Selective Removal of Metallic Single-Walled Carbon Nanotubes with Small Diameters by Using Nitric and Sulfuric Acids

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Coexistence of metallic and semiconducting carbon nanotubes has often been a bottleneck in many applications and much fundamental research. Single-walled carbon nanotubes (SWCNTs) were dissolved in HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} mixture to confirm differing reactivity between metallic (m) and semiconducting (s) SWCNTs. With HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} treatment, s-SWCNTs remained intact, while m-SWCNTs were completely removed for SWCNTs with small diameters less than 1.1 nm, which was confirmed by resonant Raman and optical absorption spectra. We also showed that nitronium ions (NO\textsubscript{2}\textsuperscript{+}) dissolved in the HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} solution could preferably attack the m-SWCNTs, which was supported by our theoretical calculation. This clear selectivity can be explained by the preferential adsorption of positively charged NO\textsubscript{2}\textsuperscript{+} on m-SWCNTs due to more available electron densities at the Fermi level in the m-SWCNTs. We report for the first time a selective removal of small-diameter m-SWCNTs by using HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} solution, which presented a striking contrast to the diameter-selective removal of SWCNTs by oxidative etching reported previously.

Introduction

The electronic structures of carbon nanotubes are determined by their chirality and diameter. Coexistence of metallic and semiconducting carbon nanotubes in the conventionally synthesized samples has been a serious obstacle in many applications and much fundamental research. Despite tremendous demand for the use of carbon nanotubes with a specific chirality in large-scale application to various devices, for instance, nanotransistors and memory devices that necessitate semiconductors, and electrodes for batteries and supercapacitors that favor the metallic ones, a chirality control has not been realized in the conventional synthesis approaches. Although several selective separation methods have been reported by posttreatment such as dielectrophoresis, surfactant, DNA, bromination, diazonium, and solution-phase oxymulation, a realistic separation method for high yield and massive quantities with a specific chirality of nanotubes is still highly desired. Furthermore, the fundamental reaction mechanism of nanotubes with adsorbates is still far from being clearly understood. In addition, according to previous reports, single-walled carbon nanotubes (SWCNTs) showed an oxidative etching effect, particularly small-diameter nanotubes. Recently, Banerjee and Wong demonstrated diameter-selective reaction of SWCNTs toward ozonation. Yudasaka et al. also reported the diameter-selective removal of SWCNTs by using light-assisted oxidation. However, these studies did not provide any evidence for selective reactivity dependent on metallicity of SWCNTs. Although Menna et al. investigated selectivity in a chemically oxidative attack of SWCNTs in a mixed solution of nitric and sulfuric acids (HNO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4}), they did not report on the metallicity-dependent selective reactivity particularly in small-diameter nanotubes and merely concluded that the nanotube diameter is the most important factor in determining their reactivity and destruction. In our previous study, we reported the effect of nitronium ion (NO\textsubscript{2}\textsuperscript{+}) in the selective removal of small-diameter metallic (m) SWCNTs. We treated the HiPco SWCNTs with nitronium hexafluoroantimonate (NO\textsubscript{2}SbF\textsubscript{6}; NHFA), which can produce NO\textsubscript{2}\textsuperscript{+}. According to the Raman spectra of the NHFA-treated HiPco SWCNTs, the semiconducting (s) SWCNTs remained intact with the NHFA treatment, while the m-SWCNTs were removed at small diameters less than 1.1 nm.

Here, we report for the first time a selective removal of m-SWCNTs with small diameters by using HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} solution, which could be achieved by adjusting the treatment conditions. We dissolved the SWCNT powder in a mixed solution of HNO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4} to determine differing reactivity between m-SWCNTs and s-SWCNTs in the solution. After HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} treatment, s-SWCNTs remained intact, while m-SWCNTs were completely destroyed and removed, especially nanotubes with diameters in a range of 0.9–1.1 nm, which was confirmed by resonant Raman spectra and optical absorption spectra. This result can be explained by the charge transfer from m-SWCNTs to NO\textsubscript{2}\textsuperscript{+} dissolved in the HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} solution, in good agreement with our theoretical calculations.

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Experimental Section

The 50 mg batches of pristine HiPco SWCNTs (Carbon Nanotechnologies Inc., two different batches) were immersed without pretreatment and stirred at room temperature in 50 mL mixtures of HNO₃ (60%)/H₂SO₄ (97%) with three different volume ratios (1:9, 1:3, and 1:2) for 12 and 48 h, respectively. This solution was filtrated through a membrane filter with a pore diameter of 10 µm and then washed with distilled water several times. After the leftover nanotubes on the filter and filtrated ones were dried, these samples were further heat-treated in Ar atmosphere for 1 h at 900 °C.

Field-emission scanning electron microscopy (FESEM) observations were carried out using a JSM6700F (JEOL) at 15 kV accelerating voltage. Raman spectroscopy measurements were performed using a microprobe RM1000 (Renishaw) at room temperature under ambient conditions. The Raman spectra were obtained by using excitation lasers with several wavelengths (514 (Ar ion laser), 633 (He–Ne laser), and 785 nm (diode laser)). To obtain optical absorption spectra (JASCO V-570), the powder sample was dissolved in 2-propanol and sprayed on the quartz substrate followed by heat treatment at 900 °C in Ar atmosphere. X-ray photoelectron spectroscopy (XPS; ESCA2000) was also taken to investigate the adsorbate effects. The measurements were done with Mg Kα excitation in a vacuum (<10⁻⁶ Pa) at room temperature. Theoretical calculations were performed within a generalized gradient approximation (GGA) using the computational package of PWSCF. We employed ultrasoft pseudopotential for ionic potentials, and the Kohn–Sham wave functions were described by plane waves with an energy cutoff of 35 Ry. The total charge of the system was maintained at zero due to the difficulties of modeling a charged system within the plane wave method. We defined an adsorption energy of molecules as $E_{ad} = E_{tot}^{(adsorbate+CNT)} - E_{tot}^{(adsorbate)} - E_{tot}^{(CNT)}$, where $E_{tot}$ is the total energy of a given system. The atomic positions were fully relaxed until the forces on each atom became less than 0.001 atomic unit.

Results and Discussion

Strong acid treatments of nanotubes have been introduced traditionally for purification, chemical oxidation, modification of lengths, and functionalization of the nanotube ends. Here we used various volume ratios of HNO₃/H₂SO₄ (1:9, 1:3, and 1:2) to investigate a selective attack of m-SWCNTs. In our approach, the HNO₃/H₂SO₄ treatment conditions (lower reaction temperature and no sonication) were rather mild, compared to the typical HNO₃/H₂SO₄ treatment for severe nanotube modification.

$$\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_2\text{O}^+ + 2\text{HSO}_4^-$$

The concentration of NO₂⁺ produced from HNO₃/H₂SO₄ solution, which is directly dependent on the volume ratio of HNO₃ and H₂SO₄, increases in the following order: HNO₃/H₂SO₄ (1:9) < HNO₃/H₂SO₄ (1:2) < HNO₃/H₂SO₄ (1:3).

By analogy, we conjecture that NO₂⁺ can attack π electrons on the carbon nanotube surface, which may lead to strong adsorption of NO₂⁺ on the nanotube surface and subsequent modification or disintegration of the nanotube wall by an oxidative etching. The most intriguing idea is that the m-SWCNTs can provoke stronger adsorption of NO₂⁺ with higher binding energy than s-SWCNTs due to more available charge density at the Fermi level which induces stronger charge transfer from SWCNT to NO₂⁺, similar to the diazonium adsorbates.

After the filtration followed by the HNO₃/H₂SO₄ (1:9) treatment, the morphology of the leftover nanotubes on the filter was similar to that of the pristine sample. However, the bundle size was slightly enlarged due to an aggregation effect in the solution (Figure 1). On the other hand, the filtrated SWCNTs in the precipitates were cut into small pieces and mostly disintegrated to carbonaceous particles, as shown in Figure 1. The leftover on the filter amounted to 65–70 wt %, depending on batches of HiPco SWCNTs used in the present study.

The selectivity in the metallicity with HNO₃/H₂SO₄ treatment can be clearly demonstrated in the resonant Raman spectra. All the samples were heat-treated in Ar gas ambient at 900 °C after the HNO₃/H₂SO₄ treatment. We identified various characteristic peaks in the radial breathing mode (RBM) using excitation lasers with three wavelengths (514, 633, and 785 nm). The diameters of SWCNTs were determined by the relation of $\omega \times \text{cm}^{-1} = 233d/\text{nm} + 14$. At 514 nm, we clearly observed two groups of s-SWCNTs near 183 cm⁻¹ and m-SWCNTs near 260 cm⁻¹ in the RBM of the pristine sample (Figure 2a) (characteristics of m- and s-SWCNTs were determined from the Kataura plot that is expressed by the relationship between transition energies and nanotube diameter). The metallic peaks (m-peaks) near 260 cm⁻¹ (diameter ~ 0.95 nm) disappeared completely after HNO₃/H₂SO₄ (1:9) treatment for 12 and 48 h and subsequent heat treatment in Ar gas ambient. On the other hand, the
semiconducting peaks (s-peaks) remained intact without a shift of the peak position, while maintaining the same intensity ratio among them. The Breit–Wigner–Fano (BWF) line at the lower energy side of G-bands was also drastically reduced, as shown in the right panel of Figure 2a, again indicating the removal of metallicity in the acid-treated samples. This phenomenon was fully reproducible with a different batch of HiPco SWCNTs. The second batch (batch 2) contained nanotubes with different diameter distributions, that is, higher metallicity at an excitation wavelength of 514 nm, as shown in the RBM (Figure 2b). The m-peaks were again mostly removed, whereas the s-peaks were significantly enlarged. Since adsorbates were fully removed by the heat treatment at 900 °C, as evidenced by the XPS data later, the removal of m-SWCNTs should be independent of the adsorbate effect. The D-band was slightly developed in this case, suggesting that the remaining SWCNTs were partially attacked during the treatment. On the other hand, the filtrated sample showed no RBM peaks and a prominently developed D-band (Figure 2c), which is characteristic of amorphous carbons. This observation is consistent with the FESEM image (Figure 1), showing that nanotubes were disintegrated into the carbonaceous particles. This can be also evidenced by the amount of loss (30–35 wt %) of the SWCNTs after the HNO3/H2SO4 treatments.

The resonant Raman spectra of the pristine sample at an excitation wavelength of 633 nm showed two m-peaks near 191 and 215 cm−1 and two s-peaks near 255 and 281 cm−1 (Figure 2d). With HNO3/H2SO4 (1:9) treatment of 12 h and subsequent heat treatment (batch 1), the s-peak near 281 cm−1 (diameter ~ 0.88 nm) was removed, suggesting that even s-SWCNTs with smaller diameters were removed. The rest of the peaks remained with a similar intensity ratio. The slight enhancement of the BWF line in the G-band after HNO3/H2SO4 treatment of 12 h reflects the reduction of s-SWCNTs (diameter ~ 0.88 nm). With longer HNO3/H2SO4 treatment of 48 h, the s-peak near 255 cm−1 (diameter ~ 0.99 nm) was rather intensified compared to the pristine sample, which was accompanied by considerable decrease of the m-peak intensity near 191 cm−1, resulting in slight decrease of the BWF line intensity. The m-peak (near 191 cm−1) should be related to both chiral and achiral (armchair and zigzag) nanotubes. According to the report by Menna et al., they assigned such an intensity decrease of the m-peak (near 191 cm−1) to higher reactivity of metallic zigzag nanotubes toward oxidation. Therefore, our result was probably associated with a lower adsorption barrier of metallic zigzag nanotubes with NO2+.

Figure 2. Raman spectra for HiPco SWCNTs. (a, b) RBM and G-band Raman spectra from the leftover on the filter for batch 1 and 2 HiPco SWCNTs at 514 nm excitation wavelength. The bottom (black), middle (blue), and top (red) lines are from the pristine, HNO3/H2SO4 (1:9) treatment for 12 h, and HNO3/H2SO4 (1:9) treatment for 48 h, respectively, followed by heat treatment at 900 °C in Ar atmosphere. (c) Raman spectrum of the filtrated sample after HNO3/H2SO4 (1:9) treatment for 12 h at 514 nm excitation wavelength. (d) Corresponding RBM and G-band Raman spectra for batch 1 and 2 HiPco SWCNTs at 633 nm excitation wavelength similar to (a). The RBMs were normalized with respect to the G-band. M_ii and S_ii correspond to metallic and semiconducting interband transitions.

less than 0.9 nm seemed to be etched away due to heavy strain, independent of metallicity (Figure 2a,b,d). Moreover, the large-diameter m-SWCNTs near 191 cm⁻¹ were reduced significantly but the m-peak at 215 cm⁻¹ was still present in the sample even after the HNO₃/H₂SO₄ treatment of 48 h, as shown in Figure 2d. Thus, the selective removal of m-SWCNTs becomes obscured at diameters greater than 1.1 nm. The similar behavior of the diameter-selective removal of m-SWCNTs was also obtained in batch 2 (Figures 2b,d and 3b).

We separated the RBM into three regions in order to explain the diameter dependence in a selective attack of SWCNTs by HNO₃/H₂SO₄ treatment, as indicated in Figures 2 and 3. In regime I, where the diameters are less than 0.9 nm, all SWCNTs were etched away. In regime II, where the diameters range from 0.9 to 1.1 nm, s-SWCNTs remained intact whereas m-SWCNTs were etched away. In regime III, where the diameters are greater than 1.1 nm, the m-SWCNTs were reduced significantly but not completely. If one uses starting SWCNTs with diameters less than 1.1 nm, only s-SWCNTs could be obtained on a large scale.

We provide a detailed analysis of the G-band in Figure 4. The pristine sample at 514 nm (Figure 4a) had two metallic (m) components (red) with a BWF line near 1513 cm⁻¹ and four semiconducting (s) components (blue) with Lorentzian lines near 1546, 1566, 1593, and 1600 cm⁻¹, similar to the previous report. Two m-components were completely removed after HNO₃/H₂SO₄ treatment, while s-components were intensified without a significant change in the peak positions. At 633 nm (Figure 4b), the pristine sample was fitted using two m-components and two s-components. After HNO₃/H₂SO₄ (1:9) treatment, the intensities of m-components were reduced, whereas those of s-components were enlarged. Therefore, these results again demonstrated the removal of small-diameter m-SWCNTs (at 514 nm) and the reduction of large-diameter m-SWCNTs (at 633 nm) in the HNO₃/H₂SO₄-treated sample.

To confirm the dependence of HNO₃/H₂SO₄ volume ratios in the diameter-selective removal of m-SWCNTs, we analyzed the RBM Raman spectra (514 and 633 nm) of SWCNTs treated with various volume ratios (1:9, 1:3, and 1:2) for 12 h (Figure 5). The RBM Raman spectra of SWCNTs treated with HNO₃/H₂SO₄ volume ratios of 1:3 and 1:2 show a tendency similar to that of the 1:9 sample. With HNO₃/H₂SO₄ treatments, m-SWCNTs are completely removed for SWCNTs with small diameters less than 1.1 nm (Figure 5a), while s-SWCNTs less than 1.1 nm remain intact (Figure 5b), regardless of HNO₃/H₂SO₄ volume ratios.

We also analyzed the RBM in Raman spectra (514, 633, and 785 nm) of the air-oxidized SWCNTs, which were heated in an air flow (350 °C, 1 h) without any further treatment (Figure S1 in the Supporting Information), to elucidate the difference in reactivity of SWCNTs between HNO₃/H₂SO₄ and simple gas-phase oxidation. After the gas-phase oxidation, the RBM peak intensities of SWCNTs with small diameters were dramatically reduced, regardless of metallicity. It is interesting to note that the gas-phase oxidation treatment clearly led to the diameter-selective removal of SWCNTs, which is in good agreement with previous studies, whereas the HNO₃/H₂SO₄ treatment strongly depended on the metallicity of SWCNTs.

Although Raman spectra provided some information for the removal of m-SWCNTs, this was excitation energy dependent due to the nature of the resonant Raman behavior and therefore could not provide quantitative information for the metallicity of SWCNTs with the limited number of excitation sources. Here
we provide optical absorption spectra to determine the overall content of m-SWCNTs. The spectrum was composed of three bands, two semiconducting $S_{11}$ and $S_{22}$ and one metallic $M_{11}$ interband transitions (Figure 6). Each subband peak is closely related to the SWCNT diameter. The diameter ranges (0.7–1.2 nm for semiconducting and 0.9–1.3 nm for metallic nanotubes) determined from the tight-binding model were in good agreement with that obtained from the Raman spectra (the agreement is better with the modified relationship between the transition energy and diameter that is based on trigonal warping effect). We emphasize that m-SWCNTs with small diameters less than 1.1 nm were removed, whereas s-SWCNTs with small diameters of up to 0.85 nm were still retained in the sample. These changes were in excellent agreement with observations from Raman spectra. Since the $S_{11}$ band might be modified more easily than the $S_{22}$ band, we extracted information for the content of m-SWCNTs using $S_{22}$ by $M_{11}/(M_{11} + S_{22})$. This value was 38% from the pristine sample, comparable to the theoretically estimated value of 30%. The content of m-SWCNTs in the acid-treated sample was significantly reduced to 20% due to removal of m-SWCNTs with small diameters.

The selective removal of m-SWCNTs can be understood by NO$_2^+$ adsorption on nanotubes. O 1s XPS spectra show that the C–O bonds near 532.3 eV are developed with HNO$_3$/H$_2$SO$_4$ (1:9) treatment and reversed after heat treatment at 900 °C (Figure 7a). This is in somewhat good contrast to the general belief that N sites in NO$_2^+$ prefer to adsorb on the nanotube surface, not O sites. N 1s XPS spectra also show that the amount of C–N related peaks is increased with HNO$_3$/H$_2$SO$_4$ (1:9) treatment of 48 h (Figure 7a). The adsorption of NO$_2^+$ involves strong charge transfer between nanotubes and nitronium ions, thus shifting the peak positions in the Raman spectra; the peak positions were recovered after heat treatment, indicating recovery of electronic structures of nanotubes (Figure S2 in the Supporting Information). Moreover, the disappeared m-peaks (514 nm) by HNO$_3$/H$_2$SO$_4$ treatment were still not visible even after post heat treatment (Figure S2), which is in good contrast to the diazonium treatment reported previously. This N 1s peak again disappeared after heat treatment. This implies that the NO$_3^-$ can be adsorbed at first on the nanotube wall in various forms and desorbed in the following heat treatment. The adsorption of NO$_2^+$ is promoted by the presence of H$_2$SO$_4$ that can be easily intercalated into the SWCNT bundles in the form of H$_2$SO$_4$. This priori intercalation process is necessary to provide more available surface for NO$_2^+$ to adsorb on the tube wall. Once NO$_2^+$, particularly oxygen sites, is adsorbed on the tube wall, the tube walls can easily be damaged and disintegrated, similar to etching processes under oxygen gas atmosphere.

To understand the adsorption energetics of the NO$_2^+$, we performed first-principles calculations for NO$_2$ adsorption on $(n,0)$ zigzag nanotubes using GGA. The nanotube can be regarded as a metallic (or semimetallic) one, when $n$ is a multiple of 3. Otherwise they are semiconducting with a finite band gap. Figure 7b shows a physisorbed NO$_2$ molecule on the nanotube wall. The computed adsorption energies ($E_{ad}$) for various sizes of nanotubes are given in Table 1. We note that $E_{ad}$ on m-SWCNTs was consistently lower than that on s-SWCNTs.

Figure 5. RBM Raman spectra at excitation wavelengths of (a) 514 and (b) 633 nm from the leftover on the filter for batch 1 HiPco SWCNTs treated with HNO$_3$/H$_2$SO$_4$ solutions of different volume ratios for 12 h, followed by heat treatment at 900 °C in Ar atmosphere. HNO$_3$ and H$_2$SO$_4$ were mixed in three different volume ratios of 1:9, 1:3, and 1:2, respectively.

Figure 6. Subtraction of baselines and Lorentzian fittings for optical absorption spectra for batch 2 HiPco SWCNTs. Absorption spectra from (a) the pristine and (b) HNO$_3$/H$_2$SO$_4$ (1:9) treated samples for 48 h, followed by heat treatment at 900 °C in Ar atmosphere. $M_{ii}$ and $S_{ii}$ correspond to metallic and semiconducting interband transitions.
oxygen atoms was chemically bound to the tube wall (Figure 7c) or an NO\textsubscript{2} molecule was attached parallel to the surface (Figure 7d). These are possible intermediate states along the path to the disintegration of nanotubes. The latter configuration involves both C–O and C–N chemical bonds, in excellent agreement with the XPS data among model systems considered here. The energy loss compared to the physisorbed configuration was attributed to the deformation of the nanotube and the NO\textsubscript{2} molecule. The adsorption could become exothermic in the bundled nanotubes in liquid state or by cooperative processes involving several molecules.\textsuperscript{38} The exothermic adsorption energetics could be also realized by an additional adsorption of hydroxyl group. The tendency of $E_{\text{ad}}$ for precursor states shown in Table 1 indicates that the curvature of the nanotube wall plays an important role in stabilizing precursor states, especially in the case of precursor (Figure 7d), where $E_{\text{ad}}$ monotonically increases with the nanotube radius. These precursor states could be transformed to strongly chemisorbed ones by being squeezed into the bundles. Therefore, the selectivity addressed by the physisorbed configuration will result in the removal of the metallic component efficiently for small-diameter nanotubes. The theoretically predicted energetics of NO\textsubscript{2} adsorption may not be directly applicable to the experiments that were done in a liquid phase. Moreover, the adsorption energy could be enhanced by the presence of the SWCNT bundles. Nevertheless, it should be stressed that this theoretical prediction is consistent with the above experimental observations that the selective removal is most clear for nanotubes with diameters less than 1.1 nm.

**Conclusions**

We have clearly presented that m-SWCNTs with small diameters less than 1.1 nm are selectively removed by using

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**Figure 7.** (a) XPS spectra of O 1s and N 1s for batch 1 HiPco SWCNTs. The pristine sample (black), HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} (1:9) treated ones for 12 h (green), and HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} (1:9) treated ones for 48 h (blue), followed by heat treatment at 900 °C in Ar atmosphere (red). (b), (c), and (d) are the geometric models for physisorbed and precursor states on the (12,0) nanotube, which were determined from the density functional calculations. The red and blue atoms indicate oxygen and nitrogen atoms, respectively.

**TABLE 1: Adsorption Energies Calculated from GGA for Various Diameters of Nanotubes**

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<th>Diameter (nm)</th>
<th>(n,0)</th>
<th>(9,0)</th>
<th>(10,0)</th>
<th>(11,0)</th>
<th>(12,0)</th>
<th>(17,0)</th>
<th>(18,0)</th>
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<tr>
<td>$E_{\text{ad}}$ (eV)</td>
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<tr>
<td>Physisorbed (Figure 7b)</td>
<td>0.39</td>
<td>−0.28</td>
<td>−0.26</td>
<td>−0.37</td>
<td>−0.29</td>
<td>−0.34</td>
<td></td>
</tr>
<tr>
<td>Precursor (Figure 7c)</td>
<td>0.12</td>
<td>0.40</td>
<td>0.46</td>
<td>0.36</td>
<td>unstable</td>
<td>unstable</td>
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<tr>
<td>Precursor (Figure 7d)</td>
<td>2.02</td>
<td>2.43</td>
<td>2.52</td>
<td>2.60</td>
<td>3.11</td>
<td>3.08</td>
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Selective Removal of Metallic SWCNTs
HNO3/H2SO4 treatment. The selective etching of small-diameter m-SWCNTs should be achieved by an attack of NO3+ during the HNO3/H2SO4 treatment, which was supported by our previous report on NHFA treatment of SWCNTs. The selective removal of small-diameter m-SWCNTs by HNO3/H2SO4 treatment was more effective compared with that by the NHFA treatment. Positively charged NO3+ preferred to selectively adsorb on m-SWCNTs with stronger binding energy compared to the counterpart s-SWCNTs. This was attributed to more available electron densities at the Fermi level in m-SWCNTs. This difference became obscured for SWCNTs with diameters greater than 1.1 nm. This strain-induced chirality separation by NO3+ was confirmed by our theoretical calculations. The small-diameter m-SWCNTs strongly bound with NO3+ by HNO3/H2SO4 treatment were destroyed and the Raman peak positions of the remaining s-SWCNTs were recovered by thermal annealing at high temperature, suggesting that the electronic structures of nanotubes are almost recovered after post heat treatment. We expect that our approach of the mild acid treatment followed by thermal annealing could provide a novel route to separate s-SWCNTs from a mixture of m- and s-SWCNTs in mass quantity, although the chirality selectivity was not clear for SWCNTs with diameters greater than 1.1 nm. The selectivity relies strongly on the nanotube diameter, and a more sophisticated process should be designed for a higher yield of s-SWCNTs. We again emphasize that the selective removal of small-diameter m-SWCNTs by NO3+ produced from HNO3/H2SO4 solution presented a striking contrast to the diameter-selective removal of SWCNTs by oxidative treatments reported previously.13–16

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Supporting Information Available: Figure S1, RBM Raman spectra (514, 633, and 785 nm) for air-oxidized HiPco SWCNTs; Figure S2, RBM Raman spectra (514 nm) for HNO3/H2SO4 (1:9) treated HiPco SWCNTs before and after heat treatment at 900 °C; Figure S3, redistribution of electronic density as calculated by Δρ = ρ(CNT+NO3) − ρ(CNT) − ρ(NO3). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes