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Experimental and theoretical studies on the structure of N-doped carbon nanotubes: Possibility of intercalated molecular N₂

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The concentration distribution and electronic structure of N atoms doped in multiwalled bamboo-like carbon nanotubes (CNTs) are examined by photon energy-dependent x-ray photoelectron spectroscopy and x-ray absorption near edge structure. The inner part of the nanotube wall has a higher N concentration and contains molecular N₂ presumably intercalated between the graphite layers. These results are supported by the self-consistent charge-density-functional-based tight-binding calculation of double-walled CNTs, showing that the intercalation of N₂ is energetically possible and the graphite-like N structure conformer becomes more stable when the inner wall is more heavily doped. © 2004 American Institute of Physics. [DOI: 10.1063/1.1835994]

Carbon nanotubes (CNTs)¹ have drawn particular attention on account of both their scientific interest and their potential applications in a field emission display,² nanoheterojunction,³ diode,⁴ interconnect,⁵ nanotransistor,⁶ and sensor.⁷ Many of these applications are based on the electrical properties of CNTs, which strongly depend on their helicity and diameter.⁸ Therefore, the control of electrical properties is very important in many applications of CNTs. The doping of CNTs with other chemical elements (e.g., B or N) is a practical and feasible way to tailor their electrical properties. Indeed, the N-doped CNTs show *n*-type behavior regardless of a tube chirality.⁹

Despite the great attention devoted to the N-doped CNT system,^{10–12} some issues require further clarification. One is the electronic structure of the doped N atoms. The diverse electronic structures of N atoms have been proposed by a number of research groups.^{13–15} These are pyridine-like, pyrrolic, and graphite-like structure (N atoms replacing C atoms in graphite layers), triple-bonded CN, and molecular N₂. Another one is the distribution of N atoms inside the CNTs. Terrones¹ group measured the N distribution across the N-doped CNTs using electron energy-loss spectroscopy (EELS), showing that the N atoms exist mainly within the inner core of CNTs.¹⁶ We reported the EELS data that the N concentration of the compartment layers is higher than that of the wall.¹⁷ These findings indicate that the electronic structure of doped N atoms is inhomogeneous inside the CNT. But there are few studies on the space-resolved distribution of the doped N atoms in CNTs. In this study, we aim to investigate the distribution of N atoms along the probing depth and their corresponding electronic structure by using photon energy-dependent x-ray photoelectron spectroscopy (XPS) as well as x-ray absorption near-edge structure

(XANES). The data strongly suggest a possibility of intercalated molecular N₂ at the inner wall.

The N-doped CNTs were grown on a silicon oxide substrate by pyrolyzing iron phthalocyanine (FeC₃₂N₈H₁₆, 97+%, Aldrich, designated as FePc hereafter) under argon (Ar)/hydrogen (H₂) flow at 900 °C.¹⁸ The size and morphology were examined by scanning electron microscopy (SEM, Hitachi S-4300) and transmission electron microscopy (TEM, Hitachi H9000-NAR). The XPS measurements were performed at the U7 beam line of the Pohang Light Source (PLS). The U7 beam line was designed to provide soft x rays in the energy range of 50–1500 eV.¹⁹ The XPS data were collected using 475, 625, and 1265 eV photon energies, with the photon flux of $\sim 6 \times 10^{11}$, $\sim 4 \times 10^{11}$, and $\sim 3 \times 10^{10}$ (photons/s/200mA), respectively. The experiment was performed in an ultrahigh vacuum chamber with a base pressure $\leq 5 \times 10^{-10}$ Torr. The analyzer was located at 55° from the surface normal. The binding energy was calibrated by using the C 1s peak (284.6 eV). In order to determine the total energy and the stable geometry, theoretical calculations were performed for the double-walled N-doped carbon nanotubes (DWNTs), (5,5)@(10,10), using a self-consistent charge-density-functional-based tight-binding (SCC-DFTB) method.²⁰ Sixteen carbon layers along the tube axis were used for periodic boundary condition calculations. The inner diameter is 7.1 Å, and the average bond length is 1.42 Å. We define an intercalation energy of N₂ molecule as $E_{\text{int}} = E_{\text{tot}}(\text{N}_2 + \text{CNT}) - E_{\text{tot}}(\text{N}_2) - E_{\text{tot}}(\text{CNT})$, where E_{tot} is the total energy of a given system.

Figure 1(a) shows SEM image of the vertically well-aligned CNTs grown on the substrate. The density of CNTs is higher than 10¹⁰/cm², and the average length is 35 ± 10 μm. The TEM image in Fig. 1(b) shows the general morphology of CNTs. The average diameter is 50 nm and the wall thickness is in the range of 10–15 nm. The high-resolution TEM (HRTEM) image shows that the graphitic sheets of CNTs are in a highly ordered crystalline structure [Fig. 1(c)]. To obtain the distribution of N atoms, we measured the XPS using

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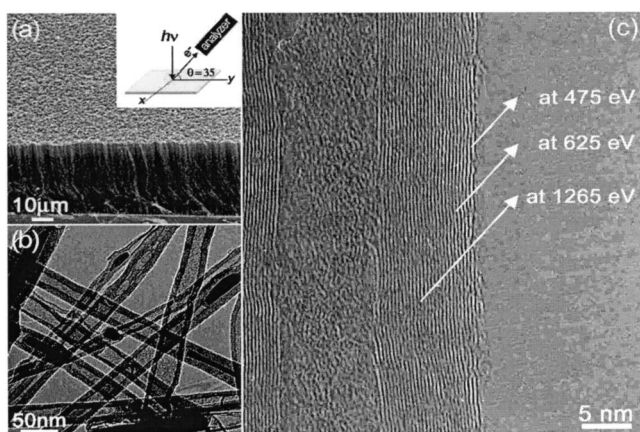


FIG. 1. (a) SEM micrograph of vertically aligned N-doped CNTs on the substrates. The inset is the scheme of the XPS measurement. (b) TEM image showing the general morphology of N-doped CNTs. (c) HRTEM image of a typical nanotube. The average probing depth for the XPS using 475, 675, and 1265 eV is indicated as arrows.

three different photon energies 475, 625, and 1265 eV. Since the escape depth of a photoelectron increases with its kinetic energy,²¹ the higher photon energy provides more information for the inner part of the wall [Fig. 1(c)]. The scheme of the XPS measurement is shown in the inset of Fig. 1(a). At 475–1265 eV photon energy, the average probing depth is in the range of 1–5 nm.

Figure 2(a) shows a typical XPS survey scan spectrum of the N-doped CNTs. The XPS data show distinct C and N 1s peaks. The N concentration, defined as $N/(C+N)$ atomic ratio %, was estimated by the area ratio of the N 1s and C 1s bands, taking into consideration of their relative sensitivities. As the photon energy increases from 475 to 1265 eV, the N concentration increases from 1.5% to 5.6%, indicating the higher N concentration in the inner part of the wall. Detailed electronic structures of N atoms can be extracted from the N 1s XPS [Fig. 2(b)]. One asymmetric band at 400.2 eV (labeled A) is observed for all photon energies, and a new band at 404.9 eV (B) is detected at 1265 eV. This shows that a new electronic structure of N atoms appears at the inner wall. According to the previous works, the band A can be assigned to chemically bonded N atoms.^{13,22} The asymmetric shape of band A suggests at least two main components such as pyridine-like and graphite-like structures.¹³ We assign the band B to the molecular N₂ by following

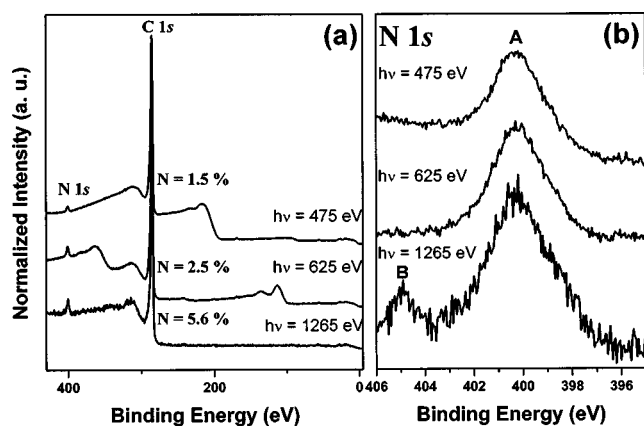


FIG. 2. XPS of the N-doped CNTs using 475, 675, and 1265 eV; (a) survey scan and (b) N 1s peak.

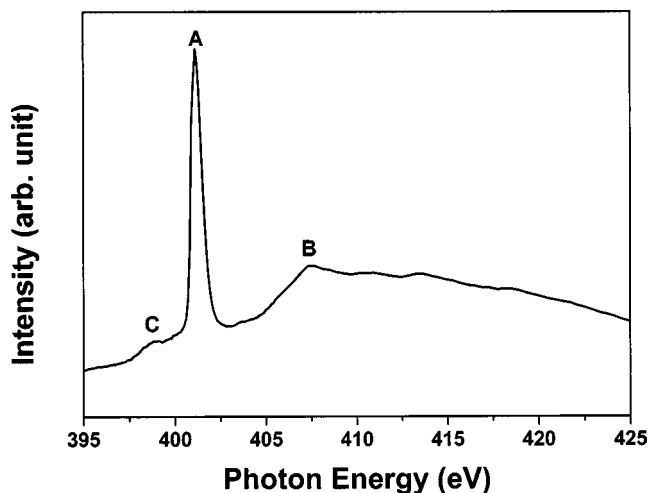


FIG. 3. N K-edge XANES spectrum of N-doped CNTs.

reason. The N 1s binding energy is 409.9 eV for free N₂ gas,²³ but the energy becomes lowered if there is extra-atomic screening effect between N 1s core hole and matrix.^{24,25} The energy lowering was observed from a number of systems; the interstitial N₂ on TiAlN (403.2 eV), physisorbed N₂ on W (403.3 eV) and graphite (403.9 eV), and chemisorbed N₂ on Re (405.2 eV) and W (405.3 eV).^{24–26} Considering the energy position and the probing depth (about 5 nm) of N 1s photoelectrons at 1265 eV, the band B suggests that molecular N₂ can exist at the interstitial and/or intercalated sites between the graphite layers. Since the graphite layers are in a highly ordered crystalline structure as shown in the HRTEM image [Fig. 1(c)], the molecular N₂ would preferentially exist as an intercalated form.

Figure 3 shows the N K-edge XANES spectrum that consists of two features (labeled A and B) centered at 401 and 407 eV and a hump (C) at 399 eV. The A/C and B features can be assigned to the transitions into unoccupied π^* and σ^* orbitals, respectively. It is well known that the π^* features of molecular N₂ and pyridine-like structures usually appear at 401.1 and 398.8 eV, respectively.^{27–29} Therefore, the position of the A and C features is close to the π^* features of molecular N₂ and pyridine-like structure, respectively. The most intense A feature reveals that the doped N atoms mainly exist as molecular N₂. However, the A feature does not show any vibrational features, indicating that the π^* level of molecular N₂ is highly perturbed by surrounding matrix. It provides additional evidence for the intercalation of molecular N₂ between the graphite layers.

The intercalation of molecular N₂ in double-walled carbon nanotubes (DWNTs) has been numerically simulated as shown in Fig. 4. Two structures, parallel and perpendicular orientation along the tube axis, were chosen. The SCC-DFTB intercalation energy is 1.37 eV for the parallel orientation and 1.68 eV for the perpendicular orientation, respectively. These energies are lower than the calculated dissociation energy (2.01 eV) of C–C bond in CNTs.³⁰ Therefore, the intercalation of molecular N₂ into the wall becomes possible without the structure destruction. The intercalated molecular N₂ prefers the parallel orientation.

In order to determine the stability of N-doped CNTs, we calculated the relative energy of three DWNT conformers whose total number of N atoms in the graphite-like structures is the same. One of the conformers contains 3% and 1% N

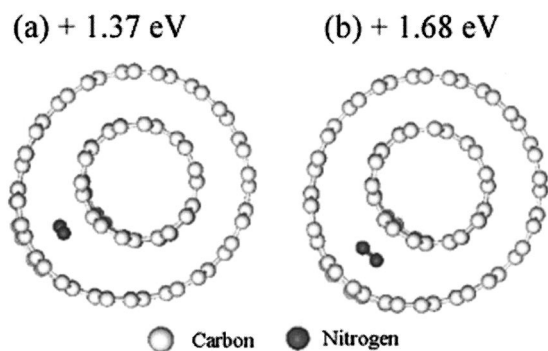


FIG. 4. Intercalation of molecular N_2 in DWNTs with (a) parallel and (b) perpendicular orientation along the tube axis.

atoms for outer and inner walls, respectively. We also considered two conformers; one with 2/4% N atoms and the other with 1/5% N atoms for outer/inner walls, respectively. The energy of these two conformers is lower than that of 3/1% N-doped conformer by -0.31 and -0.37 eV, respectively, as listed in Table I. The stability increases as the N content of the inner wall increases, which is highly consistent with our XPS data.

In summary, the concentration distribution and corresponding electronic structure of the N atoms doped in the CNTs were examined by XPS using three photon energies (475, 625, and 1265 eV). The CNTs were grown vertically aligned on the substrates using the pyrolysis of FePc at 900 °C. They have a typical bamboo-like structure, 50 nm average diameter, and 10–15 nm wall thickness. As the photon energy increases from 475 to 1265 eV, the N concentration increases from 1.5% to 5.6%, indicating the higher concentration at the inner parts of the nanotube wall. The corresponding probing depth is in the range of 1–5 nm. The molecular N_2 peak appears at the higher photon energy, suggesting the molecular N_2 intercalated between the graphite layers at the inner parts of the nanotube wall. The XANES also provides evidence for the intercalation of molecular N_2 . The SCC-DFTB calculation shows that the intercalation of molecular N_2 is energetically possible in the DWNTs. The graphite-like N structure conformer becomes more stable when the inner wall is more doped.

TABLE I. Relative energy of the N-doped DWNT conformers calculated using SCC-DFTB.^a

	Conformer A		Conformer B		Conformer C	
	Outer	Inner	Outer	Inner	Outer	Inner
N content	3%	1%	2%	4%	1%	5%
Relative energy	0 eV		-0.31 eV		-0.37 eV	

^aThe total number of graphite-like N atoms of three conformers is the same. We only vary the N content between outer and inner walls.

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