Boron-Doped Carbon Nanotubes Serving as a Novel Chemical Sensor for Formaldehyde

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To search for a novel sensor to detect the presence of formaldehyde (HCOH), we investigate reactivities of the intrinsic and boron-doped (B-doped) single-walled (8, 0) carbon nanotube (SWCNT) with HCOH using density functional theory calculations. Compared with the intrinsic SWCNT, the B-doped SWCNT presents high sensitivity to HCOH. This is attributed to the strongly chemical interaction between the electron-rich oxygen atom of HCOH and the electron-scarce boron atom of the doped SWCNT. B-doped SWCNTs are expected to be a potential candidate for detecting the presence of HCOH.

Introduction

Single-walled carbon nanotubes (SWCNTs) as chemical sensors have attracted strong interests due to their high sensitivity and fast response time toward gaseous molecules, such as O_2,[1] NH_3,[2,3] NO_2,[2,4] and SO_2.[5] The relevant sensing mechanics are attributed to the sensitive conductance change of SWCNTs caused by charge transfer between SWCNTs and gaseous molecules.[6] As found in experiments, these gaseous molecules affect the electronic transport properties of SWCNTs via physisorption or chemisorptions. However, it is a pity that a host of toxic gaseous molecules (e.g., carbon monoxide), water molecules, and some biomolecules cannot be detected by intrinsic CNT devices,[5] since they cannot be adsorbed on the surface of SWCNTs. So considerable experimental and theoretical works have focused on improving the sensing performance of SWCNTs to various desired molecules by doping or functionalizing CNTs.[6,7−11] SWCNTs coated with Pd nanoparticles become excellent H_2 sensors,[10] whereas SnO_2/SWCNTs hybrid material shows an enhanced sensitivity to NO_2.[11] Peng et al.[6] has demonstrated high sensitivity of boron-doped SWCNTs (B-doped SWCNTs) to carbon monoxide and water. Their calculated results show that B-doped SWCNTs can act as either electron acceptors or electron donors upon exposure of different molecules. Very recently, metal cluster−SWCNT assembly was proposed to be a promising method for the design of novel molecular sensors to NH_3,[12] and the B-doped SWCNT was found to present high sensitivity to gaseous cyanide molecules.[13]

HCOH is known as a common environmental pollutant and has serious toxicity, which can cause dermatitis, watery eyes, respiratory irritation, asthma, and pulmonary edema.[14,15] Animal experiments have shown that HCOH is a lung carcinogen and may cause cancer in humans.[16] So its monitoring and control of exposure, in both industrial and residential environments, are of special interest. Various methods[17−21] are available for the detection of HCOH, including spectrophotometry, polarography, gas chromatography, and fluorometry. These methods, however, are not sensitive enough, require complicated and expensive instruments, have high detection limits, or require long sampling intervals. Recently, great efforts have devoted to search rapid, simple, sensitive methods for detecting HCOH.[22,23] Here, we are interested in (1) whether there is a potential possibility of SWCNTs serving as a chemical sensor to HCOH, and (2) if not, can we find a method improving the sensitivity of SWCNTs to HCOH? To these ends, we studied the reactivities of HCOH toward both intrinsic SWCNTs and B-doped SWCNTs, which have been synthesized by substituted reaction of SWCNTs with B_2O_3.[24]

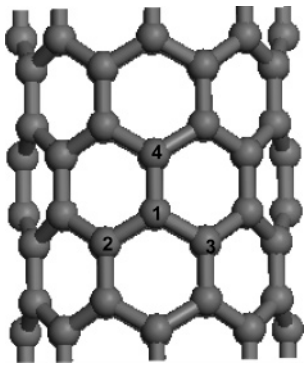

Figure 1. Structural model of the semiconducting (8, 0) carbon nanotube, where the carbon atoms in sites 1 will be replaced by a boron atom to model the B-doped SWCNTs and sites 2, 3, and 4 are the carbon atoms near the doped B atom.

Structural model of the (8, 0) carbon nanotube is shown in Figure 1, where the carbon atoms in sites 1 will be replaced by a boron atom to model the B-doped SWCNTs. We performed full geometry optimizations and property calculations on the (8, 0) intrinsic- and B-doped SWCNT systems with and without a HCOH molecule, using Perdew and Wang's local density approximation (LDA)[25] with a double numerical basis set including *p*-polarization function (denoted as DNP). As indicated by the previous theoretical calculations, LDA can accurately describe the properties of SWCNTs and their interactions with gaseous molecules.[6,12] Although the binding energies were slightly overestimated, the geometrical structures, charge distributions, and electric spectra calculated by LDA were in agreement with the generalized gradient approximation (GGA) calculations.[12] In the present calculations, the periodic-boundary

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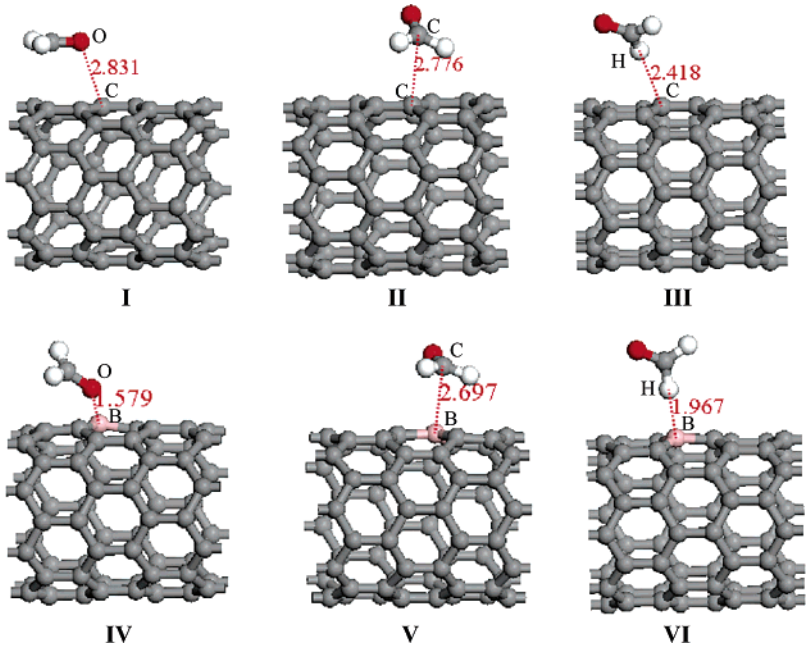

Figure 2. Optimized structures of a HCOH molecule adsorbed on the intrinsic and B-doped SWCNT: the HCOH−SWCNT systems labeled by panels I, II, and III with the O, C, and H atoms of a HCOH molecule close to SWCNT, respectively; the corresponding HCOH−B-doped SWCNT systems, labeled by panels IV, V, and VI, respectively.

TABLE 1: Calculated Data for the HCOH−SWCNT Systems and HCOH−B-Doped SWCNT Systems

	configuration[a]	E_g (eV)[b]		E_b (eV)	D (Å)	Q_T[e]
HCOH−SWCNT	I	0.576[c]	0.566	0.301	2.831	0.021
	II		0.573	0.214	2.776	0.039
	III		0.569	0.252	2.418	0.024
HCOH−B-doped SWCNT	IV	0.390[d]	0.098	0.881	1.579	0.121
	V		0.088	0.274	2.697	0.027
	VI		0.092	0.265	1.967	0.052

[a] All the configurations are given in Figure 1. [b] HOMO−LUMO energy gap calculated using Γ point. [c] HOMO−LUMO energy gap for the intrinsic SWCNT. [d] HOMO−LUMO energy gap for the B-doped SWCNT. [e] Charge transfer from HCOH to the nanotube.

condition is used with the super cell of 20 × 20 × 8.439, 24 × 24 × 8.439, and 28 × 28 × 8.439 Å^3, respectively, which includes 64 atoms in the nanotube (64 C atoms for the intrinsic SWCNT and 63 C atoms and 1 B atom for the B-doped SWCNT) with and without a HCOH molecule, respectively. The initial distance from the HCOH molecule to SWCNT surface is set to be 1.60 Å. For the B-doped SWCNT systems with and without a HCOH molecule, the spin-unrestricted calculations are performed. The Brillouin zone sampling is approximated by two k points along the tube axis, which is shown to be a good approximation for (8, 0) carbon nanotubes.[26]

To evaluate the interaction between a HCOH molecule and SWCNT or B-doped SWCNT, we calculated their binding energy (E_b), defined as

$$E_b = E(\text{SWCNT}) + E(\text{HCOH}) - E(\text{HCOH−SWCNT})$$

where E(HCOH−SWCNT) is the total energy of a HCOH molecule adsorbed on the intrinsic or B-doped SWCNT surface, and E(SWCNT) and E(HCOH) are the total energies of the intrinsic or B-doped SWCNT and a HCOH molecule, respectively. To investigate the electronic charge changes through the SWCNTs, we calculated net charge-transfer (Q_T) between the HCOH molecule and the intrinsic or B-doped SWCNT by using Mulliken population analysis.

We first compared the calculated results obtained using three different super cells. It is found that no obvious differences for the geometries E_b and Q_T are observed for the selected systems, indicating that the super cell of 20 × 20 × 8.439 Å^3 is large enough to avoid the interaction of tube and tube. So in the following sections, we only discuss the case in the super cell of 20 × 20 × 8.439 Å^3.

For the HCOH−SWCNT system, we investigated various possible adsorption geometries. Three representative configurations, in which the nanotube is close to the oxygen, carbon, and hydrogen atom of HCOH, are shown by panels I, II, and III of Figure 2, respectively. As shown in Figure 2 and Table 1, the calculated E_b values for I, II, and III are 0.301, 0.214, and 0.252 eV, respectively. And the corresponding interaction distance (D) between the SWCNT and HCOH are 2.831, 2.776, and 2.418 Å, respectively. These small E_b values and large D values indicate that HCOH undergoes physical absorption on intrinsic SWCNTs due to weak van der Waals interaction between SWCNT and HCOH. We also find that the values of Q_T in these three structures are very small, suggesting that the interaction between the HCOH and nanotubes is intrinsically electrostatic. The energy gaps (E_g) between the highest-occupied molecular orbitals (HOMOs) and the lowest-unoccupied molecular orbitals (LUMOs) calculated using the Γ point are also given in Table 1. The intrinsic (8, 0) SWCNT is found to be semiconducting with a gap of 0.576 eV, which is good agreement with 0.56 eV reported in the previous literature.[6] This fact indicates that the model and the density functional theory (DFT) method used in this paper is accurate enough for describing the SWCNT. After the adsorptions for a HCOH molecule, we cannot observe distinct changes of the energy gaps,

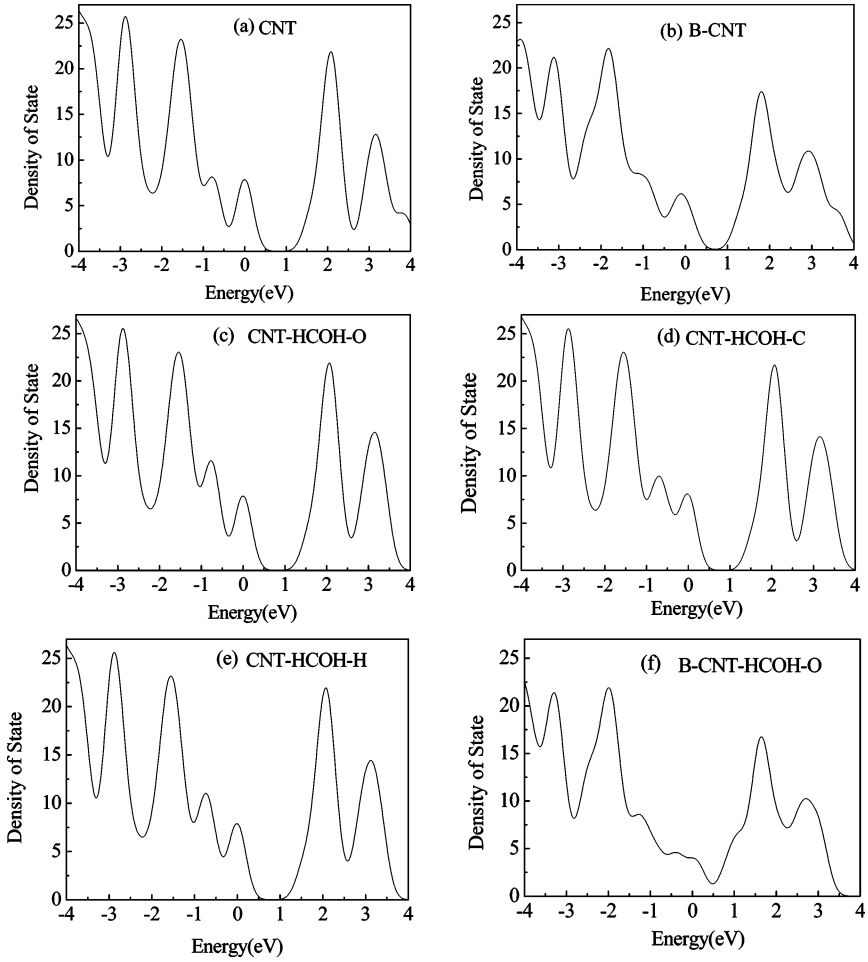

Figure 3. Calculated electronic DOSs for the intrinsic SWCNT (panel a), B-doped SWCNT (panel b), HCOH−SWCNT systems (panels c, d, and e with the O, C, and H atom of a HCOH molecule close to the SWCNT, respectively), and the B-doped-SWCNT-HCOH system IV (panel f).

indicating that the adsorptions do not change the electric properties of the intrinsic SWCNT. In other words, the intrinsic SWCNT is not sensitive to HCOH molecule.

While for the B-doped SWCNT with one carbon atom substituted by one boron atom in a super cell, the drastic changes of properties of the nanotube have been observed. For the HCOH−B-doped SWCNT system, we also obtain three stable configurations: the boron atom of the SWCNT is close to the oxygen, carbon, and hydrogen atoms of HCOH, respectively, as shown by panels IV, V, and VI of Figure 2. From Table 1, we found that the E_b values for IV, V, and VI are 0.881, 0.274, and 0.265 eV, respectively, higher than those of the corresponding HCOH−SWCNT systems. In particular, panel IV with the oxygen atom of HCOH close to the boron atom is the most stable, and its E_b increases by 0.580 eV, compared with the intrinsic SWCNT system, indicating that the interaction between HCOH and the B-doped SWCNT is much stronger than that between HCOH and the intrinsic SWCNT. In other words, the B-doped SWCNT is more sensitive to HCOH. In panel IV, the distance between the oxygen atom of HCOH and the boron atom is 1.579 Å and the B−O−C angle is 120.7°. While the corresponding interaction distance of panel V and VI is 2.697 and 1.967 Å, respectively, clearly larger than that in panel IV. These results indicate HCOH molecule prefers to the oxygen atom rather than carbon and hydrogen atoms close to B-doped SWCNT surface. As listed in Table 1, we also find the E_g for IV remarkably decreases, while the corresponding Q_T increases to 0.121, compared with the HCOH−SWCNT system, which again proves the doping of the boron atom obviously change the electronic transport properties of the SWCNT. All these changes above for panel IV conformably suggest that the interaction between HCOH and B-doped SWCNT belongs to chemisorption, in contrast to the physisorption on the intrinsic SWCNT. This is due to strong interaction between the electron-rich oxygen atom of HCOH and the electron-scarce boron atom of the doped SWCNT.

To further evaluate the electronic properties of these intrinsic and B-doped SWCNT systems, we also calculated their electronic densities of state (DOSs), as shown in Figure 3. By comparison with the intrinsic SWCNT, the DOSs of HCOH−SWCNT systems near Fermi level corresponding to I, II, and III have no distinct changes (see panels a, c, d, and e in Figure 3), which would not result in a conductance change of the nanotubes upon absorption of HCOH molecules, hence we again conclude that intrinsic SWCNTs cannot serve as sensors for detecting the presence of HCOH molecules. While for the B-doped SWCNT, we found that the band gaps near Fermi level disappear after the absorption of HCOH molecule for the energetically most favorable adsorption configuration IV (see panel f in Figure 3), indicating that the nanotube has become conductive. From an electronic view, the electronic structure of the SWCNT contains electronic holes after doping boron atoms, which is responsible of generating a *p*-type semiconductor. When it interacts with an electron-rich HCOH molecule, the π electrons of C═O in HCOH transfer to unoccupied orbital of B atom, and at the same time the π electrons in the CNT feed back into the π^* orbital of C═O in HCOH, which dramatically changes the conductance of the nanotube and

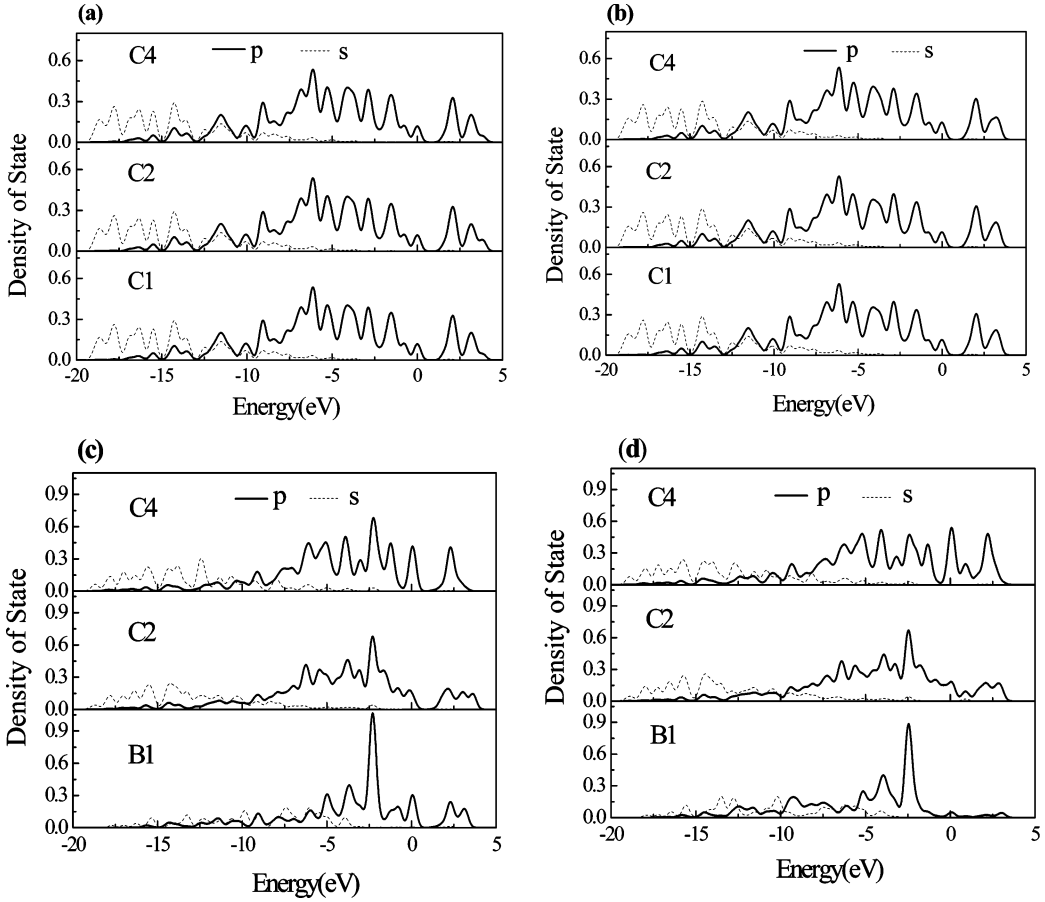

Figure 4. Calculated partial electronic DOSs for C1 (or B1), C2, and C4 atoms of the intrinsic SWCNT (panel a), SWCNT−HCOH (panel b), B-doped SWCNT (panel c), and the B-doped SWCNT−HCOH systems (panel d), respectively. The dashed and solid lines represent s and p orbitals, respectively.

makes the semiconducting B-doped SWCNT become a conductor. Thus, by detecting the conductivity change of the B-doped SWCNT systems before and after the absorption of formaldehyde, the presence of this toxic molecule can be detected. So we suggest that B-doped SWCNTs would be a promising candidate to detect the presence of HCOH molecules.

Furthermore, we studied partial densities of state (PDOS) changes of carbon atoms near B atoms in the SWCNT before and after the adsorption of a HCOH, and the positions of the atoms distributed are shown in Figure 1. Figure 4 shows the PDOS of C1 (or B1), C2, and C4 atoms of the intrinsic SWCNT (panel a), SWCNT-HCOH (panel b), B-doped SWCNT (panel c), and the energetically most favorable B-doped-SWCNT-HCOH systems (panel d), respectively. The dashed and solid lines in Figure 4 represent s and p orbitals, respectively. From Figure 4a, we find out that the PDOS of C2 atom is the same as the C4 and C1 atoms, which has a wide band gap near Fermi level, and the PDOSs in the range from −5 to 5 eV are mostly contributed from the interaction of 2p orbitals. After the adsorption of HCOH, their PDOSs do not present any change, which again prove that the intrinsic SWCNTs are insensitive to HCOH. While for the B-doped SWCNT, we find the doped B atom significantly affects the PDOS of the adjacent C atoms. The PDOSs of C2 and C4 atoms moved to the high energy level near Fermi surface, and the band gaps near Fermi level changed narrower, which indicates that the doping of B atom increases the conductivity of the SWCNT. However, the B-doped SWCNT still belong to a semiconductor. In the range from −6 to 0 eV, the 2p orbital of the B atom strongly interacts with the 2p orbital of the C1 and C2 atoms. After the absorption of HCOH molecule, the PDOSs of C2 and C4 of the B-doped SWCNT dramatically change to the continuous band above Fermi level, which is in agreement with the total DOS in Figure 3f. This suggests that the doping of B atom increases the conductive performance of the carbon atoms in SWCNT and improves the sensitivity of the SWCNT to HCOH.

We also calculated PDOSs of a HCOH molecule and O, C, and H atoms in the HCOH molecule before and after the adsorption on the B-doped-SWCNT surface, shown in parts a and b of Figure 5, respectively. From panel a of Figure 5, the PDOS of an isolated HCOH has discrete peaks corresponding to separate energy levels, which belongs to an insulator, owing to the wide band gap near the Fermi level. While when HCOH is adsorbed on the B-doped SWCNT, its PDOS presents distinct changes. The PDOS is concentrated in the range of −15 to 2.5 eV, and more importantly, it appears the 2p orbital peaks near the Fermi level, thus the HCOH molecule become conductive. We also find that O and C atoms in HCOH are mostly contributed to the change of PDOS of HCOH, which indicates O and C atoms participate in charge-transfer process of this adsorption system.

In summary, by performing DFT calculations we have established that the B-doped SWCNT is a good candidate for detecting HCOH molecules. We find that the geometric structures and electronic properties of the B-doped SWCNTs present dramatic changes after the absorption of HCOH molecule, and HCOH molecule prefers to the oxygen atom close to B-doped SWCNT surface with a tilting angle. The present

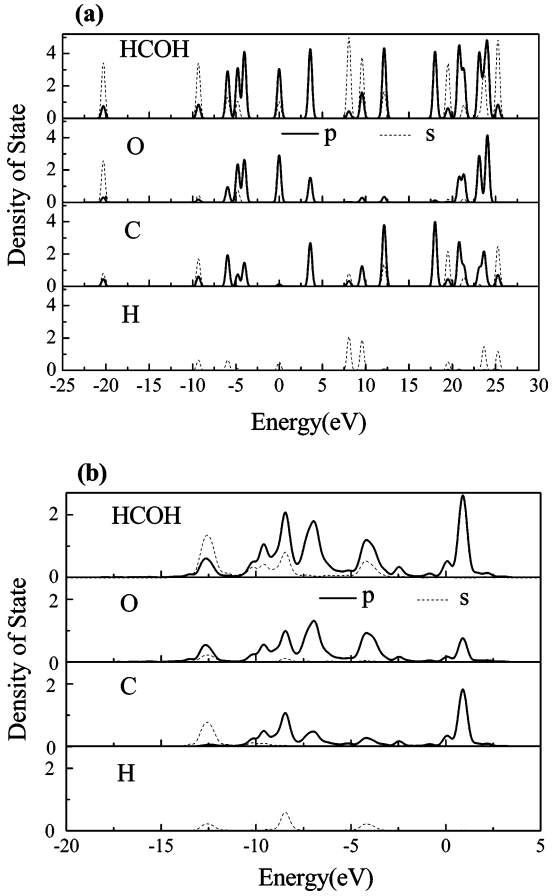

Figure 5. Calculated partial electronic density of states for a HCOH molecule and O, C, and H atoms in the HCOH molecule before (panel a) and after (panel b) the adsorption on the B-doped SWCNT surface, respectively. The dashed and solid lines represent s and p orbitals, respectively.

results are expected to provide a useful guidance to develop novel SWCNT-based sensors for the detection of HCOH molecules.

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References and Notes

(1) Collins, P. G.; Bradley, K.; Ishigami, M.; Zettl, A. *Science* **2000**, *287*, 1801.

(2) Kong, J.; Franklin, N. R.; Zhou, C. W.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. J. *Science* **2000**, *287*, 622.

(3) Feng. X.; Irle, S.; Witek, H.; Morokuma, K.; Vidic. R.; Borguet, E. *J. Am. Chem. Soc.* **2005**, *127*, 10533.

(4) Li, J.; Lu, Y. J.; Ye, Q.; Cinke, M.; Han, J.; Meyyappan, M. *Nano Lett.* **2003**, *3*, 929.

(5) Goldoni, A.; Larciprete, R.; Petaccia, L.; Lizzit, S. *J. Am. Chem. Soc.* **2003**, *125*, 11329.

(6) Peng, S.; Cho, K. *Nano Lett.* **2003**, *3*, 513.

(7) Bekyarova, E.; Davis, M.; Burch, T.; Itkis, M. E.; Zhao, B.; Sunshine S.; Haddon, R. C. *J. Phys. Chem. B* **2004**, *108*, 19717.

(8) Fagan, S. B.; Silva, L. B.; Mota, R. *Nano Lett.* **2003**, *3*, 289.

(9) Pan, H.; Feng, Y. P.; Lin, J. Y. *Phys. Rev. B* **2004**, *70*, 245425.

(10) Kong, J.; Chapline, M. G.; Dai, H. *Adv. Mater.* **2001**, *13*, 1384.

(11) Wei, B. Y.; Hsu, M. C.; Su, P. G.; Lin, H. M.; Wu, R. J.; Lai, H. J. *Sens. Actuators, B* **2004**, *101*, 81.

(12) Zhao, Q.; Nardelli, M. B.; Lu, W.; Bernholc, J. *Nano Lett.* **2005**, *5*, 847.

(13) Zhang Y. M.; Zhang D. J.; Liu C. B. *J. Phys. Chem. B* **2006**, *110*, 4671.

(14) Agathos, M.; Bernecker, H. A. *Derm. Beruf. Umwelt.* **1982**, *30*, 43.

(15) Cockcroft, D. W.; Hoeppner, V. H.; Dolovich, J. *Chest* **1982**, *82*, 49.

(16) *Registry of Toxic Effects of Chemistry Substances*; National Institute of Occupational Safety and Health: Washington, DC, 1976.

(17) Magada, B.; El-Yazbi, H. *Anal. Lett.* **1991**, *24*, 857.

(18) Li, W.; Chen, X.; Cheng, Z. *Huanjing Huaxue* **1988**, *7*, 53.

(19) Kennedy, E. R.; Hill, R. H., Jr. *Anal. Chem.* **1982**, *54*, 1739.

(20) Nieves, L.; Wentzell, M.; Peter, D.; Grouch, S. R. *Anal. Chim. Acta* **1992**, *258*, 253.

(21) Weng, J. L.; Ho, M. H. *Anal. Lett.* **1990**, *23*, 2155.

(22) Zhang, Z. Q.; Zhang, H.; He, G. F. *Talanta* **2002**, *57*, 317.

(23) Motyka, K.; Mikuka, P. *Anal. Chim. Acta* **2004**, *518*, 51−57.

(24) Han, W.; Cumings, J.; Huang, X.; Bradley, K.; Zettl, A. *Chem. Phys. Lett.* **2001**, *346*, 368.

(25) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(26) Srivastva, D.; Menon, M.; Cho, K. *Phys. Rev. Lett.* **1999**, *83*, 2973.