N-doped double-walled carbon nanotubes synthesized by chemical vapor deposition

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Abstract

High-purity N-doped double-walled carbon nanotubes (DWNTs) were synthesized by chemical vapor deposition, and investigated by synchrotron X-ray photoelectron spectroscopy (XPS). As the photon energy increases, the N content increases up to 3 at.%, indicating that the inner wall contains the higher N content than the outer wall. The graphite-like and pyridine-like N structures exist as about 1:1 ratio. The self-consistent charge-density-functional-based tight-binding calculation shows that the N-doping of the inner wall yields the more stable DWNT than that of the outer wall, which supports the XPS result.

1. Introduction

Double-walled carbon nanotubes (DWNTs), as frontier between single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs), have recently attracted much attention because of their unique structural and electrical properties [1–7]. Various methods were developed for the high-yield synthesis of DWNTs [8–12], and the transport properties were also measured for the use of nanoscale electronic devices [6,7]. The control of electrical properties is very important in many applications of carbon nanotubes (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. In fact, the N-doped CNTs show n-type behavior regardless of a tube chirality [13]. However, there are few works on the N-doped DWNTs, although arc-discharge synthesis of N-doped SWNTs has been reported [14,15].

In the present work, we first report the synthesis of N-doped DWNTs using a catalytic chemical vapor deposition method. Their electronic structures were thoroughly investigated by employing synchrotron X-ray photoelectron spectroscopy (XPS). The photon energy of XPS is variable in the range of 100–1300 eV. Since the escape depth of a photoelectron increases with its kinetic energy [16], the higher photon energy would provide more information for the inner parts of DWNTs. In order to explore the nature of band structure, we also obtained the valence band (VB) spectrum using low photon energy. Furthermore, we performed ab initio calculations on the N-doped DWNTs, (5,5)@(10,10), to explain the experimental results.

2. Experimental

Ethanol solution of Fe(NO3)3·9H2O and (NH4)6Mo7O24·4H2O was blended with MgO powder and sonicated for 30 min. The molar ratio was MgO: Fe:Mo = 20:1:0.1. The mixture was baked at 120 °C.
for 2 h and then ground to fine powders, forming the bimetallic catalyst embedded in MgO powders. The CH₄/NH₃/Ar mixture was flowed with the rate of 50/10/500 sccm, on these MgO-supported catalyst powders at 850 °C for 10–30 min. The morphology and structure of the products were examined by scanning electron microscopy (SEM, Hitachi S-4300), field-emission transmission electron microscopy (TEM, FEI TECNAI G²), and Raman spectroscopy (Renishaw RM 1000) using the 514 nm line from an Ar ion laser.

The XPS measurements were performed at the U7 (8A1) and U10 (3A1) beam lines of the pohang light source (PLS). These beam lines are designed to provide soft X-rays in the energy range of 50–1500 eV [17] and 10–1000 eV, respectively. The respective spectral resolving power ($E$/Δ$E$) of incident photons is 4000–5000 and 10000–30000. The experiment was performed in an ultra-high vacuum chamber with a base pressure ≤5 × 10⁻¹⁰. The analyzer was located at 55° from the surface normal.

Theoretical calculations were performed for (5,5)@(10,10) N-doped DWNTs, using a self-consistent charge density-functional-based tight-binding (SCC-DFTB) method [18]. The total energy and the optimized geometry were obtained for the conformers containing the different number of N atoms in two walls. Eight carbon layers along the tube axis were used for DWNTs. The inner diameter is 7.1 Å and the average bond length is 1.42 Å.

3. Results and discussion

Fig. 1a shows the SEM images for as-grown products. High-density bundles were grown completely covering the support. The diameter of the bundles is 10–20 nm. Fig. 1b corresponds to high-resolution TEM image showing that the bundles are mostly consisted of the DWNTs. A negligible amount of MWNTs was produced. The outer diameter of DWNTs is in the range of 1.5–2 nm (Fig. 1c).

Fig. 2 displays first-order Raman spectrum. It reveals the characteristic narrow G band at 1591 cm⁻¹, which is originated from the Raman active A₁g, E₁g, and E₂g axial vibrational modes of the graphite sheets [19,20]. The D band at 1340 cm⁻¹ is originated from the level of disordered carbons and its intensity is about 1/10 of that of G band. It also shows a series of peaks in the range of 150–350 cm⁻¹, which is unique to SWNTs and DWNTs arising from the radial breathing mode (RBM). Due to a cut-off filter, the peaks below 100 cm⁻¹ were not detected. Typical axial vibrational modes and RBM confirm the production of DWNTs. The diameter is estimated by the formula that the RBM frequency ($ν_{RBM}$) is proportional to the inverse diameter ($d$): $ν_{RBM}$ (cm⁻¹) = 248/$d$ (nm) [21]. The peaks at 311, 274, 259, 183, 165, and 150 cm⁻¹ correspond to 0.80, 0.91, 0.96, 1.36, 1.50, and 1.65 nm. The diameter of 1.50 and 1.65 nm may correspond to the outer wall of DWNTs.
having the inner diameter of 0.80 and 0.91 nm, respectively. The diameter is in the same range as that observed from the HRTEM images.

Fig. 3a shows the XPS survey scan spectrum using the photon energy 360, 630, 1000, and 1260 eV. It shows distinct C, N, and O 1s peaks. The respective probing depth of C 1s electrons is predicted to be about 1, 2, 4, and 5 nm [16]. The N concentration, defined as N/(C + N) at.%, is estimated by the area ratio of the N 1s and C 1s peaks, taking into consideration of their relative sensitivities. As the photon energy increases from 630 to 1260 eV, the N% increases to 2.9%. The increase of the N% with the probing depth indicates the higher N content in the more inside parts of the tubes. The O peak would be originated mainly from the MgO support, with some contribution from the dangling bonds of graphite layers such as C=O.

The fine-scanned C 1s spectrum is displayed in Fig. 3b. For all four photon energies, an asymmetric band is centered at 284.6 eV. The full width at half maximum (FWHM) increases from 0.8 to 1.5 eV, as the photon energy increases from 360 to 1260 eV. From the curve fitting by Voigt function, the band can be deconvoluted into three bands at 284.6 (PC1), 285.2 (PC2), and 286.1 eV (PC3). The strongest PC1 is assigned to the C atoms binding to C atoms (C–C), and the weaker PC2 corresponds to the C atoms binding to N atoms (C–N). We ascribe the weakest PC3 to the other binding configurations such as C=O or C≡N that can be formed at the edge of graphite layers. This assignment is consistent with our recent work of the N-doped MWNTs [22].

![Fig. 3. (a) XPS survey scan spectrum. (b) The fine-scanned C 1s peak. The data points (open circles) are fitted by two Voigt functions PC1 (red dots), PC2 (blue dots), and PC3 (green dots). The sum of deconvoluted bands is marked by the lines. (c) The fine-scanned N 1s peak. The data points (open circles) are fitted by two Voigt functions PN1 (blue dots) and PN2 (red dots). The sum of deconvoluted bands is marked by the lines. (For interpretation of the references to color in this Figure, the reader is referred to the web version of this article.)](image-url)
favorable by releasing a strain of graphite sheets. This will be explained further using the following SCC-
DFTB calculations.

The VB spectrum measured using the photon energy 133 eV is displayed in Fig. 4. The spectrum of the N-
doped DWNTs has been compared with that of the un-
doped DWNTs. The zero energy is chosen at the Fermi
level $E_f$, which is the threshold of the emission spectrum. The spectrum is normalized using the intensity at 13 eV.
The intensity of the region between 2 and 12 eV is
noticeably higher for the N-doped DWNTs than the un-
doped DWNTs. This enhanced region is separated into
two parts; region A at 2–6.5 eV and region B at 6.5–
12 eV, which attributes to C 2p and N 2p electrons associated with $\pi$ bonds in graphite structure, and to C 2p
and N 2p electrons associated with bonds, respectively
[30,31]. Thus the presence of the N-binding structure increases the intensity of the A and B regions.

Our research group had already reported the relative
energy of three (5,5)@(10,10) DWNT conformers in
which the N structure is graphite-like and the total num-
er of N atoms is 6 [32]. The energy of the conformers G1, G2, and G3 is listed in Table 2. Herein, we calculate
the relative energy of the DWNT conformers containing
the pyridine-like N atoms. Two conformers P1 and P2,
in which three N atoms replace the C atoms of the outer and inner wall, respectively, are displayed in Fig. 5. The
4% N-doping of the inner wall results in the more stable
conformer ($-0.76$ eV) than the 2% N-doping of the outer
wall, as listed in Table 2. In order to examine the ef-
fect of defects on the stability of DWNTs, we calculate
the relative energy of the conformers D1 and D2 with
one C atom lacking in the outer and inner wall, respec-
tively. The defect in the inner wall induces more stable
conformer than that in the outer wall by $1.12$ eV.

The calculation shows that the N-doping of the inner
wall is more favorable than that of the outer wall for
both graphite-like and pyridine-like N structures. The formation of N-binding structure would release the
strains of curved graphite layers, more efficiently for
the inner wall than the outer wall. The defects in the
inner wall are also favorable by the same reason. The
incorporation of N atoms preferentially in the inner wall
may be thus thermodynamically driven during the
growth. For the pyridine-like N structures, the energy
decrease corresponding to 2% N increase of the inner
wall is more significant than the case of graphite-like
N structure. Due to the deficiency of C atoms, the pyr-
idine-like N structure would release the strain better
than the graphite-like N structure. Such strain-releasing
effect becomes larger for the smaller diameter, which ex-
plains the higher fraction of the pyridine-like N struc-
ture compared to the MWNTs.

In summary, we synthesized high-purity N-doped
DWNTs on the MgO-supported Fe–Mo catalysts using
the CVD of CH$_4$/NH$_3$ mixture at 850 °C. The DWNTs
form the bundles with a diameter of 10–20 nm. The out-
er diameter is in the range of 1.5–2 nm. As the photon
energy increases, the N content increases up to 3%, indi-
cating a higher N concentration at the inner wall. The deconvolution of fine-scanned N 1s peaks shows that
the pyridine-like and graphite-like N structures exist as
1:1 ratio. The XPS valence band analysis reveals that
the doped N atoms. We calcu-
late the stability of N-doped DWNT (5,5)@(10,10)

<table>
<thead>
<tr>
<th>Photon energy (eV)</th>
<th>PC1 (C–C)</th>
<th>PC2 (C–N)</th>
<th>PC3 (defects)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position (eV)</td>
<td>FWHM (eV)</td>
<td>Area %</td>
<td>Position (eV)</td>
</tr>
<tr>
<td>360</td>
<td>284.7</td>
<td>0.49</td>
<td>58</td>
</tr>
<tr>
<td>625</td>
<td>284.6</td>
<td>0.54</td>
<td>58</td>
</tr>
<tr>
<td>1000</td>
<td>284.6</td>
<td>0.76</td>
<td>48</td>
</tr>
<tr>
<td>1260</td>
<td>284.6</td>
<td>0.92</td>
<td>47</td>
</tr>
</tbody>
</table>

PN1 (pyridine-like) | PN2 (graphite-like)

| 1000 | 398.3 | 3.1 | 42 | 400.1 | 2.8 | 58 |
| 1260 | 398.3 | 3.4 | 46 | 400.2 | 3.0 | 54 |

Fig. 4. VB spectrum of XPS using photon energy 133 eV for N-doped and undoped DWNTs. The spectrum consists of two regions; region A at 2–6.5 eV and region B at 6.5–12 eV.
conformers using SCC-DFTB method. The N doping of the inner wall than the outer wall is thermodynamically favorable, which is more significant for the pyridine-like N structure compared to the graphite-like N structure.

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**References**


### Table 2

Relative energy of the N-doped DWNT conformers calculated using SCC-DFTB

<table>
<thead>
<tr>
<th>Conformer</th>
<th>N content (%)</th>
<th>Relative energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>G2</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>G3</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>P1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>P2</td>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C deficiency (%)</th>
<th>Inner</th>
<th>Outer</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>0</td>
<td>0.6</td>
</tr>
<tr>
<td>D2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

The total number of N atoms is 6. We only vary the number between outer and inner wall ([31]). The number of N atoms replacing C atoms is 3.

Fig. 5. (a) (5,5)@(10,10) DWNT doped with pyridine-like N atoms: (a) 2% in the outer wall and (b) 4% inner wall. The energy of (b) is −0.76 eV lower than that of (a).