A diameter-dependent separation of semiconducting from metallic single-wall carbon nanotubes by using nitronium ions

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Abstract

We have reported the density-functional calculations of NO2 adsorption on single-walled carbon nanotube (SWCNTs) walls. We find that NO2 adsorption is strongly electronic structure- and strain-dependent. The NO2 adsorption on metallic nanotubes (m-SWCNTs) was energetically more favorable than that on semiconducting nanotubes (s-SWCNTs) and furthermore the adsorption became less stable with increasing diameters of nanotubes. The adsorption barrier height shows similar dependence on the electronic structure and diameter to the adsorption energy. On the base of our theoretical model, we have found a method for a diameter-selective removal of metallic single-walled carbon nanotubes (m-SWCNTs) from semiconducting (s-) ones by stirring or sonication SWCNT powder in tetramethylene sulfone (TMS)/chloroform solution with nitronium hexafluoroantimonate (NO2SbF6: NHFA) and nitronium tetrafluoroborate (NO2BF4: NTFB). Positively charged nitronium ions were intercalated into nanotube bundles, where the intercalation was promoted also by the counter ions. Nitronium ions selectively attacked the sidewall of the m-SWCNTs due to the abundant presence of electron density at the Fermi level, thus yielding stronger binding energy compared to the counterpart s-SWCNTs. The s-SWCNTs were left on the filter after filtration, whereas the m-SWCNTs were disintegrated and drained away as amorphous carbons. The effectiveness of removing m-SWCNTs was confirmed by the resonant Raman spectra and absorption spectra.

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1. Introduction

Carbon nanotubes (CNTs) have been the leading functional materials in nanoscience and nanotechnology and have been investigated most extensively compared to their counterparts such as nanoparticles and nanowires due to their scientific and technological importance, since the discovery of multiwalled carbon nanotubes by Iijima in 1991 [1], and single-walled carbon nanotubes (SWCNTs) synthesized by catalytic arc discharge [2,3]. CNTs show very wide applications in various disciplines; application areas cover very widely for field emitters [4,5], hydrogen storage [6,7], transistor [8,9], secondary battery [10,11], supercapacitor [12–14], fuel cell [15–17], gas sensor [18,19], nanocomposites [20], and nanoprobes [21]. All these applications are closely related to their unique atomic and electronic structures.
The electronic structure of CNT is determined by their chirality and diameter, which are not selectively controlled by conventional synthesis approaches. The present state of art technology for CNT synthesis always produced samples with mixing chiralities. The coexistence of metallic (m-SWCNTs) and semiconducting single-walled carbon nanotubes (s-SWCNTs) in commercially available samples has been a bottleneck for many fundamental researches and applications with high device performance, such as nanotransistors, memory devices, and chemical/bio-nanosensors. Post-treatments of samples are necessary to selective chirality separation for high performance and reproducibility of devices. Several methods of separating semiconducting nanotubes from metallic ones or vice versa using dielectrophoresis, octadecylamine (ODA), alkyl amine, bromination, porphyrins, and DNA have been reported [22–28]. Dielecrophoresis method requires a priori nanodispersion of nanotubes for high yield of separation and may not be scalable to large quantity. Preferential adsorption of ODA and DNA on semiconducting nanotubes can give rise to high separation yield but an extra work is necessary to remove additives. Bromination and porphyrins approach are easy and straightforward to understand but leaves a poor separation yield. Therefore, a realistic separation method for high yield and massive quantities of specific metallicity is still lacking.

Another approach is the functionalization that leads to transform the electronic structures of nanotubes. Strong chemisorption by hydrogenation and fluorination transformed electronic structures from m-SWCNTs to s-SWCNTs by inducing a partial sp³ hybridization [29,30]. This sometimes deteriorated the nanotube walls, leading to a disintegration into amorphous carbons or graphitic layered structures [31]. The diazonium salts have been also introduced to react with the nanotubes to extract electrons from nanotubes in the formation of a covalent ary1 bond, demonstrating chemoselective reactions with metallic versus the semiconducting nanotubes [32]. Thermal annealing of the diazonium-treated nanotubes at 300 °C cleaved the aryl moieties from the sidewalls and recovered the spectroscopic signatures of the pristine nanotubes. Small-diameter nanotubes have been selectively removed by an oxidative etching particularly with an assistance of light illumination [33,34].

We found that the treatment of SWCNTs with an appropriate volume ratio of nitric/sulfuric acids (1:9) made s-SWNTs highly enriched, as shown in Fig. 1. We clearly observed two groups of s-SWNTs near 180 cm⁻¹ and m-SWNTs near 260 cm⁻¹ in the RBM of the pristine sample (Fig. 1A). The metallic peaks near 260 cm⁻¹ (diameter ~ 0.93 nm) disappeared completely after nitric/sulfuric acids treatments for 48 h (Fig. 1B). This was a rather mild condition compared to the typical volume ratio (1:3) for severe nanotube modification. No color change was observed during the stirring SWCNTs powder in the mixture of nitric/sulfuric acids solution, demonstrating that the metal catalyst particles were not melted under the current mild acid treatment. It is well known that mixing nitric and sulfuric acids yields a high production rate of nitronium ions (NO₂⁺), which can easily attack π electrons in aromatic rings, leading to nitration, as shown in Fig. 2 [34]. By analogy, we conjecture that the nitronium ions can attack π electrons on the carbon nanotube surface, which may lead to strong adsorption of nitronium ions on the nanotube surface and subsequent modification or disintegration of the nanotube wall. The most intriguing idea is that the m-SWNTs can provoke stronger adsorption and Thus, the treatment of SWCNTs with an appropriate volume ratio of nitric/sulfuric acids (1:9) made s-SWNTs highly enriched, as shown in Fig. 1. We clearly observed two groups of s-SWNTs near 180 cm⁻¹ and m-SWNTs near 260 cm⁻¹ in the RBM of the pristine sample (Fig. 1A). The metallic peaks near 260 cm⁻¹ (diameter ~ 0.93 nm) disappeared completely after nitric/sulfuric acids treatments for 48 h (Fig. 1B). This was a rather mild condition compared to the typical volume ratio (1:3) for severe nanotube modification. No color change was observed during the stirring SWCNTs powder in the mixture of nitric/sulfuric acids solution, demonstrating that the metal catalyst particles were not melted under the current mild acid treatment. It is well known that mixing nitric and sulfuric acids yields a high production rate of nitronium ions (NO₂⁺), which can easily attack π electrons in aromatic rings, leading to nitration, as shown in Fig. 2 [34]. By analogy, we conjecture that the nitronium ions can attack π electrons on the carbon nanotube surface, which may lead to strong adsorption of nitronium ions on the nanotube surface and subsequent modification or disintegration of the nanotube wall. The most intriguing idea is that the m-SWNTs can provoke stronger adsorption and

![Fig. 1. Fitting of radial breathing mode Raman spectra (514 nm excitation) for SWNTs before and after HNO₃/H₂SO₄ treatment for 48 h.](image)

![Fig. 2. Mechanism of electrophilic aromatic substitution by nitronium ion in benzene.](image)
of nitronium ions with higher binding energy than s-SWNTs due to more available charge density at the Fermi level which induces stronger charge transfer from nanotube to nitronium ion, as shown in Fig. 3.

Our aim is to theoretically and experimentally prove our analogy about the chiral separation of SWCNTs by nitronium ions. Therefore, we have established that theoretical model to explain the electronic structure-dependent adsorptions on SWCNTs by NO2 molecules. In this report, we demonstrate a selective reactivity of NO2 molecules on the sidewall of SWCNTs by calculating the adsorption energy and adsorption barrier height. Here we also report a new method of removing small-diameter m-SWCNTs from s-SWCNTs by dispersing SWCNT powder in tetramethylenesulfone (TMS)/chloroform solution with nitronium ions \( \text{NO}_2^+ \). This method is simple and straightforward without altering electronic structures after treatment, and furthermore easily scalable for the large quantity of SWCNTs with high separation yield.

2. Experimental

2.1. Theoretical approaches

We used a self-consistent charge-density-functional-based tight-binding (SCC-DFTB) method to optimize adsorbed geometries of NO2 molecules on the SWCNT sidewall. The charge transfer was taken into account through incorporation of a self-consistent scheme for Mulliken charges based on the second-order expansion of the Kohn–Sham energy in terms of charge-density fluctuations [35]. We also used the density-functional calculations within generalized gradient approximation (GGA) to check the validity of our tight-binding calculations. We adopted Vanderbilt ultrasoft pseudopotential for ionic potentials [36,37]. The exchange-correlation energy in GGA was parameterized by Perdew and Wang's scheme [38]. The Kohn–Sham wave functions were expanded in plane waves with an energy cutoff of 35 Ry, which is necessary to maintain the accuracy of the total energy. We chose armchair and zigzag nanotubes for the calculations. The SCC-DFTB calculations were done with large supercells of 18 layers for armchair tubes and those of 20 layers for zigzag tubes along the tube axis with a periodic boundary condition. The convergence in the energy with different number of layers was tested [39]. We define an adsorption energy of molecules as

\[ E_{\text{ad}} = \frac{E_{\text{tot}}(\text{adsorbate} + \text{CNT}) - E_{\text{tot}}(\text{adsorbate}) - E_{\text{tot}}(\text{CNT})}{C_0} \]

where \( E_{\text{tot}} \) is the total energy of the system. Atoms were fully relaxed by the conjugate gradient method in SCC-DFTB and GGA calculations until the forces on each atom became less than 0.001 atomic units.

2.2. Experimental approaches

Nitronium hexafluoroantimonate (NO2SbF6; NHFA) or nitronium tetrafluoroborate (NO2BF4; NTFB) of 50 mmol was dissolved in TMS/chloroform (1:1 by weight) solution of 100 ml. The nitronium salts were ionized in the mixed solvent as follows:

\[ \text{NO}_2\text{SbF}_6 \rightarrow \text{NO}_2^+ + \text{SbF}_6^- \quad \text{or} \quad \text{NO}_2\text{BF}_4 \rightarrow \text{NO}_2^+ + \text{BF}_4^- \]

where both reactions produced nitronium ions.

The pristine HiPCO SWCNT soot of 10 mg purchased from CNI (Carbon Nanotechnologies Inc.) was suspended by either stirring for 4 weeks or sonicating for 24 h in the prepared NHFA or NTFB solution at 60 °C under N2 bubbling. After reaction, the suspension was filtered using a membrane filter with a pore diameter of 10 μm and then washed with an ethanol several times. The residual SWCNTs on the filter treated with NHFA or NTFB solution were dried in vacuum at 100 °C for overnight, and further heat-treated in a vacuum at 1000 °C for 30 min. Fig. 4 shows the sequence of procedures for the sample treatment.

The metallicity of samples was characterized by the resonant Raman spectroscopy (Renishaw, microprobe RM1000) with several wavelengths of 514.5 nm (Ar+ ion laser), 632.8 nm (He–Ne laser), and 785 nm (diode laser). Samples were further analyzed by the field-emission scanning electron microscope (FESEM; JEOL 6700F). X-ray photoelectron spectroscopy (XPS) was carried out using PHI 5100 spectrometer using Mg-Kα (1253.6 eV) line. The SWCNT powder was immersed in isopropanol solution and sonicated for dispersion for 4 h. The absorption spectras were obtained by dropping a solution on a quartz plate using UV–vis–NIR spectrophotometer (Hitachi U-3501).
3. Results and discussion

In Fig. 4, the FESEM images of the filtrated solids, and NHFA-treated SWCNTs on the filter are shown. The bundle size of the residual SWCNTs on the filter was enlarged due to an aggregation effect in solution without a distinct deformation of the nanotube walls. On the other hand, the morphology of the filtrated solid appeared somehow completely different from that of the pristine SWCNTs. The SWCNTs were hardly seen and mostly fragmented into small pieces, forming carbonaceous particles. The dispersed pristine SWCNTs in TMS/chloroform without NHFA or NTFB have not been filtrated through a membrane filter with a pore diameter of 10 μm. Therefore, we emphasized that the only nanotubes disintegrated by the NHFA were filtrated through the filter. Similar trends were observed with the NTFB treatment. It has been well known that the graphite surface can be attacked easily by nitronium ions at the graphite surface [40]. The nitronium ions capture the available π electrons in the (metallic) graphite, enhancing the binding energy with graphite surface. Since the SWCNTs have also similar π electrons on the surface except the strain effect, we expect that the nitronium ions can attack π electrons on the nanotube wall and thus provoke stable adsorption. The availability of the electrons at the Fermi level is a key factor to determine the binding nature, similar to the diazonium effect [32]. Since the m-SWCNTs have more abundant electron charge density at the Fermi level than the counterpart s-SWCNTs, we expect that nitronium ions can be adsorbed more strongly on m-SWCNT sidewalls than on s-SWCNT ones. Strong adsorption of nitronium ions may attack the m-SWCNT sidewalls, as shown in Fig. 3, and furthermore disintegrate the nanotube walls, as observed in our experiments.

The disintegrated m-SWCNTs by an attack of nitronium ions during NHFA treatment were filtrated out during the filtering process. Fig. 5A shows the Raman spectra of the filtrated solids at the excitation energy of 514 nm. The pristine sample clearly reveals the G-band near 1590 cm⁻¹, small D-band near 1330 cm⁻¹, and the radial breathing modes.
(RBM) near 100–300 cm$^{-1}$, demonstrating a typical behavior of SWCNTs. In good contrast with this, the D-band of the filtrated sample, which is a characteristic of amorphous carbons or defects, increased drastically, while the RBM peaks near 100–300 cm$^{-1}$ were completely disappeared. After heat treatment at 1000 °C, the ratio of D-band to G-band was not reduced and furthermore the RBM modes were not recovered. The XPS C1s spectra of the pristine sample in Fig. 5B show two characteristic peaks near 284.5 eV, sp$^{2}$-hybridized or graphitic carbons, and 285.3 eV, sp$^{3}$-hybridized or defective carbons [41]. This peak became broadened after NHFA treatment and furthermore the ratio of sp$^{3}$-like bonds to sp$^{2}$-like bonds was significantly increased. The broad peak near 287.5 eV and the small peak near 282 eV (carbidic carbon) [14] together with the broadened main peaks indicated the filtrated solids to be functionalized by various adsorbates. The broad peak was still maintained after heat treatment, although the intensity of the graphitic peak was increased due to the crystallization effect. These lead to the conclusion that the filtrated SWCNTs were disintegrated into amorphous carbons, in good agreements with the SEM morphology for the precipitated solids (Fig. 4). Interestingly, the amount of the sample loss after filtration was about 25–30 wt.%, close to the theoretically estimated metallic content. Similar results were obtained with NTFB treatment, although the reactivity was less effective. This implies that the anion plays an important role during reaction as an intercalator into the bundle. The anion size ($\text{SbF}_6^-$) of the NHFA is larger than $\text{BF}_4^-$ of NTFB, providing more rooms for nitronium ions to be intercalated into the bundle, as shown in Fig. 6.

Here we propose schematically a concerted pathway of the intercalation induced by the NHFA treatment as follows (Fig. 6). The NHFA was ionized in TMS/chloroform solvent into nitronium ions and hexafluoroantimonate ions as follows (Step 1) [42]. $\text{SbF}_6^-$ ions are first inserted along with solvent molecules into SWCNT bundles, where the debundling of nanotubes is enhanced by the charge transfer, similar to the sulfuric acids [43]. This provides more room for $\text{NO}_2^+$ ions to intercalate into the nanotube bundles, expanding the interlayer distances in bundles, similar to the graphite (Step 2) [30]. The $\text{NO}_2^+$ ions capture the available π electrons in the graphite, enhancing the binding energy with graphite surface. Since π electrons of SWCNT surface are similar that of the graphite, we expect that the $\text{NO}_2^+$ ions can attack π electrons on the nanotube surface and thus provoke stable adsorption. The binding of $\text{NO}_2^+$ ions with nanotubes could be promoted by an assistance of strain effect present in the tube wall. This weakens the tube–tube interactions. The nanotube dispersion into individual nanotubes or small-sized bundles is enhanced by the physical excitation with sonication.

Fig. 7 shows HRTEM images of the filtrated (precipitated) solids. We obviously see that almost SWCNT

![Fig. 6. Schematic diagram for the intercalation of NHFA.](image)

![Fig. 7. HRTEM images of the filtrated (precipitated) solids.](image)
bundles are transformed into amorphous carbonaceous particles by treatment of NHFA. We also note some graphitic phases with a lattice parameter of about 0.34 nm (red circle). The shortened SWCNT bundles with under 10 nm length are also observed (blue circle). The attack and covalent bonding of nitronium ions on sidewall of m-SWCNTs will cause the different C–C bond lengths and thus heavy strain on the m-SWCNTs wall. The local strain can be accumulated in the tube wall of the bundle due to covalent bonding of nitronium. This may enhance destruction of tube structures to those with small piece of bundles. The next step is the fragmentation of the shortened bundles into small pieces of amorphous particles or graphitic phases induced again by the continuously attack of nitronium ions.

In order to clarify the nature of metallicity of the residual sample on the filter, we investigated the resonant Raman spectra. The SWCNTs were drop casted on quartz substrate. The numbers in the Fig. 8 indicates the corresponding diameters from each peak determined by \[ \omega \text{ (cm}^{-1}) = 235/d \text{ (nm)} + 9 \] [44]. The metallic and semiconducting bands indicated by the dotted square boxes were determined from the Kataura plot [45]. We identified five distinct peaks in the RBM mode from the pristine sample at an excitation energy of 514 nm in Fig. 8A. The RBM bands can be grouped into two characters: semiconducting S_{33} band (183 and 204 cm\(^{-1}\)) and metallic M_{11} band (244, 259, and 266 cm\(^{-1}\)). Interestingly, the metallic band was completely removed after NHFA treatment, whereas the semiconducting peaks were slightly upshifted. This implies

![Fig. 8. RBMs of Raman spectra with excitation energies of 514 nm (A, D), 785 nm (B, E), and 633 nm (C, F) for the pristine sample, the residual sample on the filter after the NHFA treatment by either stirring for 4 weeks (NHFA) or sonicating for 24 h (soni-NHFA), and the residual sample with further heat treatment at 1000 °C (NHFA-HTT or soni-NHFA-HTT) in a vacuum.](image-url)
that nitronium ions could be adsorbed even on s-SWCNTs so as to upshift the peak positions due to the charge transfer to the nitronium ions, similar to an acceptor behavior [30]. After heat treatment at 1000 °C in a vacuum, the peak shift of the semiconducting band was recovered and the peak was intensified. All the adsorbates were removed after heat treatment, which will be discussed later in the XPS analysis. However, the metallic band was still not visible. Therefore, the disappearance of the metallic band was not due to the shift of the resonance, in good contrast with the previous works that the disappeared band in the RBM by the diazonium adsorption was recovered simply due to the desorption after heat treatment, leaving unaltered electronic structures of nanotubes [32,46].

Fig. 8B shows the RBM profiles at an excitation energy of 785 nm. In this case, we observed only the semiconducting S22 band (205, 216, 226, 234, and 267 cm−1) from the pristine sample. The peak intensities of the large-(1.22 nm) and small- (0.92 nm) diameter nanotubes were reduced and the peak positions were slightly upshifted after NHFA treatment. The large-diameter nanotubes form a rather large interstitial space in the bundle to provide better accessibility for adsorbates [47-49]. On the other hand, in small-diameter nanotubes, the ratio of adsorbate to nanotube is high and furthermore large strain induces strong binding energy with adsorbates [47-49]. This provokes to violate the resonance condition and shifts the peak positions. The related peak intensities were reduced as shown in figure. These peaks were fully recovered again with similar intensity ratios and peak positions after heat treatment. The binding energy of nitronium ions to the sidewall of the semiconducting nanotubes was not strong enough to destroy nanotubes during adsorption and desorption, such that the electronic structures of s-SWCNTs remained unchanged after heat treatment. We emphasize here that s-SWCNTs with small diameters of 0.92 nm were not disintegrated after treatments, whereas the corresponding metallic band with diameters less than 1.1 nm was completely removed in Fig. 8A. This strongly suggests that the nitronium ions attacked selectively the m-SWCNTs with small diameters less than 1.1 nm.

We also observed the Raman spectra with an excitation energy of 633 nm, as shown in Fig. 8C. In this case, the metallic bands at 216 cm−1 (1.16 nm) and 192 cm−1 (1.32 nm) and the semiconducting bands at 256 cm−1 (0.97 nm) and 281 cm−1 (0.88 nm) appeared in the pristine sample. The small-diameter (0.97 nm) s-SWCNTs were attacked to lead to a partial disintegration after NHFA and heat treatments, which is in good contrast with completely recovered semiconducting peak of 0.92 nm at 785 nm. The semiconducting peak at 281 cm−1 (0.88 nm) was completely disappeared. The strain is too large, 0.12 eV/atom in this case [50], such that nanotubes can be disintegrated independent of the metallicity. The metallic band was upshifted with NHFA treatment, confirming again an adsorption of nitronium ions, and was recovered again after heat treatment, similar to the semiconducting one in Fig. 8B. Yet, the preferable binding energy on m-SWCNTs to that of s-SWCNTs was not large enough to disintegrate m-SWCNTs, as predicted from theoretical calculations [51]. The selective attack of metallic nanotubes became unclear at nanotubes with diameters of greater than 1.1 nm. This inconsistent result may originate from the inhomogeneous distribution of nanotubes with different diameters in the bundle. Similar phenomena were also observed in ODA-treated samples [24]. Instead of having long stirring time of 4 weeks, we also tried short treatment time of 24 h with sonication. The effects were very similar, as shown in Fig. 8D–F. The sonication approach seemed to be more effective in removing large-diameter m-SWCNTs, as shown in Fig. 8F. The sonication generally gives a better dispersion of nanotubes and thus promotes the reaction of nanotubes with adsorbates.

So far we learned that the selective disintegration of m-SWCNTs is diameter-dependent. At small-diameter nanotubes of less than 1.1 nm, both the strain effect and the abundance of charge density at the Fermi level play a dominant role for a selective removal of metallic nanotubes. However, at large-diameter nanotubes of greater than 1.1 nm, the strain effect may be excluded. This strongly suggests that the selective adsorption on metallic nanotubes can be achieved by the abundant presence of charge density at the Fermi level and the extra strain effect should be accommodated in order to destroy the nanotube walls.

The absorption spectra in the infrared and visible ranges can provide information for metallicity of the whole sample, which cannot be obtained practically from resonant Raman data. It is well established that the optical response of SWCNTs is dominated by transitions between peaks in the electronic density of states, with momentum conservation allowing transition pairs of van Hove singularities with a mirror symmetry to the Fermi level [52–54]. Furthermore, the widths and fine structures of these absorption bands are specifically related to the distribution of diameters and chiralities of nanotubes [55,56]. The optical absorption spectra of the pristine and NHFA-treated SWCNTs were compared in Fig. 9 to distinguish the metallicity between two samples. In the pristine SWCNTs, transitions between the first and second van Hove singularities (S11 and S22) in s-SWCNTs were observed near 0.9 eV (S11) and 1.5 eV (S22), whereas the related peak (M11) in m-SWCNT was observed near 2.0 eV. Although the nanodispersion of the pristine SWCNTs was insufficient in isopropyl alcohol followed by a drop casting on quartz substrate, several subband peaks in each band were clearly visible. On the other hand, several subband peaks in the NHFA-treated SWCNTs were suppressed due to the formation of large bundles during NHFA treatment, as shown in Fig. 4. In short, the intensity of the M11 transition peak of the NHFA-treated SWCNTs was greatly suppressed due to the selective removal of m-SWCNTs. Moreover, the transition energies of the semiconducting peaks were all downshifted, suggesting that even for
semiconducting nanotubes, some portions of the small-diameter s-SWCNTs were also removed.

In order to determine the separation yield, we performed the curve fitting of the absorption spectra. The transition energy is inversely proportional to the tube diameter \[57,58\]. The diameter distribution, which is written on the fitted curves in Fig. 9A and B, clearly demonstrated the removal of small-diameter SWCNTs by the NHFA treatment. The small amount of M11 transitions at lower energy side (large diameter) still remained in the sample even after NHFA treatment. We note that the semiconducting nanotubes with small diameters near 0.95 and 1.03 nm were still visible in the NHFA-treated sample. These changes were in good agreements with the Raman data. The previous theoretical calculations demonstrated that the NO2 binding energy with the metallic nanotube was stronger than that with semiconducting nanotube due to large charge transfer and furthermore the binding energy of each chiral nanotube became weaker with increasing diameters. The separation yield of the sample can be drawn by the ratio of S22 and M11 transitions in the optical absorption spectra. Since the S11 band might be modified more easily than the S22 band \[55\], we extracted information of the separation yield from \(S_{22}/(S_{22} + M_{11})\). This value was 0.63 from the pristine sample, close to the theoretical estimate. This increased to 0.86 after the NHFA treatment followed by thermal annealing. If one starts with small-diameter nanotubes less than 1.1 nm, the yield of separation would be close to 100%. Our approach with nitronium ions in solvent is easily scalable to large quantity treatment and moreover no additive is left in the sample without altering the electronic structures of nanotubes such that the separated nanotubes can be directly used for other purposes.

We first search for the stable adsorption geometry of a single NO2 molecule to explain the experimental results. Fig. 10 shows the top view of the several stable geometries of NO2 adsorbed on the (9,0) zigzag nanotube optimized by the SCC-DFTB. The most stable configuration is shown in Fig. 10A, where a single NO2 molecule is adsorbed with the nitrogen atom placed toward the top carbon atom on the nanotube wall. The adsorption energy is \(-0.68\) eV with a bond length of 2.07 Å, and this configuration has been predicted from calculations within local density approximation \[59\]. Fig. 10B shows another stable geometry, where the nitrogen atom in NO2 is placed 3.30 Å away from the nanotube sidewall. The adsorption energy obtained by the SCC-DFTB (GGA) calculation is \(-0.05\) \((-0.39)\) eV. No appreciable structural deformation is seen during this adsorption. An interesting local geometry is obtained, when one of the oxygen atoms in NO2 approaches to the tube wall, as shown in Fig. 10C, similar to the previous report \[60\]. In this case, the adsorption is endothermic with an adsorption energy of 0.25 (0.12) eV. Yet, this configuration is locally stable, as demonstrated from the detailed study of an adsorption barrier height in

![Fig. 9. The Lorenztian curve fitting of each band for the pristine sample (A) and the NHFA-HTT sample (B). The baselines were subtracted from the background plasmons for the curve fitting. Values in the figure were the corresponding diameters of each curve determined from the tight-binding model.](image1)

![Fig. 10. Optimized structures of NO2 molecule on the sidewall of (9,0) nanotube: (A, B) physisorbed, (C) chemisorbed structures, and (D) absorption barrier for the chemisorbed structure (C). Dark, gray, and white balls indicate N, O, and C atom, respectively. Adsorption energies in eV are presented by the SCC-DFTB (GGA) calculations.](image2)
In estimating the local barrier height, we fixed one oxygen atom located near the tube wall and relaxed the other atoms in NO$_2$ molecule including all the carbon atoms in the nanotube. This calculation was repeated by moving NO$_2$ molecule close to the tube wall from a far distance. One can see from Fig. 10D that the final adsorption energy is endothermic. This geometry is kinetically limited. In this final geometry, NO$_2$ molecule itself is severely distorted, losing its binding energy (1.89 eV) and furthermore the C–C backbonds of the tube sidewall are also heavily strained with a distortion energy of 0.86 eV, where the distortion energy is defined as $E_d = E_{tot}(\text{distorted SWCNT}) - E_{tot}(\text{ideal SWCNT})$. However, the stabilization energy by the formation of a local C–O bond ($\lambda_{CO}$) on chemisorption is huge (−2.51 eV), compensating most of the energy loss by the unfavorable distortion energy factors. This suggests that this locally stable geometry could be realized by an assistance of an appropriate thermal energy. Since we are interested in the selective reactivity of nanotubes that may invoke a severe structural deformation that may lead to dissociate the nanotube walls (oxidative etching), we choose the chemisorbed geometry of Fig. 10C for the rest of calculations to investigate the selective adsorption of NO$_2$ molecule on particular nanotubes. Furthermore this endothermic adsorption becomes exothermic with an additional NO$_2$ adsorption, as will be discussed in the following section.

We also calculate the adsorption energy of armchair and zigzag nanotubes as a function of diameter, as shown in Fig. 11A. This reveals two remarkable features. One is the dependence of adsorption energy on the electronic structures. Regardless of diameters, the adsorption to metallic (armchair) nanotubes is consistently stronger than that to semiconducting ones. In particular, all ($3n,0$) zigzag nanotubes, which are zero-band gap semiconductors and simply regarded as metallic nanotubes, show adsorption energies close to those of the armchair nanotubes. Another is the dependence of adsorption energy on diameters. The adsorption becomes weaker with increasing diameters in both metallic and semiconducting nanotubes. We have done more accurate calculations for zigzag nanotubes to check the validity of the SCC-DFTB. The GGA calculations give lower adsorption energies for zigzag nanotubes than the SCC-DFTB calculations, but show similar tendency that zero-gap zigzag nanotubes have consistently lower adsorption energies than nonzero-gap zigzag ones with the same diameter dependence. This confirms the validity of our calculations using the SCC-DFTB approach.

Fig. 11B shows the adsorption barrier height as a function of diameter. The barrier heights of semiconducting nanotubes are consistently higher than those of metallic (armchair and ($3n,0$) zigzag) ones. The barrier height increases monotonically with increasing diameters in both armchair and zigzag nanotubes except the zero-gap ($3n,0$) zigzag nanotubes that their barrier heights are similar to those of armchair nanotubes. Another interesting point to note is that the barrier exists only for small-diameter nanotubes of (4,4), (5,5), (8,0), and (9,0), independent of metallicity. Others do not reveal the energy lowering after transition point upon adsorption. Yet, the locally stable structure is maintained, which may be understood by a strong C–O bond between nanotube and NO$_2$ molecule in spite of the heavy distortion energy involved in other backbonds of nanotube and NO$_2$ molecule. From this sense, NO$_2$ molecule is an unusual adsorbate particularly at large diameters, compared to other types of adsorbates that show a typical transition state. The implication of this result is rather simple from an experimental point of view. When NO$_2$ molecule has enough thermal energy to overcome the adsorption barrier height, the adsorption will take place. At small-diameter nanotubes, NO$_2$ molecule will adsorb with higher probability due to the presence of adsorption barrier. However, at large-diameter nanotubes, NO$_2$ molecules will be adsorbed with much less probability simply due to endothermic adsorption without a transition state compared to the small-diameter nanotubes. This suggests that the selective adsorption is not only energetically
controlled but also kinetically controlled and furthermore strongly diameter-dependent. Therefore, the selective adsorption could be enhanced in experiments by optimizing the reaction temperature.

4. Conclusions

We have investigated a liquid phase reaction using nitronium ions to remove metallic carbon nanotubes. We presented a separation technique that is capable of removing metallic nanotubes at small diameters less than 1.1 nm with high yield. The s-SWCNTs remained intact with NHFA treatment, while the m-SWCNTs were completely destroyed and removed, especially for nanotubes with diameters close to or less than 1.1 nm. The nitronium ion selectively adsorbed on m-SWCNTs with higher binding energy by inducing a stronger charge transfer from nanotube to nitronium ion. This is due to the higher availability of electron density at the Fermi level at the metallic nanotube to nitronium ion. This is due to the higher availability of electron density at the Fermi level at the metallic nanotube to nitronium ion. This difference becomes obscured for nanotubes with diameters greater than 1.1 nm. Our approach is straightforward with the adsorption energy of NO₂ strongly relying on the electronic structure of nanotubes, i.e., NO₂ is adsorbed more strongly on metallic tubes than on semiconducting tubes. The available charge density at the Fermi level plays an important role for a favorable adsorption particularly with an acceptor-type adsorbate. Similar selectivity is also observed in the adsorption barrier height. We conclude that the adsorption of NO₂ molecule on carbon nanotube walls is both energetics- and kinetics-limited. The diameter dependence of adsorption energetics is explained by the pyramidalization angle and the bond length between the carbon and oxygen atoms.

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References

[39] A special care was taken in the choice of the number of layers particularly for an armchair tube because of the presence of π and π* overlap at the Fermi level, which was located at 2/3 from the zone
center. It was therefore crucial to choose an effective sampling point at the Fermi level to reveal the metallic characteristics. We chose 18 (multiple of six) layers for this purpose and the total energy change from the choice of 24 layers was negligible. The total energy was saturated at these layers. It is interesting to see the dependence on the number of layers particularly on armchair nanotubes, which is related to the location of the Fermi level at 2/3 from the zone center.

[57] $S_{11} = 2a_0\hbar/\hbar_d$, $S_{22} = 4a_0\hbar/\hbar_d$, and $M_{11} = 6a_0\hbar/\hbar_d$, where $a_0$ is the carbon–carbon bond length (0.144 nm), $\hbar_0$ is the tight-binding parameter of the nearest neighbor overlap integral (2.9 ± 0.5 eV), and $d$ is diameters in nanometers.