronic Devices and Integrated Technology, Institute of MicroElectronics Chinese Academy of Sciences, by National Key Research and Development Program (Grant No. 2016YFA0201802, 2017YFB0701703), by the National Natural Science Foundation of China (Grant No. 61725404, 61574166, 61376112, 61221004, and 61674167), by the Beijing Training Project for the Leading Talents in S&T under Grant No. Z151100000315008, by the National 973 Program under Grant Nos. 2013CBA01604 and 2013CB933504, by the Strategic Priority Research Program of the Chinese Academy of Sciences, Grant No. XDB12030400, and Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM).

References

[1] J. Zhou, Q. Wang, Q. Sun, X. S. Chen, Y. Kawazoe, and P. Jena, "Ferromagnetism in semihydrogenated graphene sheet", Nano Lett., vol. 9(11), pp. 3867-3870, Aug. 2009.

[2] T. Zhang, S. Mubeen, N. V. Myung, and M. A. Deshusses, "Recent progress in carbon nanotube-based gas sensors", Nanotechnology, vol. 19, 332001, July 2008.

[3] Y. Wang, and J. T. W. Yeow, "A review of carbon nanotubes-based gas sensors", Journal of Sensors, vol. 2009, 493904, May 2009.

[4] Z. Zhou, J. J. Zhao, Z. F. Chen, X. P. Gao, T. Y. Yan, B. Wen, and P. von R. Schleyer, "Comparative study of Hydrogen adsorption on carbon and BN nanotubes", J. Phys. Chem. B, vol. 110, pp. 13363-13369, 2006.

[5] C. Y. Zhi, Y. Bando, C. C. Tang, D. Golberg, "Boron nitride nanotubes", Mater. Sci. Eng. R, vol. 70, pp. 92-111, June 2010.

[6] S. Lin, X. X. Ye, R. S. Johnson, and H. Guo, "First-principles investigations of metal (Cu, Ag, Au, Pt, Rh, Pd, Fe, Co, and Ir) doped hexagonal boron nitride nanosheets: stability and catalysis of CO oxidation", J. Phys. Chem. C, vol. 117, pp. 17319-17326, July 2013.

[7] A. A. Peyghan, A. Soltani, A. A. Pahlevani, Y. Kanani, S. Khajeh, "A first-principles study of the adsorption behavior of CO on Al- and Ga-doped single-walled BN nanotubes", Appl. Surf. Sci., vol. 270, , pp. 25-32, Dec. 2013.

[8] O. Leenaerts, B. Partoens, and F. M. Peeters, "Adsorption of H2O, NH3, CO, NO2, and NO on graphene: A first-principles study", Phys. Rev. B, vol. 77, 125416, Mar. 2008.

[9] S. J. Zhao, J. M. Xue, W. Kang, "Gas adsorption on MoS2 monolayer from first-principles calculations", Chem. Phys. Lett., vol. 595-596, pp. 35-42, Feb. 2014.

[10] Y. Cai, Q. Ke, G. Zhang, and Y. W. Zhang, "Energetics, charge transfer, and magnetism of small molecules physisorbed on phosphorene", J. Phys. Chem. C, vol. 119, pp. 3102-3110, Jan. 2015.

[11] Y. Xie, Y. P. Huo, J. M. Zhang, "First-principles study of CO and NO adsorption on transition metals doped (8,0) boron nitride nanotube", Applied Surface Science, vol. 258, pp. 6391-6397, Mar. 2012

[12] P. Srivastava, N. K. Jaiswal, V. Sharma, "First-principles investigation of armchair boron nitride nanoribbons for sensing PH3 gas molecules", Superlattices and Microstructures, vol. 73, pp. 350-358, June 2014.

[13] R. Chowdhury, and S. Adhikari, "Boron-nitride nanotubes as Zeptogram-scale bionanosensors: theoretical investigations", IEEE Transactons on Nanotechnology, vol. 10, pp. 659-667, July 2011.

[14] N. D. Lu, L. Li, P. X. Sun, M. Wang, Q. Liu, H. B. Lv, S. B. Long, W. Banerjee, and M. Liu, "Carrier-transport-path-induce switching parameter fluctuation in oxide-based resistive switching memory," Mater. Res. Express, vol. 2, pp 046304, Apr. 2015.

[15] N. D. Lu, L. Li, P. X. Sun, M. Wang, Q. Liu, H. B. Lv, S. B. Long, and M. Liu, "A novel method of identifying the carrier transprot path in metal oxide resistive random access memory," J. Phys. D: Appl. Phys., vol. 48, pp 065101, Jan . 2015.

[16] S. Liu, N. D. Lu, X. L. Zhao, H. Xu, W. Banerjee, H. B. Lv, S. B. Long, Q. J. Li, Q. Liu and M. Liu, "Eliminating Negative-SET Behavior by Suppressing Nanofilament Overgrowth in Cation-Based Memory," Advanced Materials, vol. 28, pp 10623-10629, Oct. 2016.

[17] W. Wei, X. C. Chuai, N. D. Lu, Y. Wang, L. Li, C. Ye, and M. Liu, "Simualtion of doping effect for HfO_2-based RRAM based on first-principles calculations", SISPAD 2017, September 7-9, 2017, Kamakura, Japan, pp21-24.

[18] W. Hu, N. Xia, X. J. Wu, Z. Y. Lia, and J. L. Yang, "Silicene as a highly sensitive molecule sensor for NH_3, NO and NO_2", Phys. Chem. Chem. Phys., vol. 16, pp. 6957-6962, Jan. 2014.

[19] E. Montes, and U. Schwingenschlögl, "Superior selectivity and sensitivity of blue phosphorus nanotubes in gas sensing applications", J. Mater. Chem. C, vol. 5, pp. 5365-5371, May. 2017.

[20] M. Solimannejad, M, Noormohammadbeigi, "Boron nitride nanotube (BNNT) as a sensor of hydroperoxyl radical (HO_2): A DFT study", Journal of the Iranian Chemical Society, vol. 14(2), Feb. 2017, pp. 471-476

[21] Q. Wang, Q. Sun, P. Jena, Y. Kawazoe, "Potential of AlN nanostructures as hydrogen storage materials", ACS Nano, vol. 3(3), pp. 621-626, March 2009.