ELECTRONIC-STRUCTURE ENGINEERING OF CARBON NANOTUBES

KAY HYEOK AN
Center for Nanotubes and Nanostructured Composites, Department of Physics
Institute of Basic Science, Sungkyunkwan University, Suwon 440-746, Korea
khan1028@skku.edu

YOUNG HEE LEE
Center for Nanotubes and Nanostructured Composites, Department of Physics
Advanced Institute of Nanotechnology
Sungkyunkwan University, Suwon 440-746, Korea
younghee@skku.edu

Received 15 June 2006

A review for controlling electronic structures and chirality separation of carbon nanotubes (CNTs) is presented with the subject divided into three topics. The first topic introduces the electronic structures of CNTs and the analytical techniques to identify the chirality of CNTs. The second topic discusses band gap engineering techniques using the sidewall functionalization of CNTs. The third topic concerns several approaches in chiral and diameter-dependent separation of CNTs. The electronic-structure engineering is of critical importance for a variety of technological applications of CNTs including, for example, field-effect transistor, chemical/bio-nanosensors, the electrical conductivity and charge dissipation in polymer/CNT composites, and flexible transparent conducting films. This paper is intended to concisely review the recent advances in the experimental and theoretical CNT researches concerned with the band gap engineering and chiral separation techniques of CNTs.

Keywords: Carbon nanotubes; chirality separation; band gap engineering.

1. Introduction

Carbon nanotubes (CNTs) have been the leading functional materials in nanoscience and nanotechnology and investigated most extensively due to their scientific and technological importance, compared to their counterparts such as nanoparticles and nanowires, since the discovery of multi-walled carbon nanotubes (MWCNTs) by Iijima in 1991 and single-walled carbon nanotubes (SWCNTs) synthesized by catalytic arc discharge.\(^1\)\(^-\)\(^3\) 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,\(^18\)\(^,\)\(^19\) composite,\(^20\) and nanoprobes.\(^21\) All these applications are closely related to their unique atomic and electronic structures. Carbon nanotube is a semi-one-dimensional self-assembly, which is naturally formed in a cylindrical form of graphene sheet with high aspect ratio (1000–10 000) and has extremely small diameters of a few nanometers for SWCNTs and a few tens nanometers for MWCNTs.

The electronic structure of CNT is determined by their chirality and diameter, and in general cannot be selectively controlled by conventional synthesis approaches. The present state of art
technology for CNT synthesis always produces samples with mixing chiralities. The coexistence of metallic (m-) and semiconducting (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 for 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, nitronium ions and DNA have been reported.22-27

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 sp$^3$ hybridization.28,29 In this review, we try to summarize the recent efforts for chiral and diameter-dependent separation by several research groups.

1.1. Atomic structure of carbon nanotubes

The simplest way of specifying the structure of an individual carbon nanotube is to specify a translational vector, which we label $C_n$, joining two equivalent points on the original graphene lattice. The cylinder can be produced by rolling up the sheet such that two end-points of the vector are superimposed. Because of the symmetry of honeycomb lattice, many of the cylinders produced in this way will be equivalent, but there is an “irreducible wedge” comprising one graphene lattice, within which unique tube structures are defined. Figure 1 shows a small part of this irreducible wedge, with points on the lattice labeled according to the notation of Dresselhaus et al.$$^{30}$ Each pair of integers $(n, m)$ represents a possible tube structure. Thus, the length of the chiral vector $C_h$ can be expressed as $C_h = n \mathbf{a}_1 + m \mathbf{a}_2$, where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit cell base vectors of the graphene sheet, and $m \leq n$. It can be seen in Fig. 1 that $m = 0$ for all zigzag tubes, while $n = m$ for all armchair tubes. All other tubes are chiral. Since $||\mathbf{a}_1|| = ||\mathbf{a}_2|| = (\sqrt{3})a_{C-C} = 0.246$ nm, where $a_{C-C}$ is the nearest-neighbor C–C distance (1.421 Å in graphite), the magnitude of $C_h$ in nanometers is:

$$C_h = 0.246\sqrt{(n^2 + mn + m^2)} \quad (1)$$

and the diameter, $d_t$, is given by

$$d_t = \frac{0.246\sqrt{(n^2 + mn + m^2)}}{\pi} \quad (2)$$

The chiral angle, $\theta$, is given by

$$\theta = \sin^{-1}\frac{\sqrt{3}m}{2\sqrt{(n^2 + mn + m^2)}} \quad (3)$$

Figure 1 also shows some examples of the constructed tubes with $(n, m)$. When $\theta = 30^\circ$, “armchair” nanotube (name from the edge armchair shape) is generated. When $\theta = 0^\circ$, “zigzag” nanotube is generated. For nanotubes with other than 0 or 30$^\circ$, chiral nanotube is generated.

1.2. One-dimensional electronic structure of carbon nanotubes

Electronic band structure calculations predict that the $(n, m)$ indices determine the metallic or semiconducting behavior of CNTs. Zigzag $(n, 0)$ CNTs $(\theta = 0)$ should have two distinct types of behavior: the tube will be zero-gap semiconducting, when $n/3$ is an integer, and otherwise semiconductors with a finite band gap. As $C_h$ rotates away from $(n, 0)$, chiral $(n, m)$ CNTs are possible with electronic properties similar to the zigzag tubes, that is, when $(n - m)/3$ is an integer, the tubes are metallic, and otherwise semiconducting. The gaps of the semiconducting $(n, 0)$ and $(n, m)$ tubes should depend inversely on diameter. Finally, when $C_h$ rotates $30^\circ$ relative to $(n, 0)$, $\theta = 30^\circ$, $n = m$. The $(n, 0)$ armchair tubes are expected to be truly metallic with band crossings at $k_5 = ±2/3$ of the one-dimensional Brillouin zone.$$^{31}$
The intriguing electrical properties of CNTs are due to the peculiar electronic structure of a graphene layer. Its band structure and the hexagonal shape of its first Brillouin zone are shown in Fig. 2. In most directions in \( k \)-space, as in the \( \Gamma - M \) direction, the electrons encounter a semiconductor-like band gap. In the \( \Gamma - K \) direction and in five other directions that pass through the Fermi points, or \( K \)-points, the electrons have free motion, and the graphene behaves as a metal.

In CNTs, we need to take into account the confinement of the electrons around the circumference of the CNT. This is accomplished by introducing a new quantization condition, namely \( k_c C_h = 2 \pi q \), where \( k_c \) is the wavevector in the circumferential direction, and \( q \), an integer. In other words, the momentum is quantized along the circumferential direction due to periodic boundary condition. Thus, each band of graphene \( \{ \sigma, \sigma^*, \pi, \pi^* \} \) splits into a number of one-dimensional (1D) subbands labeled by \( q \). Therefore, only a particular set of states, which are parallel to the corresponding tube axis with a spacing of \( 2/d \), are allowed. On the basis of this simple scheme, if one of the allowed wavevectors passes through the Fermi points of the graphene layer, the CNT should be metallic, and otherwise it should be semiconducting.

For the \((n, n)\) armchair tube, the allowed wavevectors in the circumferential direction are given by the following periodic boundary condition:

\[
n \sqrt{3} k_y a = 2 \pi q \quad (q = 1, 2, \ldots, 2n).
\]

Thus, for the \((9, 0)\) nanotube, there are nine lines of allowed wavevectors, as shown in Fig. 3(b). The energy dispersion relation for this case is shown in Fig. 3, where the bands are assigned to an irreducible representation of the \( D_{5d} \) point group. There are two \( A \) bands and eight \( E \) bands making a total of 18. The valence and conduction bands meet at \( k = 0 \), so that in this case the tube is metal. The reason for this is clear from Fig. 2(b), where it can be seen that one of the lines of allowed wavevectors for this tube passes through a \( K \) point. This is not the case for all zigzag tubes, and only occur when \( n \) is divisible by three. Thus, for the \((10, 0)\) tube there is an energy gap between the valence and conduction bands at \( k = 0 \), as shown in Fig. 4, and the tube would be expected to be a semiconductor.

For armchair tubes, the orientation of the Brillouin zone means that there will always be one set of allowed vectors passing through the \( K \) point, which leads to the conclusion that all armchair tubes are metallic. The energy dispersion relation for an \((5, 5)\) armchair tube is shown in Fig. 3. Each band can be assigned to an irreducible representation of the \( D_{5d} \) point group, and is labeled accordingly in the figure. The \( A \) bands are nondegenerate and the \( E \) bands are doubly degenerate, so the total number of valence bands in this case is 10; the + and − labels denote the unfolded and folded bands, respectively. It can be seen that the valence and conduction bands meet at a position which is two-thirds of the distance from \( k = 0 \) to the zone boundary at \( k = \pi/a \). Calculations show that all armchair tubes have a similar band structure.

On the other hand, for the \((n, 0)\) zigzag tube the allowed wavevectors can be written as follows:

\[
nk_y a = 2 \pi q \quad (q = 1, 2, \ldots, 2n).
\]

Thus, for the \((9, 0)\) tube, there are nine lines of allowed wavevectors, as shown in Fig. 3(b). The energy dispersion relation for this case is shown in Fig. 3, where the bands are assigned to an irreducible representation of the \( D_{9d} \) point group. There are two \( A \) bands and eight \( E \) bands making a total of 18. The valence and conduction bands meet at \( k = 0 \), so that in this case the tube is metal. The reason for this is clear from Fig. 2(b), where it can be seen that one of the lines of allowed wavevectors for this tube passes through a \( K \) point. This is not the case for all zigzag tubes, and only occur when \( n \) is divisible by three. Thus, for the \((10, 0)\) tube there is an energy gap between the valence and conduction bands at \( k = 0 \), as shown in Fig. 4, and the tube would be expected to be a semiconductor.

![Fig. 2. (a) Band-structure of the 2D graphene sheet in 3D representation and (b) illustration of allowed \( k \) values in Brillouin zone.](image)

![Fig. 3. Band-structure of (a) the \((5, 5)\), (b) the \((9, 0)\), and (c) the \((10, 0)\) nanotube.](image)
(a) \((n, m) = (10, 0)\)

(b) \((n, m) = (9, 0)\)

(c) Fig. 4. Density of states of (a) the (9, 0), (b) the (10, 0) nanotube, and (c) the subband energy gaps of 1D electronic bands for a particular \((n, m)\) armchair nanotube.

The SWCNT is a quasi 1D material. This 1D nature of the nanotube results in several spikes (van Hove singularities) in the electronic density of states (EDOS). One intriguing property of the EDOS is that these subband peak positions are uniquely determined by a diameter and chirality of the carbon nanotubes. The tight binding calculations of the EDOS for (10, 0) and (9, 0) and a series of armchair tubes were presented in Fig. 4 (Fermi energy \(E_F = 0\) eV).

In spite of the similar diameter of (10, 0) and (9, 0) zigzag nanotubes, we see the significant different peak positions in the subband energies. We note that (10, 0) nanotube is a semiconductor with a finite size of the band gap, whereas (9, 0) nanotube is a metal or zero-gap semiconductor, i.e., a finite state near the Fermi level. As the nanotube diameter increases in the armchair tubes, the singularities move closer together. In the case of larger diameter tubes, the singularities are merged, become smeared out, and the DOS approaches to that of a graphene layer. On the other hand, for small diameter nanotubes, the 1D “spikes” in the EDOS are well separated, especially near \(E_F\). The allowed optical transitions are from \(v_i\) to \(c_i\) by selection rules. Thus the electronic structures of 1D nanotubes are closely related to the optical properties.

The band gap of the zigzag nanotubes with \(n = 3k\), which are supposed to be zero-gap semiconductors, was widened due to the strains with decreasing the tube diameters. An empirical fitting formula of the band gap for semiconducting nanotubes is \(E_g = 1 (\text{eV})/d \text{ (nm)}\).\(^{33}\)

2. Analytical Techniques in Determining Chirality of CNTs

One-dimensional electronic structure of carbon nanotubes opens a new possibility for rich nanoscience and nanotechnology. As described in the previous paragraph, 1D van Hove singularity could be detected by a resonant Raman spectrum due to its specific dependence on the chirality and diameter. Resonant Raman scattering occurs when the energy of the incident photon matches the energy of strong optical absorption electronic transitions. The optical absorption is invoked between electronic states \((v_i\) to \(c_i\)\) whose character is determined primarily by 1D quantum confinement phenomena. Large tube diameter would not exhibit electronic quantum confinement effects. Therefore, the Raman features for an ensemble of larger diameter nanotubes would be found at the same Raman bands upon variation of the laser excitation frequency. Diameter and chirality-selective resonant Raman scattering process is a direct consequence of the 1D electronic quantum-confinement in small diameter SWCNTs.\(^{34}\)

Raman spectroscopy has been the most powerful tool and has been extensively studied for the analysis of atomic and electronic structures of carbon nanotubes. Raman spectra of the SWCNTs is mainly composed of Radial breathing mode (RBM) near 200 \text{cm}^{-1}, disorder-band (D-band) near 1320 \text{cm}^{-1}, and tangential band (G-band) near 1590 \text{cm}^{-1}. The most essential information for the diameter distribution of the sample is expressed by the RBM. The diameter of the nanotube \((d_i)\) is inversely proportional to the RBM frequency, \(i.e., \omega \text{ (cm}^{-1}) = a/d_i \text{ (nm)} + b\), where \(a\) and \(b\) are the proportionality constants. These constants are slightly different from group to group and dependent on the degree of bundles of the sample.\(^{35-37}\) The RBM frequencies are varied with different excitation laser energies. This is a clear evidence of resonant Raman spectra. CNTs are composed of various diameters.
and chiralities. CNTs whose subband transition energies \( E_n = c_i - v_i \) coincide with the laser excitation energies are excited and show the resonant Raman scattering.

The dependence of \( E_{\text{ii}} \) on the diameter and chirality is shown in the so-called “Kataura” plot as shown in Fig. 5.38 By performing tight-binding (TB) calculations using only \( \pi-\pi \) interactions for the graphene sheet with periodic boundary condition, we get the useful information for \( E_n \) with diameter as follows:

\[
E_{11}(S) = \frac{2\gamma_0 a_{\text{CC}}}{d_t}, \quad E_{11}(M) = \frac{6\gamma_0 a_{\text{CC}}}{d_t},
\]

\[
E_{22}(S) = \frac{4\gamma_0 a_{\text{CC}}}{d_t}, \quad E_{22}(M) = \frac{12\gamma_0 a_{\text{CC}}}{d_t},
\]

\[
E_{33}(S) = \frac{8\gamma_0 a_{\text{CC}}}{d_t}, \quad E_{33}(M) = \frac{18\gamma_0 a_{\text{CC}}}{d_t},
\]

\[
d(\text{nm}) = \frac{0.246(n^2 + nm + m^2)^{1/2}}{\pi},
\]

where \( S \) and \( M \) stand for semiconducting and metallic tubes, respectively, and \( \gamma_0 \) is a TB overlap interaction parameter and can be ranged to be 2.4–2.9 eV, \( a_{\text{CC}} \) is the nearest neighbor distance of graphite, \( d_t \) is the diameter of the nanotube.32,39

The Kataura plot is very useful in determining the chiral indexing of carbon nanotubes.38 For instance, the sample contains carbon nanotubes with different chirality and diameter. However, only the corresponding nanotubes are excited by the Raman scattering with a given laser excitation. Once the diameter is determined from the RBM frequency, we can determine the chirality of nanotubes by the Kataura plot with corresponding subband energy. Since this is a simple TB approach, some corrections have been done with more accurate method.40 No excitonic contributions are incorporated in this approach. The excitonic effect will be more severe at small diameter tubes.41

Recently, Samsonidze et al. have found that the Kataura plot calculated from the conventional TB approximation have two major problems.42 First, the experimental \( E_{22}(S)/E_{11}(S) \) ratio in the large \( d_t \) limit is less than 2, while the TB \( E_{22}(S)/E_{11}(S) \) ratio approaches 2 with increasing \( d_t \) (the “ratio” problem). Second, the empirical spread of the \( E_n(S) \) energies within the same \( 2n + m = \) constant family is much larger than the corresponding spread of the TB \( E_n(S) \) energies at constant \( d_t \) (the “family spread” problem). Therefore, they have tried providing a theoretical basis to account for PL empirical fit that can be safely applied to many experiments using the extended tight-binding model (ETB). This ETB has included the curvature effect of SWCNT sidewall, which is missed in conventional TB, by extending the basis set to the atomic orbitals according to the Slater–Koster formalism.

They have calculated bond lengths and angles to vary, the optical transition energies \( E_{\text{ii}} \) in SWCNTs as a function of inverse tube diameter using ETB.42 After geometrical structure optimization, the \( 2n + m = \) constant family behavior observed in photoluminescence (PL) experiments is obtained, and the detailed agreement between calculations and PL experiments is achieved after including many-body corrections. Table 1 shows the chiral assignment \((n, m)\) by ETB. The \( E_{\text{ii}} \) energies observed follow “family” patterns for SWCNTs with \( 2n + m = 3p + r \), where \( p \) is an integer and \( r = 0, 1, 2 \) define metallic, semiconducting type, and semiconducting type SWCNTs, respectively.

One method for distinguishing m-SWCNTs from semiconducting ones in any given sample is to analyze the line shape of the tangential G-band feature in Raman spectra.43 The G-band of semiconducting nanotubes has been extensively studied, and is well accounted by using Lorentzian oscillators to describe the six Raman-active modes, identified by polarization studies of the symmetries of the various line-shape components.44 Some researchers fitted the Raman line shape for metallic SWCNTs using Lorentzians, while others used a Breit–Wigner–Fano (BWF) line shape to fit the lower frequency component of the G-band spectrum.44 Two Raman components are needed to
Table 1. Chiral assignments \((n, m)\) by ETB.

<table>
<thead>
<tr>
<th>Family Index</th>
<th>Chiral ((2n + m))</th>
<th>((n, m))</th>
<th>(\omega_{\text{RBM}}) (cm(^{-1}))</th>
<th>(E_f^l) (eV)</th>
<th>(d_{\text{in}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26 (10,6)</td>
<td>21.79</td>
<td>203</td>
<td>1.64</td>
<td>1.11</td>
<td>1.65</td>
</tr>
<tr>
<td>26 (11,4)</td>
<td>14.92</td>
<td>215</td>
<td>1.58</td>
<td>1.07</td>
<td>1.58</td>
</tr>
<tr>
<td>26 (12,2)</td>
<td>7.59</td>
<td>222</td>
<td>1.58</td>
<td>1.04</td>
<td>1.58</td>
</tr>
<tr>
<td>26 (13,0)</td>
<td>0.00</td>
<td>227</td>
<td>1.7</td>
<td>1.03</td>
<td>1.7</td>
</tr>
<tr>
<td>25 (9,7)</td>
<td>25.87</td>
<td>216</td>
<td>1.73</td>
<td>1.10</td>
<td>1.73</td>
</tr>
<tr>
<td>25 (10,5)</td>
<td>19.11</td>
<td>225</td>
<td>1.57</td>
<td>1.03</td>
<td>1.57</td>
</tr>
<tr>
<td>25 (11,3)</td>
<td>11.74</td>
<td>232</td>
<td>1.55</td>
<td>1.01</td>
<td>1.55</td>
</tr>
<tr>
<td>25 (12,1)</td>
<td>3.96</td>
<td>237</td>
<td>1.55</td>
<td>1.01</td>
<td>1.55</td>
</tr>
<tr>
<td>23 (8,7)</td>
<td>21.79</td>
<td>203</td>
<td>1.64</td>
<td>1.11</td>
<td>1.64</td>
</tr>
<tr>
<td>23 (11,1)</td>
<td>4.31</td>
<td>257</td>
<td>1.92</td>
<td>0.92</td>
<td>1.92</td>
</tr>
<tr>
<td>23 (9,5)</td>
<td>20.63</td>
<td>242</td>
<td>1.72</td>
<td>0.98</td>
<td>1.72</td>
</tr>
<tr>
<td>23 (10,3)</td>
<td>12.73</td>
<td>252</td>
<td>2.03</td>
<td>0.94</td>
<td>2.03</td>
</tr>
<tr>
<td>22 (9,6)</td>
<td>25.28</td>
<td>245</td>
<td>2.43</td>
<td>0.97</td>
<td>2.43</td>
</tr>
<tr>
<td>22 (12,2)</td>
<td>7.59</td>
<td>222</td>
<td>1.58</td>
<td>1.04</td>
<td>1.58</td>
</tr>
<tr>
<td>22 (13,0)</td>
<td>0.00</td>
<td>227</td>
<td>1.7</td>
<td>1.03</td>
<td>1.7</td>
</tr>
<tr>
<td>21 (7,7)</td>
<td>25.87</td>
<td>216</td>
<td>1.73</td>
<td>1.10</td>
<td>1.73</td>
</tr>
<tr>
<td>21 (8,5)</td>
<td>19.11</td>
<td>225</td>
<td>1.57</td>
<td>1.03</td>
<td>1.57</td>
</tr>
<tr>
<td>21 (10,1)</td>
<td>4.31</td>
<td>257</td>
<td>1.92</td>
<td>0.92</td>
<td>1.92</td>
</tr>
<tr>
<td>21 (9,3)</td>
<td>20.63</td>
<td>242</td>
<td>1.72</td>
<td>0.98</td>
<td>1.72</td>
</tr>
<tr>
<td>20 (7,6)</td>
<td>21.79</td>
<td>203</td>
<td>1.64</td>
<td>1.11</td>
<td>1.64</td>
</tr>
<tr>
<td>20 (8,4)</td>
<td>14.92</td>
<td>215</td>
<td>1.58</td>
<td>1.07</td>
<td>1.58</td>
</tr>
<tr>
<td>20 (9,2)</td>
<td>7.59</td>
<td>222</td>
<td>1.58</td>
<td>1.04</td>
<td>1.58</td>
</tr>
<tr>
<td>20 (10,0)</td>
<td>0.00</td>
<td>227</td>
<td>1.7</td>
<td>1.03</td>
<td>1.7</td>
</tr>
<tr>
<td>19 (6,5)</td>
<td>25.87</td>
<td>216</td>
<td>1.73</td>
<td>1.10</td>
<td>1.73</td>
</tr>
<tr>
<td>19 (8,3)</td>
<td>12.73</td>
<td>252</td>
<td>2.03</td>
<td>0.94</td>
<td>2.03</td>
</tr>
<tr>
<td>19 (9,1)</td>
<td>4.31</td>
<td>257</td>
<td>1.92</td>
<td>0.92</td>
<td>1.92</td>
</tr>
<tr>
<td>19 (10,3)</td>
<td>12.73</td>
<td>252</td>
<td>2.03</td>
<td>0.94</td>
<td>2.03</td>
</tr>
<tr>
<td>18 (8,6)</td>
<td>21.79</td>
<td>203</td>
<td>1.64</td>
<td>1.11</td>
<td>1.64</td>
</tr>
</tbody>
</table>

The mean electronic properties of bulk samples of SWCNTs have been established by optical absorption spectroscopy. The UV–visible–NIR spectroscopy is an important tool for characterizing the electronic band structure of SWCNTs. As described in the previous paragraph, due to the 1D nature of the SWCNTs, their electronic structure exhibits clear van Hove singularities. The energetic separation of the pairs of van Hove singularities is inversely proportional to the tube diameter. The optical response of the SWCNT is dominated by transitions between peaks in EDOS of the valence and conduction bands, with momentum conservation only allowing transitions pairs of singularities which are symmetrically placed with respect to the Fermi level. Thus, following van Hove singularities, the optical transitions in SWCNT are also inversely proportional to the nanotube diameter.

The existence of several peaks below 0.3 eV is related to inter-band transitions between van Hove singularities in the valance band of both metallic and semiconducting tubes. Figure 6 shows a typical optical absorption spectrum of HiPco sample after subtraction of \(\pi\) plasmons. The raw data are shown in the inset. Three broad SWCNT-related peaks have been found at energies in agreement with \(S_{11}\), \(S_{22}\), \(M_{11}\).

Fig. 6. A typical optical absorption spectrum of SWCNTs after background correction. The inset shows the raw data.
3. Band Gap Engineering of SWCNTs by Sidewall Functionalization

The functionalization of CNT sidewall can be realized by either chemisorption or physisorption. This relies on the choice of functional group. Physisorption has weaker binding energy than chemisorption and hence the adsorbates could be easily removed in physisorption and the original electronic structures are presumably fully recovered. Sodium dodecyl sulfate (SDS), sodium dodecylbenzenesulfonate (NaDDBS), tetrahydrofuran solutions of amine, such as octadecylamine (ODA), octylamine, propylamine, and isopropylamine have been used to disperse CNT bundles or to separate metallic nanotubes from semiconducting ones.22–24 The nanotubes usually remain intact after treatment and electronic structures are recovered after removal of adsorbates. On the other hand, adsorbates such as diazonium, nitronium ions, SOCl₂ that contain oxygen atoms, leads to chemisorption and sometimes deteriorate the nanotube walls.53,54 The adsorbates are hardly removable. In this case, the electronic structures of nanotubes are not usually recovered except some special cases. A considerable charge transfer between CNTs and adsorbates takes place for both cases. This can be measured by XPS, Raman spectroscopy and absorption spectroscopy. Chemisorption can be also achieved by some atomic species such as hydrogen and fluorine atoms.26,29 In this the transformation of electronic structures is prominent and sometimes useful for some applications to electronic devices. Another advantage of functionalization is to modify the surface tension. The pristine nanotubes are hydrophobic in nature due to their van der Waals interaction. Functionalization leads to transform the hydrophobic surface to hydrophilic one by ionizing CNT surface. Some recent reports, summarized in Table 2, on these functionalization approaches will be described in the next paragraph.

3.1. Hydrogenation of nanotube sidewalls

Realization of CNT-based transistors requires preexisting semiconducting CNTs, which are not selectively grown by the conventional synthesis approaches. While CNT heterojunction and cross-junction formed with different chiralities have demonstrated the required performance for CNT transistors, these relied on a junction formation accidentally obtained during sample preparation. It has been proposed that hydrogen functionalization of CNTs can transform the electronic structure systematically from metallic (narrow-gap semiconducting) to semiconducting (large-gap semiconducting).55

In the hydrogenation of SWCNT shown in Fig. 7, the SWCNT-metal junction is fabricated on a silicon substrate by electron beam lithography, where one half of the CNT is buried in SiO₂ layer of 100 nm and the other half is exposed to air.28 The exposed CNT is functionalized by
Table 2. Summaries of band gap engineering of SWCNTs using various methods reported recent years.

<table>
<thead>
<tr>
<th>Research group</th>
<th>Used methods</th>
<th>CNT dispersion Type</th>
<th>Analytical method</th>
<th>Type of controlled CNTs</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lee in SKKU</td>
<td>Hydrogenation using H atom</td>
<td>—</td>
<td>$I$–$V$ characteristics of FET</td>
<td>m-SWCNT</td>
<td>28, 61</td>
</tr>
<tr>
<td>Strano in University of Illinois</td>
<td>Functionalization using diazonium salt</td>
<td>SDS</td>
<td>Absorption spectra, Raman spectra (532 nm)</td>
<td>m-SWCNT</td>
<td>53</td>
</tr>
<tr>
<td>Lee in SKKU</td>
<td>Functionalization using F\textsubscript{2} gas</td>
<td>—</td>
<td>Raman spectra (1064 nm), XPS, conductivity measurement</td>
<td>m-SWCNT</td>
<td>29, 63</td>
</tr>
<tr>
<td>Weglikowska in Max-Planck-Institute</td>
<td>Chemical modification by SOCl\textsubscript{2} solution</td>
<td>Suspension in SOCl\textsubscript{2} solution</td>
<td>Raman spectra, conductivity and thermoelectric power measurement, NEXAFS</td>
<td>s-SWCNT</td>
<td>54</td>
</tr>
</tbody>
</table>

Fig. 7. (a) Scanning electron microscope (SEM) image of the CNT–metal contact, where half of the CNT was buried by SiO\textsubscript{2} with a thickness of 100 nm. (b) typical $I$–$V$ curves for both samples of MS and SS measured at 288 K after hydrogenation. The inset shows $I$–$V$ curves of the pristine samples, which show an ohmic contact near room temperature. After hydrogenation both samples show rectifying behavior. (c) the differential conductance of the hydrogenated MS sample as a function of source–drain voltage at 4.2 K and the pristine one at 5.6 K (inset), and (d) the differential conductance of the SS sample. The units in the insets are the same as those of graphs.

the atomic hydrogen and the half of the SWCNT buried in SiO\textsubscript{2} remained intact. Atomic hydrogen is supplied by flowing hydrogen gas through hot tungsten filament. Two samples are hydrogenated: one is metallic (MS sample) and another is semiconducting with an energy gap of 0.8 eV (SS sample). Both samples reveal an ohmic behavior at near room temperature, as shown in the inset of Fig. 7(b), with a resistance of 155 kΩ for the pristine MS sample and 10 MΩ for the pristine SS sample. The $I$–$V$ (current–voltage) characteristics are significantly changed after hydrogenation, as shown in Fig. 7(b). Rectifying effects are observed for both samples. The anisotropy is five and ten for the respective MS and SS samples, i.e., the rectifying effect is more prominent in the SS sample. Both samples are operable as a rectifier at room temperature. The differential conductance, $dI/dV$ is finite near the zero-bias region at 5.6 K in the pristine MS sample (inset of Fig. 7(c)), suggesting this sample to be nearly metallic. The pristine SS sample reveals a vanishing conductance near the gap region (inset of Fig. 7(d)), suggesting it to be a semiconducting CNT. It is estimated that the contact barrier height $\phi_b$ between the metal electrode and the pristine CNT from an Arrhenius plot and an extrapolation to zero-drain voltage by assuming that $I$–$V$–$T$ (current–voltage–temperature) characteristics follow the thermionic electron emission model and $\phi_b$ is proportional to the square root of the drain voltage. The contact barriers are determined to be 14 and 60 meV for the pristine MS and SS samples, respectively. Since two metal–CNT contacts are formed in series, the energy gap can be defined as half of the zero-conductance region confined by the abrupt increase in the conductance at low temperature, as shown in the inset of Fig. 7(d). After hydrogenation, an energy gap of 1.88 eV is clearly observed in the MS sample and the conductance increases almost linearly above the gap region, as shown in Fig. 7(c). The energy gap is...
Band gap engineering by sidewall functionalization can be explained in terms of the band structure of pure and hydrogenated CNTs. In intramolecular junction between pure and hydrogenated CNTs, as shown in Figs. 8(a) and 8(b), the carbon atoms at the hydrogenated CNT side accept extra charges from the adsorbed hydrogen atoms but not from the carbon atoms at the metallic CNT side. Still more charges (0.03 e per carbon atom) accumulates at the interface layer in the metallic sample than in the semiconducting sample, as expected. Therefore a weak band bending is expected in the metal–semiconducting junction, whereas the band bending may be negligible in the semiconducting–semiconducting junction. Following the metal-induced gap states model, the Schottky barrier height is mostly determined by the charge neutrality condition and the charge transfer depends on the difference of electronegativities between the metal and semiconductor.

Most semiconductors do not follow the simple Schottky model and therefore it may be reasonable to adopt the above model in constructing the junction band diagram. In this model, the junction barrier height is equivalent to the band offset. The junction is abrupt with an interface region of one or two monolayers, as shown in Figs. 8(a) and 8(b). Some charges may transfer from the metallic CNT to the semiconducting one in the metallic sample, resulting in the sharp band bending at the region of the semiconducting CNT. The charge transfer may be negligible in the semiconducting sample, which may result in a small spike at the junction. Band gap engineering may be realized by changing hydrogen coverage on CNT surface.

Figure 9 presents density functional calculations for band gap modulation as a function of hydrogen coverage. At low coverage, the band gap modulation is hardly observable. The electronic transformation from sp$^2$ to sp$^3$ hybridization is not enough to open the band gap. At coverage greater than 0.5, the band gap starts opening. The degree of band gap opening relies on the absorption patterns. This requires further investigation.

3.2. Diazonium treatment

It has been proposed that the electronic structure of SWCNTs could be also modified by functionalization using diazonium salts. Water-soluble diazonium salts can extract electrons from nanotubes in the formation of a covalent aryl bond and thereby
Fig. 10. (a) The reaction model of diazonium reagents with SWCNTs. Low-wave number Raman spectra at 532-nm excitation of the starting solution (b) and after diazonium treatment (c).

demonstrate highly chemoselective reactions with metallic versus the semiconducting tubes, shown in Fig. 10(a). This bond forms with extremely high affinity for electrons with energies near the Fermi level. The reactant forms a charge-transfer complex at the nanotube surface, where electron donation from nanotubes stabilizes the transition state and accelerates the forward rate. Once the bond symmetry of the nanotube is disrupted by the formation of this defect, adjacent carbons increase in reactivity, and the initial selectivity is amplified as the entire nanotube is functionalized. Under carefully controlled conditions, this behavior can be exploited to obtain highly selective functionalization of metallic and semimetallic species to the exclusion of semiconductors.

The sidewall functionalization of nanotubes disrupts the oscillator strength that gives rise to resonantly enhanced, low-frequency Raman lines that are distinct for species of a particular diameter. This causes the mode to decay accordingly as the particular \((n, m)\) nanotube reacts. Figures 10(b) and 10(c) analogously show the solution-phase Raman spectra at 532 nm with each reactant addition after steady state. The relative rates of the decays of these features reveal unprecedented reactivity differences between chiral semimetallic species.

Raman spectroscopy probes nanotubes with nearly identical transition energies, and these differences reveal a curvature-dependent stabilization of the charge-transfer complex that may ultimately be exploited to separate semimetallic and metallic species. After reaction with diazonium salts, metallic species have decayed, and only one low-frequency Raman mode for semiconductor \((9, 2)\) remains unaffected. Therefore, it is realized that the diazonium reagents functionalize SWCNTs suspended in aqueous solution with high selectivity and enable manipulation according to electronic structure. Metallic SWCNTs are shown to react to the near exclusion of semiconducting ones under controlled conditions. Selectivity is dictated by the availability of electrons near the Fermi level to stabilize a charge-transfer transition state preceding bond formation. Thermal pyrolysis of the reacted material at 300°C in an atmosphere of inert gas cleaves the aryl moieties from the sidewall and restores the spectroscopic signatures of the aromatic, pristine nanotubes. The electronic transitions in the absorption spectrum are restored, indicating the loss of the side group and a restoration of the original electronic structure of the nanotube. Although the selectivity was demonstrated with several excitation energies, a complete analysis requires the continuous Raman spectroscopy. For instance, the selectivity at an excitation energy of 633 nm usually leads to inconsistent with other excitation energies. The origin for this ambiguity remains unanswered.

3.3. Fluorination of nanotube sidewalls

The change of atomic and electronic structures of fluorinated SWCNTs using X-ray photoemission spectroscopy (XPS) and electrical resistivity measurements have been investigated. The SWCNT powder was fluorinated by \(F_2\) gas under 0.2 bar for 10 min at a temperature range of 150–300°C.

Figures 11(a) and 11(b) show the resistivity measured by the four-point probe method at room temperature and the XPS valence band spectra of the undoped and fluorinated CNTs, respectively. It can be seen that the resistivity rises with increasing reaction temperature. Figure 11(b) presents that the valence band edge shifts to the higher binding-energy side with increasing reaction temperature, implying the increase of band gap. The electronic properties are altered by fluorination so as to decrease the conductivity of the individual CNTs. Consequently, the XPS data have shown a significant reduction in the electronic density of states near the Fermi level with increasing F-doping content, indicating a clear transformation of the electronic structures from metallic to semiconducting ones. The density functional calculations suggest that the band
Fig. 11. (a) The resistivity measured by the four-point probe method from the pelletized fluorinated samples at room temperature. (b) The XPS valence band spectra for the undoped and fluorinated CNTs at various reaction temperatures.

The structures are severely modified with fluorination, revealing a transformation to another type of metallic tubes and semiconducting ones depending on the fluorination pattern types. Since the fluorination involves a strong chemical bonding, the carbon–carbon back bonds are severely distorted, leading to a disintegration of nanotube structures to graphitic layers.

Figure 12(a) presents two stable geometries, stripe- and ladder-types, of fluorinated armchair nanotube (5, 5) at coverage of 0.5. Figure 12(b) shows the band structures and the corresponding DOSs for particularly controversial stripe- and ladder-types in the armchair tube. The band shape is significantly modified with fluorine adsorption. For instance, the DOS is finite near the Fermi level with band edges at $G$ point and $Z$ point, and more importantly bands are closely overlapped, giving rise to the modulation of the bands, unlike the spike-type spread band in an ideal (5, 5) tube due to the 1D confinement. The ladder-type clearly shows the energy gap. The adsorption energies of the stripe- and ladder-types are not much different from each other. Both stripe- and ladder-types in the armchair tubes may coexist in the fluorinated sample, which increases the resistivity of the sample by reducing the number of nanotubes with metallic properties.

3.4. Transition from semiconducting to metallic SWCNTs by SOCl$_2$ absorption

The chemical modification by SOCl$_2$ of an entangled network of purified SWCNTs has been suggested to provide a simple way to significantly improve the electrical conductivity. The purified SWCNTs was stirred in SOCl$_2$ solution at 45°C for 24 h. The temperature dependence of the SWCNT resistance is shown in Fig. 13(a). These results show that the resistance of the pristine sample decreases continuously with increasing temperature, reflecting a semiconducting character of the sample. In the SOCl$_2$-treated sample, on the other hand, a nonmetallic behavior is observed only below 150 K. At higher temperatures they observe resistance increasing with increasing temperature, indicating a crossover to metallic behavior.

Figure 13(b) represents the temperature dependence of the thermoelectric power. These results provide experimental evidence for the shift of the Fermi level and the doping effect of SOCl$_2$ on the SWCNTs. A positive sign of the thermopower indicates that holes are major charge carriers in both pristine and modified nanotube samples. The formation of charge-transfer complexes within the nanotube bundles leads to a charge redistribution in the system, resulting in electron depletion of the sp$^2$-bonded carbon nanotubes. This $p$-type doping effect promotes a Fermi level shift into the valence band, resulting in the transition from semiconducting to metallic behavior.
4. Chiral Separation and Diameter-Dependent Separation of SWCNTs

There are two approaches for the chiral separation of SWCNTs using chirality-dependent adsorption and chemical reaction. Some recent reports, summarized in Table 3, on these two approaches will be described in the next paragraph.

4.1. Chiral selective adsorption

4.1.1. DNA-assisted separation

It has been reported that a single-stranded DNA (ssDNA) interacts strongly with CNTs to form a stable DNA–CNT hybrid that effectively nanodisperses CNTs in aqueous solution. An oligonucleotide sequence is self-assembled into a highly ordered structure on CNTs, allowing not only improved metal from semiconducting tube separation but also diameter-dependent separation. Wrapping of CNTs by ssDNA is found to be sequence-dependent. A systematic search of the ssDNA library selected a sequence d(GT)n,n = 10 to 45 that self-assembles into a helical structure around individual nanotubes in such a way that the electrostatics of the DNA–CNT hybrid depends on tube diameter and electronic properties, enabling nanotube separation by anion exchange chromatography.

Figure 13 shows the UV–vis–near IR absorption spectra of fractionated DNA–CNTs. The systematic spectral change from early fractions to late fractions is a direct evidence for structure-based CNT separation. Three regions are identified, first interband transitions for metals, M_{11} (400 to 650 nm), and first and second interband transitions for semiconductors, S_{11} (900 to 1600 nm) and S_{22} (550 to 900 nm), respectively. The starting material yielded a spectrum typical of singly dispersed CNTs in aqueous solution, with multiple peaks arising from different types of CNTs overlapping across the entire spectrum. In contrast, the spectrum from an early fraction f_{35} has only one major peak centered at 980 nm in the S_{11} region, corresponding to the S_{11} transition from the smallest diameter semiconducting tubes found in HiPco CNTs. Additionally M_{11} transitions are enhanced, indicating an enrichment in metallic tubes. The S_{11} region from later fractions (f_{36}, f_{39}, and f_{45}) shows a systematic shift of intensity toward longer wavelength. The S_{11} transition wavelength is proportional to the tube diameter, the observed shift indicates a gradual increase in average semiconducting tube diameter from early to late fractions. There is also a simultaneous decrease in the M_{11} intensities in late fractions, corresponding to a depletion of metallic tubes. An evaluation of the metal or semiconductor enrichment is also carried out based on resonance Raman measurements.

4.1.2. Amine solvents assisted separation method

Recently, amine-assisted separation method involving a dispersion–centrifugation process in a THF solution of amine, such as octylamine, propylamine, and isopropylamine has been reported. This method is very similar to the separation method using ODA, which has an amine group. In case of ODA method, when CNTs are dispersed in THF with ODA, s-enriched SWCNTs bundles are more prone to supernatant. Because the affinity of amine groups for semiconducting SWCNTs contribute additional stability to the physisorbed ODA. In the amine-assisted method, however, it is emphasized that m-SWCNTs are more strongly adsorbed by amines than s-SWCNTs. The complex
<table>
<thead>
<tr>
<th>Research group</th>
<th>Separation method</th>
<th>CNT dispersion method</th>
<th>Analytical method</th>
<th>Type of separated CNTs</th>
<th>Separation yield</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zheng in DuPont</td>
<td>Chromatography of wrapped SWCNTs by ssDNA</td>
<td>CNT dispersed in aqueous solution using ssDNA</td>
<td>Absorption spectra, Raman spectra (785 nm, 501.9 nm)</td>
<td>s-SWCNT and m-SWCNTs</td>
<td>Metal: ~87%</td>
<td>27</td>
</tr>
<tr>
<td>Papadimitrakopoulos in University of Connecticut</td>
<td>Noncovalent functionalization using ODA</td>
<td>Sonication in THF solution</td>
<td>Absorption spectra, Raman spectra (514 nm, 785 nm)</td>
<td>s-SWCNT</td>
<td>Semi: ~91%</td>
<td>23</td>
</tr>
<tr>
<td>Maeda in Tokyo Gakugei University</td>
<td>Centrifugation in THF solution of amine</td>
<td>Sonication in THF solution of amine</td>
<td>Absorption spectra, Raman spectra (514 nm)</td>
<td>m-SWCNT</td>
<td>Metal: ~87%</td>
<td>24</td>
</tr>
<tr>
<td>Papadimitrakopoulos in University of Connecticut</td>
<td>Precipitation in DMF or DMA solution</td>
<td>Sonication in DMF or DMA solution</td>
<td>Raman spectra</td>
<td>s-SWCNT and m-SWCNTs</td>
<td>—</td>
<td>64</td>
</tr>
<tr>
<td>Krupke in Institute for Nanotechnology</td>
<td>Reversing current dielectrophoresis</td>
<td>Sonication in D2O solution of SDS</td>
<td>Raman spectra (514 nm)</td>
<td>m-SWCNT</td>
<td>Metal: ~86%</td>
<td>22</td>
</tr>
<tr>
<td>Doorn in Los Alamos National Laboratory</td>
<td>Redox reaction with azobenzeno compounds</td>
<td>Sonication in D2O solution of SDS</td>
<td>Absorption and fluorescence spectra, Raman spectra</td>
<td>s-SWCNT</td>
<td>—</td>
<td>66</td>
</tr>
<tr>
<td>Lee in SKKU</td>
<td>Reaction with nitronium ions</td>
<td>Stirring in solution of nitronium ions</td>
<td>Absorption spectra, Raman spectra (514 nm, 633 nm, 785 nm)</td>
<td>s-SWCNT</td>
<td>M11/(S22 + M11) = 0.37 100% less than 1.1 nm</td>
<td>26, 67</td>
</tr>
<tr>
<td>Kataura in AIST</td>
<td>Reaction with hydrogen peroxide</td>
<td>Sonication in hydrogen peroxide</td>
<td>Absorption spectra, Raman spectra (2.71 eV, 2.06 eV)</td>
<td>m-SWCNT</td>
<td>Metal: ~80%</td>
<td>71</td>
</tr>
<tr>
<td>Tour in Rice University</td>
<td>Filtration of the functionalized SWCNTs through silica gel</td>
<td>Sonication in H2O solution of SDS</td>
<td>Absorption spectra, Raman spectra (514 nm, 633 nm, 780 nm)</td>
<td>s-SWCNT</td>
<td>—</td>
<td>72</td>
</tr>
<tr>
<td>Rinzler in University of Florida</td>
<td>Bromination using Br2 solution</td>
<td>Sonication in H2O solution of Triton X-100</td>
<td>Absorption spectra, conductivity measurement</td>
<td>m-SWCNT</td>
<td>—</td>
<td>74</td>
</tr>
<tr>
<td>Lee in SKKU</td>
<td>Fluorination using F2 gas</td>
<td>—</td>
<td>Absorption spectra, Raman spectra (514 nm, 633 nm, 785 nm)</td>
<td>s-SWCNT</td>
<td>Semi: ~86%</td>
<td>73</td>
</tr>
</tbody>
</table>
of amine and as-prepared metallic SWCNTs may have a higher solubility in organic solvents than the case of semiconducting SWCNTs, suggesting a possible separation of metallic from semiconducting SWCNTs.

Figure 15(a) displays the vis–NIR spectra of AP-SWCNTs, a supernatant solution of SWCNTs treated with propylamine (labeled by SWCNTs-PS1), and a supernatant solution of SWCNTs treated twice by the dispersion–centrifugation process with propylamine (labeled by SWCNTs-PS2). Compared with SWCNTs-OS1 and SWCNTs-OS5, much stronger absorption peaks were observed in the metallic $M_{11}$ band for SWCNTs-PS1 and SWCNTs-PS2. Meanwhile, the characteristic absorption peaks of the semiconducting $S_{11}$ band even disappear in SWCNTs-PS2. These results indicate that the metallic SWCNTs are more effectively separated from semiconducting SWCNTs by using propylamine. Interestingly, SWCNTs-PS2 shows different color (purple) from AP-SWCNTs (see Figs. 15(b) and 15(c)). They also carried out the dispersion–centrifugation process in a 3.0 M solution of iso-propylamine in THF and hexane (4:1). As shown in Fig. 15(d), treatment of SWCNTs in a mixed solvent (SWCNTs-PH) seems to provide a higher separation. For a thorough determination of separation yield, a charge-transfer due to adsorbates that invokes deviation of the resonance condition in Raman spectra should be taken into consideration. More systematic approach with Raman spectroscopy with several excitation energies has been provided.31

Papadimitrakopoulos and co-workers have also reported amine-assisted separation method using $N,N$-dimethylformamide (DMF) solution.64 They dispersed acid-treated and washed SWCNTs into DMF media (0.01 mg/ml), which typically contains ca. 15, 0.2, and 0.1 ppm of water, $N,N$-dimethylaniline (DMA), and oxalic acid, respectively. The excess DMA renders DMF basic with pH of ca. 10. This solution was sonicated for 20 min and then allowed to settle for two days. The supernatant was carefully separated from the precipitant,
intending to separate the fine dispersed SWCNTs from their large bundles. They found that m-SWCNTs were enriched in supernatant fraction in the opposite of ODA method. The underlying mechanism for this separation is the physicochemical properties of charge-stabilized SWCNT dispersions in DMF. With the establishment of the reversible nature of the redox chemistry, which was suggested by Zheng et al., SWCNT\textsuperscript{n+} + (n/2)H\textsubscript{2}O ⇌ SWCNT + nH\textsuperscript{+} + (n/4)O\textsubscript{2}, amine-induced pH changes as well as variations in H\textsubscript{2}O and O\textsubscript{2} concentration in DMF are shown to cause differential partial-reduction trends according to nanotube diameter and metallicity. At a pH of 10, the \((n, m)\)-SWCNTs that resist complete reduction to their undoped state remain in suspension while the rest that lose their charges populate the precipitate.

4.1.3. Alternating current dielectrophoresis

So far we have discussed chemical approaches that usually involve inevitable modification of electronic structures to some degree. The adsorption is often strong such that they cannot be removed from CNTs by mild conditions. One physical approach is developed to separate metallic from semiconducting SWCNTs from suspension using alternating current dielectrophoresis. This method takes advantage of the difference of the relative dielectric constants of two species with respect to the solvent, resulting in an opposite movement of metallic and semiconducting tubes along the electric field gradient. Metallic tubes are attracted toward a microelectrode array, leaving semiconducting tubes in the solvent. Microelectrodes are prepared with standard electron-beam lithography and wired to a function generator. For the ac dielectrophoresis, the generator was operated at a frequency of 10 MHz and a peak-to-peak voltage of 10 V. After the generator was switched on, a drop of suspension of individual SWCNTs is applied to the chip. After a delay of 10 min, the drop is gently blown off the surface by a stream of nitrogen gas, and the generator is switched off. The resulting sample is characterized with a confocal Raman microscope excited with 514.5 nm. These Raman spectra are shown in Fig. 16.

Figure 16(a) shows the RBM regions obtained by averaging ten single Raman spectra measured on different spots of the aligned SWCNTs and on the reference sample. The variations between the individual spectra are within a few percent owing to the large number of tubes measured within the laser spot. The reference spectrum shows two bands, with one band (red) dominated by a feature at 187 cm\textsuperscript{−1}, which is associated to semiconducting, and the other band (blue) consisting of three peaks at 247, 263 and 271 cm\textsuperscript{−1}, which are assigned to metallic tubes. The metallic peaks are intensified in the deposited sample, and this is again strongly supported by the metallic BWF line shape in G-mode, as shown in Fig. 16(b). The metallic tubes are enriched up to 80%, indicating that only a small fraction of tubes is present as bundles. It is observed that about 100 pg of metallic tubes are deposited, out of roughly 100 ng of tubes present in the drop. The issue remains in obtaining large quantity of
separated materials with high separation yield. This is again closely related to how well the CNTs are nanodispersed.

4.2. **Chiral selective chemical reactions**

4.2.1. **Chiral selective redox chemistry**

The different band gap and chemical reactivity between metallic and semiconducting nanotubes can be a new means of chirality separation. Diameter-dependent pyramidalization, π-orbital misalignment effects and charge-transfer can be an important factor of chiral selective reactivity of CNTs. Doorn and co-workers have well demonstrated a new class of electron-transfer reactions between nanotubes and organic acceptors, broadening the growing range of nanotube redox studies.

Doorn and co-workers studied the reactivity of HiPco nanotubes, suspended in SDS solution, with a number of organic charge-transfer molecules, including 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TFTCQ), mordant yellow 10 (MY) and 4-amino-1,1-azobenzene-3,4-disulphonic acid (AB). They monitored nanotube spectral changes induced by reaction with these small molecules using fluorescence (excited at 785 nm) and absorption spectroscopy. A method of selectively and reversibly doping SWCNTs, thereby controlling their electronic properties through redox reactions with small organic electron–acceptor molecules, is described. The selectivity stems from the varying reactivity of each nanotube type based on differences in band gap and electronic properties that depend on their diameter and chirality. Redox doping by means of electron-transfer between an acceptor molecule and an electron donor (the nanotube) results in bleaching of nanotube fluorescence and absorbance spectra. Chiral selectivity in the redox reaction is shown to result from band gap dependence in the electron-transfer kinetics.

Figure 17 shows the NIR absorbance spectrum of SWCNTs bleached from the original spectrum and frozen with the addition of 0.1 µmol of AB to 1 ml of 14 mg/l SWCNTs. Under these conditions, the spectral distribution remained stable for an hour after AB addition. A second addition of 0.1 µmol of AB shifted the stable distribution further, to larger band gap chiralities. Thus, the tuned redox reactivity results in a spectral enrichment of larger-band gap nanotubes. Coupling such chemistry to separation processes may be an effective method.

They initially focused on spectral behaviors in aqueous solutions under ambient oxygen conditions. In addition to the organic–acceptor molecules, other species present in the aqueous suspension of nanotubes play an important role in the bleaching and recovery of SWCNT spectra. They have also carefully watched the effect of oxygen on selective redox reaction and recognized that oxygen plays an important role in charge-transfer associated with pH-induced bleaching of nanotube absorbance and fluorescence spectra. It is proposed that the chiral-dependent redox kinetics has implications for potentially using solution-phase redox chemistry for pinning the absolute potential of the Fermi level, as well as for future applications in chiral selective separations. Control over the reaction kinetics by adjustment of relative concentrations and tuning the reduction potentials of acceptor species can result in selectable distributions of reacted and unreacted nanotube chiralities.

4.2.2. **Diameter-selective separation using nitronium ions**

Recently, two novel methods have been proposed for a diameter-selective removal of m-SWCNTs from s-SWCNTs using nitronium ions. These separation techniques are capable of nearly 100% separation of semiconducting from metallic nanotubes for small diameter nanotubes.
Lee and coworkers have found that the treatment of SWCNTs with an appropriate volume ratio of nitric/sulfuric acids (1:9) made s-SWCNTs highly enriched, as shown in Fig. 18. Two groups of s-SWCNTs near 180 cm\(^{-1}\) and m-SWCNTs near 260 cm\(^{-1}\) in the RBM of Raman spectra are clearly observed in the pristine sample (Fig. 18(a)). The metallic peaks near 260 cm\(^{-1}\) (diameter ∼ 0.93 nm) disappeared completely after nitric/sulfuric acids treatments for 48 h (Fig. 18(b)). It is well known that mixing nitric and sulfuric acids yield a high production rate of nitronium ions (NO$_2^+$), which can easily attack π electrons in aromatic rings. By analogy, 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-SWCNTs can provoke stronger adsorption of nitronium ions with higher binding energy than s-SWCNTs due to more available charge density at the Fermi level which induces stronger charge-transfer from nanotube to nitronium ion, as shown in Fig. 19.

Lee’s group has conducted another approach to experimentally prove their analogy about the chiral separation of SWCNTs by nitronium ions.

![Fig. 18. RBM of Raman spectra at 514 nm excitation wavelength for (a) pristine sample and (b) HNO$_3$/H$_2$SO$_4$ (1:9) treated sample for 48 h, followed by heat treatment at 900°C in Ar atmosphere.](image)

Fig. 18. The schematic band structures of metallic and semiconducting nanotubes (top) and the schematic diagram of the preferential binding of nitronium ion on metallic tube (bottom).

Nitronium hexafluoro-antimonate (NO$_2$SbF$_6$:NHFA) or nitronium tetrafluoroborate (NO$_2$BF$_4$:NTFB) of 40 mmol is dissolved in TMS/chloroform (1:1 by weight) solution of 100 ml. The nitronium salts were ionized in the mixed solvent as follows:

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

where both reactions produced nitronium ions.

The pristine SWCNT soot of 10 mg is suspended by sonicating for 24 h in the prepared NHFA or NTFB solution at 60°C. After reaction, the suspension is filtered using a membrane filter with a pore diameter of 10 µm and then washed with ethanol several times. The residual SWCNTs on the filter treated with NHFA or NTFB solution are dried in vacuum at 100°C for overnight, and further heat-treated in a vacuum at 1000°C for 30 min. In order to clarify the nature of metalliclicity of the residual sample on the filter, they have investigated the resonant Raman spectra. They have identified five distinct peaks in the RBM.
mode from the pristine sample at an excitation energy of 514 nm in Fig. 20(a). 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 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. After heat treatment at 1000°C in a vacuum, the peak shift of the semiconducting band was recovered and the peak was intensified. 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.

Figure 20(b) shows the RBM profiles at an excitation energy of 785 nm. In this case, only the semiconducting $S_{22}$ bands (205, 216, 226, 234, and 267 cm$^{-1}$) are observed 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. However, 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. They have emphasized 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. 20(a). This strongly suggests that the nitronium ions attacked selectively the m-SWCNTs with small diameters less than 1.1 nm. They have also observed the Raman spectra with an excitation energy of 633 nm, as shown in Fig. 20(c). 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,\textsuperscript{69} 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. 20(b). 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.\textsuperscript{70} 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.\textsuperscript{62}

They have also conducted the density-functional calculations of NO\textsubscript{2} adsorption on SWCNT walls to theoretically prove the chiral separation of SWCNTs by nitronium ions.\textsuperscript{70} They have found that NO\textsubscript{2} adsorption is strongly electronic structure- and strain-dependent. The NO\textsubscript{2} adsorption on m-SWCNTs was energetically more favorable than that on s-SWCNTs and furthermore the adsorption became less stable with increasing diameters of nanotubes, as shown in Fig. 21. The adsorption barrier height shows similar dependence on the electronic structure and diameter to the adsorption energy. The selective adsorption of nitronium ion 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. This 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.

Absorption spectra again revealed the metallicity of the pristine and NHFA-treated SWCNTs, shown in Fig. 22. In the pristine SWCNTs, transitions between the first and second van Hove singularities (S\textsubscript{11} and S\textsubscript{22}) in s-SWCNTs were observed near 0.9 eV (S\textsubscript{11}) and 1.5 eV (S\textsubscript{22}), whereas the related peak (M\textsubscript{11}) in m-SWCNT was observed near 2.0 eV, shown in Fig. 22(a). On the other hand, the intensity of the M\textsubscript{11} 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, they performed the curve fitting of the absorption spectra. The transition energy is inversely proportional to the tube diameter.\textsuperscript{47,48} The diameter distribution, which is written on the fitted curves in Figs. 22(a) and 22(b), clearly demonstrated the removal of small-diameter SWCNTs by the NHFA treatment. The small amount of M\textsubscript{11} transitions at lower energy side (large diameter) still remained in the sample even after NHFA treatment. 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 separation yield of the sample can be drawn by the ratio of S\textsubscript{22} and M\textsubscript{11} transitions in the optical absorption spectra.
Since the $S_{11}$ band might be modified more easily than the $S_{22}$ band, they extracted information of the separation yield from $M_{11}/(S_{22} + M_{11})$. This value was 0.37 from the pristine sample, close to the theoretical estimate. This was reduced to 0.14 after the NHFA treatment followed by thermal annealing. They have insisted that if one starts with small-diameter nanotubes less than 1.1 nm, the yield of separation would be close to 100%.

4.2.3. Selection of metallic SWCNTs using hydrogen peroxide

Recently $H_2O_2$ treatment of SWCNTs at varying heating times has revealed the selectivity in oxidation by increasing the concentration of metallic SWCNTs in the final product. Figure 23 shows the optical absorption spectra of the SWCNT thin films treated with $H_2O_2$ at different treatment intervals. The peak photon energies of $S_{11}$ and $S_{22}$ absorption bands have shifted to a lower energy as a result of prolonged $H_2O_2$ treatment. This means that the high energy side of $S_{11}$ and $S_{22}$ peaks decreased more rapidly than the low-energy side. On the contrary, the intensity of the $M_{11}$ absorption band increased with increasing oxidation time relative to $S_{11}$ and $S_{22}$ peaks.

This phenomenon of the $H_2O_2$-induced oxidation of SWCNTs is beneficial from two perspectives: the low temperature combustion of SWCNTs without the formation of byproducts and the enhanced chemical reactivity of SWCNTs afforded by hole-doping. Thus, SWCNT oxidation by $H_2O_2$ is more effective for thinner s-SWCNTs, because of the higher chemical reactivity resulting from curvature effects and the higher DOS caused by hole-doping. Finally, they have obtained greater than 80 wt% of m-SWCNTs by selective oxidation of s-SWCNT with $H_2O_2$.

4.2.4. Separation using polarity difference of functionalized SWCNTs

Separation techniques using simple filtration of the functionalized SWCNTs through silica gel have been introduced by Tour et al. This separation uses nanotube sidewall functionalization employing two different strategies. In the first approach (method I), a crude mixture of metallic and semiconducting SWCNTs was heavily
functionalized with 4-tert-butylphenyl addends to impart solubility to the entire sample of SWCNTs. Two major polarity fractions were rapidly filtered through silica gel, with the solvent being removed in vacuo, heated to 700°C to remove the addends, and analyzed spectroscopically. The second approach (method II) uses two different azonium salts, 4-tert-butylbenzenediazonium tetrafluoroborate (a nonpolar moiety) and 4-(2’-hydroxyethyl)benzenediazonium tetrafluoroborate (a polar moiety), appended selectively onto the different SWCNTs by means of titration and monitoring by UV analysis throughout the functionalization process. The different addends accentuate the polarity differences between the band-gap-based types permitting their partial separation on silica gel. Thermal treatment regenerated pristine SWCNTs in enriched fractions. The processed samples were analyzed and characterized by Raman spectroscopy.

The Raman RBMs generated from separation methods I and II are shown in Fig. 24. This underscores the observation that both separation methods provide similar enrichment levels when viewing at 633 nm. At 514.5 nm, the operationally simpler separation method I provides a more narrow distribution of SWCNT types in favor of the (8, 5) metallic, while separation method II affords more of the (12, 6) and (9, 3) metallics in addition to the (8, 5) metallic. Likewise, at 780 nm, separation method I appears more discriminating in favor of the (11, 3) semiconductor.

They have rationalized the functionalized metallics being less polar than the functionalized semiconductors in separation method II because the semiconductors had hydroxylated addends. They have also presumed that some m-SWCNTs are more heavily functionalized than the s-SWCNTs in separation method I, therefore making them less polar and more prone to migration on silica gel.

4.2.5. Separation via halogenations

Recently a gas phase reaction was introduced to selectively remove m-SWCNTs by fluorine gas, followed by a heat treatment. The metallicity of the processed samples was characterized by the resonant Raman spectroscopy with several wavelengths of 514.5, 632.8 and 785 nm and absorption spectra. Peaks of m-SWCNTs near 244 and 266 cm$^{-1}$ in the RBMs with an excitation wavelength of 514.5 nm were greatly suppressed with fluorination and completely disappeared after heat treatment, as shown in Fig. 25. On the other hand, the s-SWCNTs with small diameters less than 1 nm were still retained in the sample after fluorination, which was confirmed by Raman spectroscopy.

![Fig. 24. Comparison chart of the Raman spectra at varying wavelengths of the starting SWNT (left column, prepared from the SDS/SWCNTs by flocculation with acetone), the regenerated (TGA pan) SWNTs from separation method I (middle column), and separation method II (right column).](image-url)
Fig. 25. Raman spectra at 514 nm excitation wavelength. (a) RBM regions of the raw SWCNTs which was deconvoluted with several peaks (Lorentzian), fluorinated SWCNTs for 30 min, and fluorinated SWCNTs followed by the heat treatment at 600 and 900 °C from the bottom spectrum. The box indicates the range of semiconducting and metallic components determined from Kataura plot. (b) G-band regions with same notations to the RBMs.

at excitation energies of 633 and 785 nm. Moreover, the D-band decreased after annealing the fluorinated SWCNTs at 600°C, which were associated with release of the fluorine atoms during heat treatment. The removal of m-SWCNTs became obscured at nanotubes with diameters greater than 1 nm. Adsorption of fluorine gas on m-SWCNTs was promoted by the large charge transfer from metallic nanotubes to fluorine molecule due to more abundant electron density at the Fermi level compared to the counterpart semiconducting nanotubes. The absorption data also demonstrated the similar diameter dependence in the selectivity to the Raman spectra.

Rinzler et al. have also developed a separation method using charge-transfer doping using bromine solution. A diluted quantity of bromine was vigorously stirred into nanotubes in a surfactant-stabilized aqueous suspension followed by 12 h of centrifugation at 24 000 g. The supernatant and sediment from this centrifugation were separately collected and then analyzed by absorption spectra. They have found that the semiconducting nanotube content has been substantially enhanced in the supernatant sample at the expense of that in the sediment. The additional Br associated with the metallic nanotubes interferes with their surfactant stabilization, resulting in increasing density of metallic nanotubes.

The separation method relies on chemical discrimination in the charge-transfer complex formation between bromine and the metallic versus semiconducting nanotubes and takes advantage of the resulting density difference to effect a centrifugation-based separation. However, the separation efficiency is very low, and the amount of the separated metallic SWCNTs is quite small in this technique.

5. Summary

Since the discovery of CNTs, the particular electronic properties have attracted much attention. The extraordinary properties of carbon nanotubes and their electronic structure have been well established. It has been verified that electronic properties of nanotubes depend on tube diameter, helicity, and wrapping angle. The main barriers to realize full applications of CNTs are nanodispersion, sorting length, and the electronic structure control of CNTs. The problem for solving main barriers is particularly difficult because of their small size and small differences in diameter and chirality.

One of the important challenges in CNT research field is to realize the control of electronic structures of CNTs. Separation of metallic from semiconducting SWCNTs or vice versa is of critical importance fundamentally and technologically. Although several approaches have been tried so far for this issue, many problems still remain unanswered; low separation efficiency, very small amount of separated SWCNTs, and difficulty in removing the remnant reagents. In principle of several separation methods, a complete separation between metallic and semiconducting SWCNTs could be realized if all nanotubes in the suspension are present as individual ones, namely nanodispersion. The continuous development of nanotechnologies in field of physics, chemistry, and biology will make it possible to accurately control or manipulate at the atomic or molecular levels (in the length scale of 1–100 nm range). These coming new nanotechnologies may accelerate the complete chiral separation of CNTs. It is certain that the chiral separation techniques of CNTs shed new light on nanomaterial sciences, which can play a determinative role in application of CNTs.

Acknowledgments

This research was supported by a grant of No. 05K1401-00412 from Center for Nanoscale Mechatronics and Manufacturing, one of the 21st Century Frontier Research Programs, in part by the Center for Nanotubes and Nanostructured Composites at
Sungkyunkwan University, and in part by Environmental Technology project of MOE.

References