ON-CHIP SEPARATION/CONVERSION OF SINGLE-WALLED CARBON NANOTUBE

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING
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<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
</tr>
<tr>
<td>AY</td>
<td>Acid Yellow 9</td>
</tr>
<tr>
<td>CoMoCAT</td>
<td>Cobalt Molybdenum Catalysts</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon Nanotubes</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>D</td>
<td>Depletable</td>
</tr>
<tr>
<td>DEP</td>
<td>Dielectrophoresis</td>
</tr>
<tr>
<td>DGU</td>
<td>Density Gradient Ultracentrifugation</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DI water</td>
<td>Deionization Water</td>
</tr>
<tr>
<td>ssDNA</td>
<td>Single-stranded DNA</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of Electronic State</td>
</tr>
<tr>
<td>EAQ</td>
<td>2-Ethylanthraquinone</td>
</tr>
<tr>
<td>FETs</td>
<td>Field-effect Transistors</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>HFI</td>
<td>Heptadecafluoro-1-iodooctane</td>
</tr>
<tr>
<td>MWNTs</td>
<td>Multi-walled Carbon Nanotubes</td>
</tr>
<tr>
<td>ND</td>
<td>Nondepletable</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>SDB</td>
<td>Sodium Dodecyl-benzenesulfonate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscope</td>
</tr>
<tr>
<td>SWNTs</td>
<td>Single-walled Carbon Nanotubes</td>
</tr>
<tr>
<td>M-SWNT</td>
<td>Metallic Single-walled Carbon Nanotube</td>
</tr>
<tr>
<td>S-SWNT</td>
<td>Semiconducting Single-walled Carbon Nanotube</td>
</tr>
<tr>
<td>TFTs</td>
<td>Thin-film Transistors</td>
</tr>
<tr>
<td>UV-vis-NIR</td>
<td>Ultraviolet-visible-Near-Infrared</td>
</tr>
<tr>
<td>VHS</td>
<td>Van Hove Singularities</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor-Liquid-Solid</td>
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Abstract

Due to their unique structure and excellent properties, single-walled carbon nanotubes (SWNTs) have great potential on nanoelectronics applications. Now it is still difficult to control the electronic type of SWNTs by direct synthesis techniques, and post-synthetic treatment is required to obtain pure semiconducting SWNTs for FET devices. The post-synthetic separation/conversion methods can be roughly divided into two groups. One group is solution-based separation method. The other one is on-chip based separation or conversion process. Comparing with the solution-based methods, on-chip based separations or conversions are more simple and direct due to not involving purification, surfactant and sonication issues, which can degrade performance of SWNT-based FET. Thus, this thesis focuses on developing on-chip based separation or conversion technologies to obtain SWNT FET with good performance.

Firstly, we present an approach to convert metallic SWNTs to semiconducting ones in-situ to improve device field effect behaviour, using an aromatic compound (2-ethylantraquinone - EAQ) which is a mild radical initiator. We show that the reaction between EAQ-generated radicals and SWNTs is diameter and metallicity dependent; in the diameter regime (0.8 to 1.0 nm), the EAQ-generated radicals preferentially attack the metallic SWNTs over semiconducting ones and convert them to semiconducting, as evidenced by several orders (10 and 10^4) increase in the on/off ratio.

In the following, we demonstrate a simple and scalable method to improve the switching of SWNT-based FET devices by in-situ conversion of metallic SWNTs to
SWNT/adsorbed molecule complexes which exhibit semiconducting behaviour using electron-acceptor molecules. This approach, using 4-Amino-1,1’-azobenzene-3,4’-disulfonic acid sodium salt (Acid Yellow 9, AY) as electron-acceptor, is found to be diameter dependent and is highly effective for M-SWNTs with diameters in the range 1.4nm to 2.6nm. The enhancements of on/off ratio in FET devices after AY treatment generally ranged between 10 and $10^3$. Single SWNT-FET devices used here enable the precise characterization of AY treatment with different nanotube diameters and metallicity.

Lastly, we showed that a UV irradiation induced radical methods can effectively in situ silence M-SWNTs with diameter smaller than 1.4 nm with Heptadecafluoro-1-iodooctane (HFI). Perfluoroalkyl radicals’ covalent binding to sidewall of SWNTs was monitored by Raman and XPS spectra. This approach was found to be electronic dependent in the diameter range from 1.2 nm to 1.4 nm, in which the intensity of electrons near Fermi level dictates chemical reactivity of SWNTs. This method combined with our previous AY method can be applied to SWNTs network-based devices, and the resulting devices shows significantly enhanced on/off ratio. So it provides a promising technique to realize high-performance SWNT-based electronics.
Chapter 1

Introduction and Literature Review

As one of the most versatile elements in the chart of chemical elements, carbon can be found in almost every aspect in people’s daily living. Carbon has a rich chemistry due to the type and number of bonds it can form with other elements. Sigma bond (σ) and pi (π) bond can be formed when carbon binds. Two σ bonds and two π bonds can be formed in an sp\(^1\) hybridized carbon atom, three σ bonds and one π bond are shaped in an sp\(^2\) hybridized carbon atom, and four σ bonds can be formed in an sp\(^3\) hybridized carbon atoms. The properties and geometry of carbon allotropes depend on the number and type of the bonds.

Before 1991, graphite, diamond and buckyball are three known allotropes of solid carbon. Graphite is consisted of two-dimensional planar sheets of sp\(^2\) hybridized carbon atoms in a hexagonal lattice. The force between any two planar sheets is Van der Waals effect. This made graphite slippery and electrically conductive. In contrast, diamond has a tetrahedral structure, consisting of sp\(^3\) hybridized carbon atoms. This crystalline structure makes diamond the hardest substance known. The third allotrope of carbon is buckyball, which is first discovered in 1985 by Smalley and coworkers at Rice University.\(^2\) C\(^{60}\) is the first buckyball to be discovered, which is a soccer ball-shaped molecule with 60 sp\(^2\) hybridized carbon atoms bonded together in 20 hexagons and 12 pentagons. Because of
the discovery of buckyball, Smalley, Curl and Kroto were jointly awarded the Nobel Prize in Chemistry in 1996.

In 1991, Japanese scientist Sumio Iijima accidentally discovered carbon nanotubes, when he used transmission electron microscopy (TEM) to examined soot from an arc discharge chamber. Initially, Iijima observed only Multi-Walled carbon nanotubes (MWNT) consisting of 2 to 20 layers. In 1993, Iijima’s group and Bethune’s group simultaneously and independently reported their work on the synthesis of single walled carbon nanotubes (SWNTs), which have a diameter of about 1nm. Those discoveries and works led more researchers all over the world to study physical, electronic, mechanical, chemical and optical properties of carbon nanotubes in the following two decades.
1.1 SWNTs

Carbon nanotubes exist in two different forms: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Here, we focus on the SWNTs. SWNT can be considered by rolling a graphene sheet into a seamless cylinder along a chiral vector \((n, m)\) in the sheet plane as shown in figure 1-1a. The electronic structure and electrical properties of SWNTs are determined by the chiral vector, which are key parameters of carbon nanotubes. Depending on the chirality with different value of \(n\) and \(m\), SWNT can be metallic or semiconducting. \(n\) and \(m\) are also called indexes and can be used to calculate the diameter \((d_t)\) and chiral angle \((\theta)\) of a SWNT from the following equations:

\[
d_t = 0.0783\sqrt{(m^2 + mn + n^2)} \quad (1-1)
\]

\[
\theta = \tan^{-1}(\sqrt{3}m/(2n + m)) \quad (1-2)
\]

According to chiral angle, SWNT can be classified into three types differentiated by their electronic properties: armchair \((n=m, \theta=30^\circ)\), zig-zag \((m=0, n>0, \text{ and } \theta=0^\circ)\), and chiral \((0<|m|<n, 0^\circ < \theta < 30^\circ)\) (figure 1-1 b, c and d). Armchair SWNT is metallic and its band gap is zero. Zig-zag and chiral SWNT can be semimetal with a finite band gap if its chiral index \((n, m)\) meets \(n-m=3l\) \((l=1,2,3\cdots)\), and semiconductor in all other cases. For semimetallic and semiconducting SWNT, the band gap \((E_{11})\) is inversely related with the
diameter of nanotubes (figure 1-2). Different band gap corresponds with different electronic behavior as shown in figure 1-3.

**Figure 1-1** (a) Schematic honeycomb structure of a graphene sheet, \((a_1, a_2)\) represent lattice unit vectors of the graphene sheet. Folding of the \((8,8), (8,0)\) and \((10,2)\) vectors leading to armchair (b), zigzag (c) and chiral (d) SWNT, respectively.\(^6\)
In the diameter range smaller than 2 nm, there are more than two hundred chiral species in commonly synthesized carbon nanotube samples. The diversities have become an obstacle for their applications. For instance, SWNT-based field-effect transistor (FET) devices require highly pure semiconducting nanotubes with specific band gaps as active device channel components. To overcome the obstacle, a number of selective synthesis and post-synthetic separation methods have been studied.

**Figure 1-2** Electronic density of states calculated with a tight binding model for (8, 8), (9, 9), (10, 10) and (11, 11) armchair nanotubes. The Fermi energy I located at 0 eV. Wave vector-conserving optical transitions can occur between mirror image spikes, that is, $v_1 \rightarrow c_1$ and $v_2 \rightarrow c_2$. \(^1\)

In the diameter range smaller than 2 nm, there are more than two hundred chiral species in commonly synthesized carbon nanotube samples. The diversities have become an obstacle for their applications. For instance, SWNT-based field-effect transistor (FET) devices require highly pure semiconducting nanotubes with specific band gaps as active device channel components. To overcome the obstacle, a number of selective synthesis and post-synthetic separation methods have been studied.
Figure 1-3 Calculated gap energies between mirror-image spikes in DOS for $\gamma=2.75$ eV. Semiconducting SWNTs are open circles; metallic SWNTs are solid circles with armchair SWNTs as double circles.$^{12}$
1.2 SWNT Synthesis Methods

Usually there are different individual structures, morphologies and properties in as-synthesis SWNTs samples. The methods of synthesis and further processing also determine the SWNTs species and properties. Up to date, a large number of preparation methods have been reported to obtain the desired SWNTs with special properties, which can be used for scientific studies and technological application. During the last two decades, researchers have done a wide variety of endeavor to try to prepare high-quality SWNTs with high yield. Now there are mainly three common-use preparation methods to synthesize SWNTs. The first method is arc discharge. The Second one is laser ablation. Lastly we will intensively introduce chemical vapor deposition (CVD) methods, including its growth mechanism.

1.2.1 Arc Discharge

As the first method that can synthesis both MWNTs and SWNTs, arc discharge can produce gram level for MWNTs and SWNTs. In arc discharge method, usually a low voltage is applied between graphite cathode and anode electrodes with 1 mm gap. During the reaction process, an inert atmosphere such as He or Ar is needed under the pressure of 100 to 1000 torr. A schematic of arc discharge system is shown in Figure 1-4. Iijima’s group and Bethune’s group firstly observed SWNTs produced by this method. Both of them figured out that metal catalyst absorbed in anode electrode is requisite for the synthesis of the SWNTs. Iijima used iron as the catalyst under mixture gas of methane and
argon. For Bethune, cobalt was utilized in the He atmosphere. The diameter of SWNTs produced by arc discharge can be tubed by changing the ratio of Ar and He gas, obtaining smaller diameter under big Ar ratio.\textsuperscript{15} Waldorff \textit{et al.} reported the yield of SWNTs can be tuned by changing overall gas pressure.\textsuperscript{16} Journet \textit{et al.} used Y and Ni mixture as the catalyst, and produced SWNTs with 90\% yield.\textsuperscript{17} The SWNTs from arc discharge method are pretty “dirty”, and the long-time purification is required before application.

\textbf{Figure 1-4} Schematic of an Arc discharge setup.
1.2.2 Laser Ablation

Under inert atmosphere, metal and graphite composite target placed in the high-temp furnace is vaporized with a high power laser beam. A schematic of laser ablation system is shown in Figure 1-5. During the reaction process, generated metal nanoparticles can catalyze the growth of SWNTs. Laser ablation method also obtains many by-products, of which there are amorphous carbon, graphitic carbon, fullerenes and bucky onions surrounding metal catalyst. Those by-products need to be removed before utilization. Smalley group at Rice University was the first to utilize laser ablation methods to produce gram-level SWNTs.\textsuperscript{18} In their report, they used Co/Ni as catalyst with 1.2% of weight ratio under \(~500\) torr of Ar or He inert atmosphere. The diameter of SWNTs produced by laser ablation depends on

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{laser_ablation.png}
\caption{Schematic of a laser ablation system.}
\end{figure}
reaction temperature. In fact, laser ablation and arc discharge share similar growth mechanism.

1.2.3 Chemical Vapor Deposition (CVD)

CVD is the most commonly used method for commercial production of SWNTs. Since Dai et al. firstly used CVD process to successfully obtain SWNTs, researchers from all over the world have published large numbers of works on CVD of SWNTs. The CVD method involves the decomposition of gaseous carbon source under extreme high temperature, and the metal nanoparticle on the substrate can catalyze the carbon nanotube’s growth. A schematic of laser ablation system is shown in Figure 1-6. During CVD growth method, there are several key factors, such as catalyst type, carbon source, and growth temperature, which can determine the quality, yield, diameter and chirality of as-grown SWNTs.

Figure 1-6 Schematic of a CVD system.
According to the catalyst location in SWNTs growth process, CVD can be classified into two basic types. One is substrate growth, and the other is gas phase growth. In the substrate growth, the metal catalyst nanoparticles are deposited on the substrate surface. In contrast, the catalyst and SWNTs initiation and continuous growth process occur in the mid-air. The underlying growth mechanism for both is similar, including surface carbon and bulk carbon diffusion. For surface carbon diffusion, the generated carbon from decomposing carbon source is nucleated on the side of metal nanoparticle, which remains a solid under low temperature. Since carbon source is continually decomposed and nucleated on the particle, the SWNTs can grow longer and longer.

In substrate growth, when SWNT starts to growth, either base growth or tip growth will occur as shown in figure 1-7. In base growth the metal catalyst remains on the surface of substrate, and SWNTs will extend into air or along the substrate surface. While in the tip growth, the catalyst particles float in the mid-air, and the end of SWNTs stuck to the substrate surface.

Many kinds of catalytic species have been reported to synthesis SWNTs with CVD method. Fe, Co and Ni are the three most common-used metal catalysts. Their bimetallic or trimetallic mixture with Y, Mo and Ru also can be used to produce massive SWNTs with high yield. Especially, Co/Mo catalyst has been intensively studied. However, the different catalyst’s effect to SWNTs’ growth still has much more room to explore, and our understanding is still not complete.
Figure 1-7 Schematic of base and tip growth of SWNTs on the substrate.

The first carbon source for SWNTs growth by CVD method is carbon monoxide. After that, researchers have reported to use methane, ethylene, acetylene, ethanol, methanol and benzene as carbon source for CVD growth. Different carbon source has different reactivity. For example, ethylene or acetylene is much more reactive, comparing with methane. So at low temperature of 550 °C, ethylene can be used to produce
SWNTs.\textsuperscript{32}  However, methane is not reported below 680 °C. \textsuperscript{33} Some carbon sources contain oxygen element, which can remove amorphous carbon during SWNTs growth process to increase the yield and length of carbon nanotubes. For instance, ethanol has been reported to use as carbon source to prepare centimetre-scale SWNTs as shown in figure 1-8.\textsuperscript{34}

Since the discovery of carbon nanotubes in 1991, synthesis methods have been greatly enhanced. Commercial usage of SWNT with high yield and high purity has been realized. However, electronic-type and diameter control synthesis of SWNTs still face many challenges and technic issues, which impedes the practical application of SWNT-based FET and interconnects, so more works need to do.

\textbf{Figure 1-8} (a) Image of 4.8-cm-long Si substrate on which a 4-cm SWNT was grown. (b) SEM image of the beginning section of the long SWNT.\textsuperscript{34}
1.3 Applications in CNT-based Electronics

Due to their unique structure and excellent properties, SWNTs have great potential on many applications. Researchers from all over the world have devoted a large number of time and energy to try to realize those potential applications, such as carbon nanotube-based electronics,\textsuperscript{35-46} carbon nanotube-based sensors,\textsuperscript{47-69} carbon nanotube in energy,\textsuperscript{70-87} mechanical\textsuperscript{88-95} and biological\textsuperscript{50,96-110} applications.

In this section, we will focus on the carbon nanotube-based electronics, especially SWNT-based FET device. Depending on the direction SWNTs are rolled, they can be either metallic SWNT (M-SWNT) or semiconducting SWNT (S-SWNT). The Van Hove singularities (vHS) are consisted of the electronic density of states (DOS) of individual SWNT. For armchair M-SWNT, DOS is continuous near the Fermi Level as shown in figure 1-9; otherwise, M-SWNT has a

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{dos.png}
\caption{A schematic of the electronic density of states (DOS) for M-SWNT and S-SWNT. $E_F$ is Fermi level. $M_{11}$ denotes the lowest energy transition for M-SWNT, and $S_{11}$ is the first energy transition for S-SWNT.\textsuperscript{111}}
\end{figure}
small band gap (~50 meV) due to the curvature-induced mixing of \( \pi-\sigma \) orbitals. There is an obviously big band gap (over 500 meV) in the DOS of S-SWNT as shown in Figure 1-9. The current density of an individual carbon nanotube can reach up to \( 10^9 \) A/cm\(^2\). Semiconducting SWNTs are the ideal materials for next-generation FET due to their mobility as high as 79000 cm\(^2\)V\(^{-1}\)s\(^{-1}\). Figure 1-10 shows a typical carbon nanotube-based FET device, consisting of three electrodes (source, drain and gate), dielectric layer and semiconducting SWNT. Dekker \textit{et al.} firstly reported SWNT-based FET in 1998, and soon after, Avouris’ group in IBM also demonstrated SWNT-FET. Both of them dispersed carbon nanotubes produced by laser ablation.
method in a solvent, and deposited onto a Si/SiO2 substrate with metal contact. Some semiconducting carbon nanotubes can connect source and drain electrodes, resulting in P-type FET in air with on/off ratio of several orders. Since SWNT-based FET was firstly demonstrated in the experiment, the academic community and industrial circles have invested a wide variety of time and money to realize its practical application in the past two decades. Significant progress has been achieved in understanding conduction through SWNT-based electronic devices, and better-performance SWNT-FET has also been fabricated. In addition, we are on the way to SWNT-based logic circuit. Nevertheless, three are still large obstacles and challenges for carbon nanotube to completely replace silicon. Among those challenges, the central issue for fabricating high-performance SWNT-based FET is to minimize the presence or influence of metallic SWNT in the active channel.
1.4 Post-synthetic Separation/conversion Methods

So far, it is still difficult to control the electronic type of SWNTs by direct synthesis techniques, and post-synthetic treatment is required to obtain pure semiconducting SWNTs for FET devices. The post-synthetic separation/conversion methods can be roughly divided into two groups. One group is solution-based separation method. The other one is on-chip based separation or conversion process.

1.4.1 Solution-based Separation Techniques

A variety of solution-based techniques have been reported to separate SWNTs, including selective covalent reaction, selective non-covalent adsorption, electrophoretic separation, chromatography method, and density gradient ultracentrifugation (DGU). In the following, we will briefly review two most popular solution-based techniques: selective covalent reaction method and DGU.

For selective covalent reaction method, diazonium salts are the most reported chemicals. During the reaction, diazonium salts can generate radicals, which will selectively form covalent bond with metallic SWNTs. When diazonium radicals are covalently attached to the sidewall of M-SWNT, the conjugated π-system of SWNT will be interrupted, leading to the decay of transitions between the vHS of M-SWNT as shown in the figure 1.1. Metallic SWNTs have a higher DOS at the Fermi Level than their
semiconducting counterparts, and this high availability of electrons in M-SWNT is more helpful to stabilize the charge-transfer state between diazonium radicals SWNTs prior to covalent-bond formation. So theoretically, metallic SWNT can be preferentially functionalized by controlling the reaction condition.

![UV-vis-NIR spectrum of SDS-suspend SWNTs after diazonium reaction.](image)

**Figure 1-11** UV-vis-NIR spectrum of SDS-suspend SWNTs after diazonium reaction.

DGU separates SWNTs via the differences in the sedimentation coefficient in a constant density medium. A few factors, such as molecular weight, buoyant density, will affect the sedimentation coefficient. The separation result is determined by SWNT structure, surfactant type, pH values and density gradient medium. In 2005, Arnold *et al.* successfully achieved electronic-type separation SWNTs with co-surfactant of sodium cholate and sodium dodecyl sulphate via DGU method as shown in figure 1-12. To date, DGU is the main sorting method that can deliver high single type SWNTs. However, its technological limitations are bounded by its scalability and economic viability.
Figure 1-12 (a) SWNTs encapsulated with co-surfactant are separated by electronic type by DGU. (b) Optical spectra confirm sorting as metallic fractions are peaked in the M11 region whereas semiconducting ones are peaked in $S_{22}$ and $S_{33}$ regions.\textsuperscript{141}

For the solution-based separation methods, the well-monodisperse SWNT solution is the essential prerequisite to obtain excellent separation result. Usually there are a variety of impurities in the pristine SWNT samples, such as catalyst particles, carbonaceous by-products. To obtain pure SWNTs for FET devices, strong acids and alkaline were employed to remove the impurities in pristine samples.\textsuperscript{142-144} The purification treatment can lead to the defect to the structure of SWNT, and affect or even destroy the performance of SWNT-based FET. Also the surfactant is required to obtain relatively high-concentration SWNT solution. However, it is highly difficult to completely remove
the surfactant after separation. The surfactant, which wraps the sidewall of SWNTs, can also affect the performance of devices. The probe sonication is used to debundle the SWNTs. This high-energy released from probe sonication is highly helpful to disperse SWNTs while destroying the prefect structure of SWNTs. Purification treatment, surfactant wrapping and high-energy sonication are the three common disadvantages for solution-based separation techniques.

1.4.2 On-chip Based Separation or conversion Method

In contrast to the solution-based methods, on-chip based separations are more simple and direct due to not involving purification, surfactant and sonication. Especially this method is more suitable for CVD-grown SWNTs. CVD synthesis technique is highly compatible for the industrial process of electronic devices. All the work, including SWNT growth, device fabrication and separation/conversion, can be finished in the substrate for on-chip methods. This method can facilitate the real application of SWNT-based devices.

Electrical Breakdown

In 2001, Collins et al. firstly utilized electrical-breakdown method to selectively remove the single carbon cells from MWNTs and tailor the property of SWNT bundles. By applying high bias, eight cells of a MWNT are sequentially broken. Figure 1-13a shows the relationship between staircase of current and time. They also selectively removed metallic fraction from SWNTs ropes or bundles by applying positive gate bias to
turn off the semiconducting tubes while a large voltage applied between the source and drain electrode to destroy metallic ones. As shown in figure 1-13b, the G (current) was decreased as the M-SWNTs were destroyed.\textsuperscript{38} This method has been widely used to improve the on/off ratio for aligned SWNTs and random networks.\textsuperscript{145-148} It should be mentioned that electrical breakdown destroys carbon nanotube by over self-heating. Duo to oxygen in the air, this method is not controllable to remove all the M-SWNTs while keeping all the S-SWNTs intact. Usually a much bigger-than-normal bias is applied in order to remove all metallic tubes, and it is unavoidable to destroy lots of semiconducting ones. Also this method is highly difficult to scale up to apply to chips with a large of transistors.

\textbf{Figure 1-13} (a) The partial electrical breakdown of a MWNT at constant voltage stress proceeds in a series of discrete steps corresponding to the loss of individual carbon shells from the MWNT. (b) Stressing a mixture of S-SWNTs and M-SWNTs while simultaneously gating the bundle to turn off S-SWNTs and destroy M-SWNTs.\textsuperscript{38}
Irradiation

Huang et al. was the first to selectively remove metallic tubes from mixture of both M- and S-SWNTs with laser irradiation (514.5 nm for Ar$^+$ and 632.8 nm for He-Ne). In his experiments, three source of commercially available purified SWNTs with different diameter were used, and his results indicates metallic tubes with bigger chiral angles can be selectively removed. Liu’s group employed long-arc xenon lamp (0.18-11 µm) to preferentially destroy on-chip M-SWNTs from high-density SWNT arrays grown by CVD method. Their works showed long-time irradiation can significantly decrease the content of metallic tubes in the CVD-grown SWNTs, and the on/off ratio of the corresponding FET devices can increase from less than 10 to more than 2000 as shown in figure 1-14. Microwave was also reported to selectively etch metallic tubes with higher chiral angels rather than the corresponding semiconducting ones. Due to much higher dielectric constant of metallic tubes than the corresponding semiconducting ones, M-SWNTs are easier to couple with microwaves, and preferentially eliminated. So far, the mechanism of selectivity is not well understood yet. The damage of some semiconducting tubes is unavoidable under light irradiation.

![Figure 1-14](image_url)  
**Figure 1-14** $I_{dr}$-$V_g$ curve after different irradiation times of a FET device.
Plasmon Etching

Dai’s group firstly used methane plasma to selectively etch metallic tubes over semiconducting ones in the diameter range from 1.4 to 2 nm. SWNT-based devices were treated by methane plasma at 400 °C, and then annealed at 600 °C in vacuum, the on/off ratio of devices was increased by more than 4 orders due to removal of M-SWNTs as shown in figure 1-15a. According to their observation, the etching is diameter and electronic dependant. For small-diameter tubes below 1.4 nm, both metallic and semiconducting were removed, and no electronic-type selectivity is observed. For medium-diameter range between 1.4 and 2 nm, M-SWNTs were selectively etching over S-SWNTs. For SWNTs with large diameter above 2 nm, all the tubes were intact and the on/off ratio of the devices has no significant change. The fate of metallic and semiconducting SWNTs in different range is illustrated in figure 1-15b. Dai and co-workers attributed the diameter sensitivity to the different radius of curvature and strain energy in the C-C bonding. For the electronic selectivity of medium-diameter SWNTs, more abundant delocalized electronic states and higher formation energies of M-SWNTs over S-SWNTs played an important role. This plasma etching method is scalable and efficient in selectively removing M-SWNTs.
Selective chemical functionalization

Due to the different electronic structures, M-SWNTs and S-SWNT has shown different chemical reactivity. Diazonium salts were used to selectively react with M-SWNTs by Strano et al. in 2003.\textsuperscript{118} For the mechanism of chemical reaction, they proposed diazonium compound can extract electrons from carbon nanotube to form covalent aryl bonds. There is charge-transfer process from SWNTs to diazonium cations. Metallic tubes have higher DOS near Fermi level, which is more helpful to stabilize the charge-transfer transition state and accelerates the forward reaction rates. So metallic tube is more reactive than the semiconducting. In the following research, osmium tetroxide,\textsuperscript{120} azomechine ylides,\textsuperscript{153} hydrogen peroxide,\textsuperscript{154} nitric and sulfuric acid,\textsuperscript{155} and fluorinated polyolefins\textsuperscript{156} were also reported to preferentially react with metallic tubes. When metallic tubes are selectively functionalized, their structure can be dramatically changed and their conductance can be lost. Selective chemical functionalization of M-SWNTs provides another choice to
enhance performance of the SWNT-based devices. Liu’s group directly immersed SWNT-based devices into 4-bromobenzenediazonium tetrafluoroborate aqueous solution under stirring. After reaction, the on-state conductance for the device significantly decreased as shown in figure 1-16a. By carefully controlling reaction condition, they found on/off ratio of the device was greatly increased as seen in figure 1-16b. They attributed this to the electrical destruction of metallic tube causing by selective covalent functionalization from diazonium radicals. It is worth to point out that this selective chemical functionalization is reversible. The on/off ratio can be recovered by annealing. Liu et al. provided a simple way for on-chip fabrication of high-performance SWNT FET by removal of m-SWNTs. However, there is still much room to explore for this method. For instance, in which diameter range the selectivity is the best. And the characterization of SWNTs before and after treatment is also needed.

Figure 1-16 (a) Gate dependence curves of the devices: (A) before the diazonium reaction; (B) after the reaction with diazonium reagent (3.7 mM); (C) after further reaction. (b) (A) before the
diazonium reaction; (B) after the first reaction with diazonium reagent \(5.3 \times 10^{-7} \mu M\); (C) after a second reaction; (D) after annealing.\(^{157}\)

**Metal-Semiconductor Conversion**

So far, most of on-chip sorting methods involve removal or destruction of M-SWNTs to try to obtain pure semiconducting tubes in the devices. Obviously, another strategy to achieve high-performance SWNT-based FET is to convert metallic to semiconducting tubes by tailoring band structure of SWNTs. Researchers have done some studies from both experiments and theoretical calculation about metal-semiconductor transition.\(^{158-164}\) By transforming sp\(^2\) carbon atoms in \(\pi-\pi\) conjugation system into sp\(^3\) hybridized configuration, it would be possible to open the bandgap of metallic tubes. Haddon’s group has reported that introducing defect sites on the sidewalls of metallic SWNTs by covalent chemical reaction could open a gap at the Fermi level.\(^{165,166}\) Barboza et al. found direct experimental observation of the semiconductor-metal conversion in SWNT via compression with AFM tip.\(^{160}\) Lu at al. showed a metal-to-semiconductor transition can be achieved by a combined effect of breaking of mirror symmetry and bond formation between the flattened faces in the squashed SWNT, using tight-binding molecular dynamics and the Green’s function method.\(^{158}\) Manna et al. investigated the charge-transfer effect on the electronic structure of metallic (5,5) and semiconducting (8,0) SWNTs via surface adsorption of various organic donor-acceptor molecules using *ab initio* density functional theory, and found (8,0) S-SWNT (5,5) and M-SWNT could converse into metallic and semiconducting tubes respectively upon adsorption by doping of organic molecular.\(^{164}\) Hydrogen plasma was also used to achieve metal-to-
semiconductor transition for SWNTs. Ionized hydrogen generated by plasma is highly reactive to form C-H bond with carbon nanotubes, causing bandgap opening of M-SWNTs. Also they found M-SWNT could be recovered by the breaking of C-H bond after annealing as shown in figure 1-17. Due to high reactivity of hydrogen plasma, it is unavoidable to destroy original semiconducting tubes.

Figure 1-17 $I_d$-$V_g$ curve of a metallic SWNT converts to semiconducting after hydrogen treatment and recovered after annealing at 700 °C.  

Zhou’s group demonstrated the conversion from M-SWNT to S-SWNT by light-induced oxidation, which opens the band gap of metallic tube by transforming $sp^2$ into $sp^3$ carbon atoms to achieve $\pi$-electron localization. They proposed a typical conversion
process as shown in figure 1-18a. It is worth to point out that there is little change in on-state current and on/off ratio for FET devices after light irradiation in vacuum. Only in the air the increase of on/off ratio can be observed as shown in figure 1-18b. This indicates oxygen and water molecules are the prerequisites for the conversion.

![Figure 1-18](image.png)

**Figure 1-18** (a) Schematic showing light-induced oxidation of the nanotube sidewalls. Possible chemical groups were introduced on the sidewall upon \( \text{sp}^2-\text{sp}^3 \) rehybridization by light-induced oxidation. (b) Comparison of typical \( I_{ds}-V_G \) characteristics of two SWNT-based FET before and after irradiation in air and in vacuum.\(^{163}\)

The conversion from metallic to semiconducting carbon nanotube was also realized with helical wrapping of single-stranded DNA (ssSNA) by binding to the surface of tube’s sidewall via \( \pi-\pi \) stacking.\(^{161}\) Water molecules were found to be critical to achieve the transition in the hybrid consisting of ssDNA and carbon nanotubes. The author compared the transfer characteristic of a FET device with metallic behavior in both dry and wet state in the absence of ssDNA wrapping. The results indicated there was little change for \( I_{ds}-V_g \) curve of this metallic tube without ssDNA warping whether in dry or wet state as shown in figure 1-19a. In figure 1-19b, \( I_{ds}-V_g \) curve for another metallic tube remained flat for
ssDNA-SWNT hybrids in the dry state, however the electric behavior of the same metallic tube was successfully converted into semiconductor in the wet state upon ssDNA wrapping. The observation indicated hydration is important to achieve transition from metallic to semiconducting state. The author also demonstrated the transition was reversible between M-SWNT and S-SWNT via repeated hydration and dehydration. They attributed the metal-semiconductor conversion by ssDNA wrapping in the presence of water to the charge transfer between carbon nanotube and ssDNA and helical perturbation causing by ssDNA wrapping. They proposed when phosphate group with negative charge moved closer to surface of nanotube under the assistance of water hydration, consequently the electron transfer from metallic tubes to negatively charged phosphate group occurred, causing metal-semiconductor conversion with a band gap opening. According to their first-principles calculation, the band gap opening could reach up to 30 meV for the metallic (6,6) SWNT resulting from the helical wrapping of ssDNA.

![Figure 1-19](image.png)

**Figure 1-19** Dependence of current of the ssDNA-SWNT hybrid on gate voltage. (a) A metallic behavior with SWNTs without DNA. (b) A p-type semiconductor behavior with the ssDNA-SWNT hybrid.
Chapter 2

On-chip diameter-dependent conversion of metallic to semiconducting single-walled carbon nanotube by immersion in 2-ethylantraquinone

2.1 Abstract

The key hurdle to the practical use of as-grown single-walled carbon nanotubes (SWNTs) for high performance nanoelectronics is the unavoidable presence of metallic nanotubes with current synthesis methods. We present a simple approach to convert metallic SWNTs to semiconducting ones in situ to improve device field effect behaviour, using an aromatic compound (2-ethylantraquinone - EAQ) which is a mild radical initiator. We show that the reaction between EAQ-generated radicals and SWNTs is diameter and metallicity dependent; in the medium-diameter regime (0.8 to 1.0 nm), the EAQ-generated radicals preferentially attack the metallic SWNTs over semiconducting ones and convert them to semiconducting, as evidenced by several orders (10 and $10^4$) increase in the on/off ratio.

Parts of the following work in this chapter were presented in a similar form in my published article in the journal of *RSC advances*.167
2.2 Introduction

Single-walled carbon nanotubes (SWNTs) have attracted great interest due to their extraordinary electrical properties\textsuperscript{168} and their promising applications in future electronics have been extensively explored.\textsuperscript{169-172} In particular, comparing with current Si-based devices, SWNT-based field-effect transistors (SWNT-FETs) have shown unique advantages.\textsuperscript{173} Despite significant progresses being made toward SWNT-based circuits,\textsuperscript{37, 174, 175} there are still obstacles for exploiting their full potential in real application. A central issue for obtaining superior FET devices is to minimize the presence or influence of metallic SWNTs (M-SWNTs) in the active channels.

To tackle this issue, various approaches have been developed, including solution-based pre-sorting or pre-separation of the two types of nanotubes,\textsuperscript{141, 176} selective synthesis of semiconducting SWNTs (S-SWNTs),\textsuperscript{177, 178} selective chemical modifications,\textsuperscript{179-181} electrical breakdown of M-SWNTs,\textsuperscript{182} or selective etching of M-SWNTs by methane plasma\textsuperscript{183} and light irradiation.\textsuperscript{184, 185} An appealing alternative is to convert M-SWNTs into S-SWNTs in situ, which has been realized using electron irradiation\textsuperscript{186} and hydrogen plasma\textsuperscript{187, 188}. Recently, the transition of SWNT from metallic to semiconducting was also achieved through helical wrapping of DNA\textsuperscript{189}. However, electron irradiation is highly difficult to scale up due to limited size of electron beam. Hydrogen plasma is aggressive and cannot be controlled precisely.
2.3 Experimental Methods

2.3.1. Materials Preparation and Device Fabrication

SWNTs were grown on the silicon wafer with 400 nm oxide layer using CVD method. Briefly, the catalyst consisted of ferritin (Aldrich; diluted with de-ionized water at a volumetric ratio of 1:2000) was deposited onto the SiO$_2$–Si surface. The wafer was then heated to 800 °C in a quartz tube to oxidize ferritin into iron oxide nanoparticles. Growth temperature is 925 °C. Ethanol was released into the quartz tube as a carbon source. Growth time is 5 mins. After CVD growth, we used microfabrication techniques to pattern source-drain (S-D) electrode pads to contact SWNTs. We chose Ti/Au (10nm/20nm) as the contact metal in the current work. The channel length is 5μm, and the width is 6μm.

2-Ethylanthraquinone (EAQ) and other chemicals were purchased from Sigma-Aldrich. EAQ (30mg) was dissolved in a mixture of Dimethylformamide (DMF, 25ml) and DI water (5ml) by water-bath sonication for 10 mins. SWNT-based devices were immersed in the EAQ/DMF solution. Then the sample was placed in ambient condition (under the light and air) for several days. When finishing, the wafer was taken out of the solution, and washed with DMF, ethanol, and DI water. Then the wafer was dried in the oven through overnight to completely remove the solvent.
To obtain FTIR signal of detectable amplitude, we used CoMoCAT carbon nanotubes purchased from Southwest Nanotechnologies. CoMoCAT tubes were dispersed in DMF/DI water solution with or without EAQ, respectively. After reaction for 7 days, the solution was filtered through a PTFE membrane (0.2 µm), and rinsed with DMF, ethanol, and DI water. SWNTs solid was transferred to quartz substrates, and dried at 120 °C in the vacuum oven before FTIR characterization.

2.3.2. Characterization

Raman spectra of the samples were measured with a Renishaw Ramanscope in the backscattering configuration, and Stokes spectra of the samples were obtained with 633 nm lasers. Atomic force microscopy (AFM) was conducted using a MFP 3D microscope (Asylum Research, Santa Barbara, CA) with a cantilever (Arrow NC, Nanoworld) in ac mode. All electrical measurements were carried out in ambient conditions using a Keithley semiconductor parameter analyzer, model 4200-SCS. Fourier transform infrared (FTIR) spectra were obtained on a Nicolet 5700 FT-IR instrument equipped with attenuated total reflectance (ATR) accessory. Scanning electron microscopy (SEM) analysis was performed on a JEOL JSM-6700F Field-Emission Scanning Electron Microscope (FE-SEM) operating at 1 kV. All electrical measurements were carried out in ambient condition using a Keithley semiconductor parameter analyzer model 4200-SCS.


2.4 Results and Discussions

In this chapter, we demonstrate the use of 2-ethylanthraquinone (EAQ) (Figure 2-1a) to fulfil the on-chip metal-to-semiconductor transition of individual as-grown SWNTs for application in field effect transistors. This approach is simple, mild and easily scalable to whole wafers (illustrated in Figure 2-1b). Figure 2-1c shows the transfer characteristics (drain current $I_{ds}$ versus gate voltage $V_g$) for a typical device, with a single metallic SWNT as the conducting channel, before and after 7-day EAQ treatment. The scanning electron microscopy (SEM) of the device is also shown in Figure 2-1c inset. We observed a considerable increase in the channel current on/off ratio ($I_{on}/I_{off}$) from ~1.47 to ~$1.63 \times 10^3$ after EAQ treatment. The increase of on/off ratio implies the conversion from M-SWNTs to S-SWNTs.

![Figure 2-1](image)

**Figure 2-1** (a) Structure of 2-ethylanthraquinone (EAQ). (b) Schematic illustration of the treatment process for SWNT-FET in the EAQ solution. (c) Transfer characteristics ($V_{ds} = 0.5V$) of
a single metallic SWNT-FETs before (black) and after (red) EAQ treatment. The on/off ratio increased from $\sim 1.47$ to $\sim 1.63 \times 10^3$. Inset is SEM image of the SWNT-FET.

Here, we applied electrical measurements and Raman characterizations to investigate the effect of EAQ treatment to SWNTs in the channel of FET devices. With SWNTs, the Raman spectroscopy\textsuperscript{191-195} can detect the distinct vibration modes and their defects by G and D bands respectively. Figures 2-2a and 2-2b show the Raman spectra and $I_{ds}$-$V_g$ curves of a single metallic nanotube device before and after EAQ treatment. The Raman spectra reveals an increase in the D band intensity (1329.6 cm$^{-1}$) and a decrease in the G band intensity (1592.4 cm$^{-1}$), accompanied by a G band upshift of 3.5 cm$^{-1}$. There is a 4-fold decrease in the ratio between the G and D band intensities ($I_G/I_D$) after EAQ treatment (Figure 2-2a), which can be attributed to an increase in the defect density on the SWNT sidewall.\textsuperscript{187} We suggest that EAQ treatment introduced disorder on the SWNT wall, and thus increased the D band density. The $I_{ds}$-$V_g$ curve (Figure 2-2b) shows a decrease in nanotube’s conductance, and a significant increase in the gate-voltage dependence after EAQ treatment. These observations can be attributed to that defects introduced by conversion of sp$^2$ hybridized carbon structure to sp$^3$ structure in SWNT through covalent chemistry should strongly affect Fermi level of metallic tubes, and can result in localization of $\pi$-electrons, and consequently, opening up the band gap of SWNT.\textsuperscript{187, 196} The conversion of sp$^2$ to sp$^3$ structure transforms the nature of the nanotube from metallic to semiconducting.\textsuperscript{196-198}
Figure 2-2 (a) Raman spectra showing D band and G band of a single metallic SWNT in the FET device before (black) and after (red) EAQ treatment. Inset is SEM image of the metallic single-tube device. (b) Current (Ids) versus gate voltage (Vg) characteristics of the device (inset of a) before (black) and after (red) EAQ treatment, showing decrease of the overall conductance and $I_{on}/I_{off}$ improvement from 1.5 to 10.7. The stronger gate bias dependence of device indicated metal-to-semiconductor conversion of SWNT.
We treated 64 as-synthesized single-SWNT devices by immersing them into EAQ solution for seven days. Here, a “Lost” device is the one with $I_{on} < 100\text{pA}$ at $V_{ds} = 0.5\text{V}$. The “lost” devices have very low on/off ratio ($I_{on}/I_{off} \approx 1$) since their $I_{ds}$-$V_g$ curve is flat. “Depletable” (D) devices are defined as having $I_{on} > 1\text{nA}$ and $I_{on}/I_{off} \geq 10$, and “Nondepletable” (ND) devices are those with $I_{on}/I_{off} < 10$. We observed five different device behaviours after the treatment, including D→Lost (becoming electrically nonconductive (Fig 2-3a)), ND→Lost (Fig 2-3b), ND→D (nondepletable becomes depletable) (Fig 2-3c), ND→ND (Fig 2-3d), and D→D (Fig 2-3e).

AFM measurements were carried out to obtain the diameters of SWNTs in the channel of devices. No visible etching and change in the SWNTs diameters were observed after EAQ treatment in all AFM images.

We found that the D→Lost devices were composed of predominantly small-diameter semiconducting SWNTs (S-SWNTs) with d<0.80nm (Fig 2-3a inset and 2-4a). For the ND→Lost devices which are composed of initially metallic nanotubes instead (Fig 2-3b), AFM analysis shows that the diameters of these tubes were also relatively small, with a diameter range from 0.6 to 0.8nm (Fig 2-3b inset, Fig 2-4b).

It is well-accepted that SWNTs with smaller diameters are preferentially reactive over larger ones due to C-C bonding’s higher strain and the higher radius of curvature.\textsuperscript{183, 199} Our results are in support of this notion. The smaller-diameter SWNTs (0.60nm<d<0.80nm), whether metallic or semiconducting, were nondiscriminatingly overreacted in our studies, and finally losing electrical conductance.
For the medium diameter nanotubes (0.8nm<d<1.00nm), the metallic species (Fig 2-3c inset) became switchable after the chemical treatment so that devices underwent ND→D change after EAQ treatment, indicating conversion of the nanotubes from metallic to semiconducting. For the ND→ND devices (Fig 2-3d), most of the nanotubes had large diameters (d>1.00nm, in Fig 2-4d). This suggests that large-diameter metallic SWNTs (1.00nm<d<1.60nm) are likely inert to EAQ treatment. On the other hand, in D→D devices, the semiconducting tubes (Fig 2-3e inset) were observed to have a wider diameter span from 0.80nm to 1.60nm (Fig 2-4e) and these devices preserved the gate-voltage dependence after the treatment. In figure 2-4f, the changes of on/off ratio (I_{on}/I_{off}) before (black) and after (red) EAQ treatment can be easily observed.

In the small-diameter range (0.60nm<d<0.80nm), both metallic SWNTs in ND devices and semiconducting SWNTs in D devices lost conductance (ND→Lost and D→Lost). For D→Lost devices, I_{on}/I_{off} decreased a lot. For ND→Lost devices, I_{on}/I_{off} had little change before and after treatment since I_{on}/I_{off} of ND devices is nearly 1 and I_{on}/I_{off} of lost devices is also about 1.

In the medium-diameter range (0.80nm<d<1.00nm), I_{on}/I_{off} in ND devices with metallic SWNT improved several orders (10 to 10⁴) after EAQ treatment, indicting conversion from metallic to semiconducting ones (ND→D). High I_{on}/I_{off} in D devices with semiconducting SWNT was preserved (D→D), implying semiconducting SWNT was inert to EAQ treatment.
In the large-diameter range (1.00nm<d<1.60nm), $I_{on}/I_{off}$ in both ND and D devices were nearly no change (ND→ND and D→D), exhibiting large-diameter SWNTs kept their electronic property.

Figure 2-3 (a to e) Ids-Vg curves (Vds = 0.5V) showing five different device behaviours before (black) and after (red) EAQ treatment. Insets in each diagram are AFM images of the SWNT in the device channel and surface height plot showing the tube diameter. The scale bars are 500 nm.
Figure 2-4 (a to e) Diameter distribution (from AFM measurements) of SWNTs in devices grouped by their behaviour under EAQ treatment. The smaller-diameter (0.60nm-0.80nm) SWNTs (a and b), whether metallic or semiconducting, were “lost” after treatment. In ND→D devices (c), the metallic tubes, mainly in the medium-diameter regime (from 0.80nm to 1.00nm), were
converted into semiconducting ones by EAQ treatment. Large metallic SWNTs with diameter between 1.00nm and 1.60nm in ND devices (d) were only slightly affected by EAQ treatment. D→D devices (e) exhibited a wider diameter distribution spanning medium and large regimes, indicating that semiconducting SWNTs of medium diameter were less reactive than metallic tubes of the same diameters. (f) on/off ratio \(I_{on}/I_{off}\) versus SWNT diameter before (black) and after (red) EAQ treatment. In the small-diameter range (0.60nm<\(d<0.80\)nm), both metallic SWNTs in ND devices and semiconducting SWNTs in D devices lost conductance (ND→Lost and D→Lost). For D→Lost devices, \(I_{on}/I_{off}\) decreased a lot. For ND→Lost devices, \(I_{on}/I_{off}\) had little change before and after treatment. In the medium-diameter range (0.80nm<\(d<1.00\)nm), \(I_{on}/I_{off}\) in ND devices with metallic SWNT improved several orders (10 to \(10^4\)) after EAQ treatment. High \(I_{on}/I_{off}\) in D devices with semiconducting SWNT was preserved (D→D). In the large-diameter range (1.00nm<\(d<1.60\)nm), \(I_{on}/I_{off}\) in both ND and D devices were nearly no change (ND→ND and D→D).

Taken together, our results suggest that only in the medium-diameter regime (0.80nm to 1.00nm), metallic tubes are preferentially reactive over semiconducting ones in EAQ solution (Fig 2-4a – 2-4e). In other words, in this regime, the effect of EAQ treatment depends on the electronic properties of nanotubes. In contrast, in the large diameter range (1.00nm<\(d<1.60\)nm), both M- and S-SWNTs were nearly unaffected after EAQ treatment. According to first-principle calculations, M-SWNTs have higher formation energy than same-diameter S-SWNTs.\(^{200, 201}\) Also, more abundant delocalized electronic states of M-SWNTs result in their higher chemical reactivity.\(^{201}\) The reactivity difference diminishes for SWNTs with large diameters,\(^{183, 200}\) consistent with reduced chemical selectivity seen here for large-diameter SWNTs.

The behavior of these EAQ treated devices is relatively stable. The devices after EAQ treatment show similar behavior even after annealing (in Ar, 300 °C, 30 mins). The
devices cannot be converted back to metallic after high temperature annealing. This is different from previous studies using dizonium salt.\textsuperscript{179}

According to Ab Initio Calculation, binding energy between EAQ and metallic/semiconducting SWNT is zero, which means, EAQ does not bind to the semiconducting or metallic SWNT.\textsuperscript{202,203} So when we investigate the mechanism of tube conversion, charge transfer between EAQ and SWNT can be ruled out. It is well-known that EAQ can generate radicals under light.\textsuperscript{203,204} We attribute the observed metal-to-semiconductor conversion to the attack of light-induced radicals toward the sidewall of M-SWNTs, which alters the carbon lattice structure by covalently adding chemical functionalities, and consequently open up or increase the band gap of M-SWNTs.\textsuperscript{165,205} Such reaction process is illustrated in Figures 2-5a. In the FTIR spectroscopy (Figure 2-5b), increased absorption in the region 3100-3600 cm\textsuperscript{-1} was observed on CoMoCAT SWNTs samples after EAQ treatment, indicating the abundant existence of oxygenated functionalities in treated SWNTs mainly in the form of hydroxyl groups. Addition of oxygen functionalities to SWNTs’ sidewall could withdraw electrons from SWNTs,\textsuperscript{206,207} resulting in upshift of Raman G band of nanotube as observed in Figure 2-2a.\textsuperscript{208,209}
Figure 2-5 (a) Schematic illustration of the reaction mechanism in the EAQ treatment process. (b) FTIR spectra of SWNTs before (black) and after (red) EAQ treatment.
2.5 Conclusion

In summary, this work demonstrates a simple and scalable method to improve the switching of SWNT-based FET devices by in situ converting as-grown metallic SWNTs to semiconducting ones using photoinitiated radicals. This approach was found to be diameter dependent and highly effective among SWNTs with medium diameters of 0.80nm to 1.00nm, in which regime the density of states near the Fermi level dictates the reactivity of SWNTs, and M-SWNTs with more abundant density of states show preferential reactivity over s-SWNTs. The enhancements of on/off ratio in FET devices after EAQ treatment generally ranged between 10 and $10^4$. Comparing to other radical treatment methods, this process is mild. This approach provides a possibility to achieve SWNT-based integrated circuits.
Chapter 3

In-situ charge-transfer induced transition from metallic to semiconducting Single-Walled Carbon Nanotubes

3.1 Abstract

Single-walled carbon nanotubes (SWNTs) are regarded to be potential building blocks for future electronics due to their exceptional electrical, physical and mechanical properties. A major obstacle to their practical use for high performance nanoelectronics is the presence of both metallic SWNTs (M-SWNT) and semiconducting SWNTs (S-SWNT) in as-grown SWNT samples. Most metallicity-based SWNT sorting techniques involve suspension of the nanotubes in solutions which generally also result in nanotube defects. As-grown SWNTs typically have far superior conductivity or carrier mobility than solution-suspended SWNTs but thus far, there is no simple or reproducible method to remove the electronic inhomogeneity in these as-grown nanotubes. We present a simple in-situ method using an organic electron-acceptor compound, acid yellow (AY), to convert SWNTs from metallic to semiconducting to improve device field effect behaviour. By simply immersing the as-synthesized SWNTs (still attached to a wafer) into an AY solution, the originally metallic nanotubes behave like semiconducting ones. Using Raman spectroscopy, atomic force microscopy and single nanotube transistor device measurements, we show that the charge-transfer interaction between SWNTs and the organic electron-acceptor compound AY is diameter-dependent; in the large-diameter regime (1.40 to 2.60 nm), modulated metallic SWNTs exhibit semiconducting behavior,
as evidenced by a pronounced field effect in the I-V characteristics and up to three orders of magnitude increase in the on/off ratio of single M-SWNT field-effect transistors (FET). This method presents a simple viable route towards fabrication of switchable transistors with as-synthesized SWNTs.

Parts of the following work in this chapter were presented in a similar form in my published article in the journal of *Chemistry of Materials*.210
3.2 Introduction

Single-walled carbon nanotubes (SWNTs) are regarded to be potential building blocks for future electronics due to their exceptional electrical, mechanical, chemical and thermal properties. Promising applications of SWNTs in nanoelectronics, thin-film flexible electronics, and bioelectronics have been demonstrated. In particular, SWNT-based field-effect transistors (SWNT-FETs) have shown performance, superior to those of current silicon-based complementary metal oxide semiconductor (CMOS) devices. Despite significant progress made in constructing SWNT-based circuits, there are still obstacles to exploitation of their full potential in practical applications. A central shortcoming of nanotube FET devices is the presence or influence of metallic SWNTs (M-SWNTs) in the active channels. Most SWNT synthesis methods produce electronically inhomogeneous mixtures with metallic (M) and semiconducting (S) species co-mingled.

To tackle this issue, various approaches have been developed, including solution-based pre-sorting or pre-separation of the two types of nanotubes, selective synthesis of semiconducting SWNTs (S-SWNTs), selective chemical modifications, in-situ electrical breakdown of M-SWNTs, or in-situ selective etching of M-SWNTs by methane plasma and light irradiation. An appealing alternative is to convert M-SWNTs into S-SWNTs in-situ, which has been realized using electron irradiation and hydrogen plasma. Recently, the conversion of SWNT from metallic to semiconducting has been achieved through helical wrapping with DNA and radical-
induced reaction\textsuperscript{216}. However, electron irradiation is highly difficult to scale up due to limited size of the electron beam. Hydrogen plasma is aggressive and cannot be controlled precisely. The wrapped DNA method requires hydration for field effect. Radical-induced reaction damages small-diameter S-SWNTs, rendering them nonconductive.
3.3 Experimental Methods

3.3.1. Materials Preparation and Device Fabrication

SWNTs were grown on a silicon wafer with 400 nm oxide layer using CVD method. Briefly, ferritin catalyst precursor (Aldrich; diluted with de-ionized water at a volumetric ratio of 1:2000) was deposited onto the SiO$_2$–Si surface. The wafer was then heated to 800 °C in a quartz tube to oxidize the ferritin into iron oxide nanoparticles. The CVD growth temperature was 925 °C. Ethanol was released into the quartz tube as a carbon source. The growth time was 5 mins. After CVD growth, microfabrication techniques was used to pattern source-drain (S-D) electrode pads (of Ti/Au, 10nm/20nm) to contact individual SWNTs. The channel gap was 5μm.

Arc discharge SWNTs were purchased from Carbon Solutions, Inc. 4-Amino-1,1′-azobenzene-3,4′-disulfonic acid sodium salt (AY) and other chemicals were purchased from Sigma-Aldrich. AY (30mg) was dissolved in Dimethylformamide (DMF, 25ml) by water-bath sonication for 10 mins. SWNT-based devices were immersed in the AY/DMF solution under ambient conditions (exposed to light and air) for 60 mins. After AY treatment, the wafer was removed from the solution and blown dry with Ar gas. Then the wafer was further dried in a vacuum oven overnight to completely remove the solvent. Arc-SWNTs were dispersed in DMF solution with or without AY. After 60 mins, the solution was filtered through a PTFE membrane (0.2 μm). PTFE membranes with SWNT solids were dried in a vacuum oven overnight before Raman characterization.
To obtain SWNTs film, 1 mg of Arc-SWNTs was dispersed in 25 mL of 1,2-dichloroethane (anhydrous, 99.8% Sigma-Adrich) via probe-ultrasonication (Sonics & Materials Inc., Model: VCX 130) for 5 hs. After sonication, SWNTs suspensions were centrifuged for 15 mins at 10000g. The supernatant was sprayed onto a quartz substrate with an N₂ gas brush pistol (Fuso Seiki Co., Ltd.). Then the substrate with SWNTs film were heat in a vacuum oven to 250 °C for 1h for UV−vis−NIR measurement before AY treatment. Five 1ml drops of AY solution was placed onto the SWNTs film. After 60 mins, the solvent was spin-coated at 2500 rpm for 10s. Then the substrate with SWNTs film was placed in a vacuum oven for 1h for UV−vis−NIR measurement after AY treatment.

3.3.2. Characterization

Raman spectra of the samples were measured with a Renishaw Ramanscope in the backscattering configuration, and Stokes spectra of the samples were obtained with 633 nm laser excitation. Atomic force microscopy (AFM) was conducted using a MFP 3D microscope (Asylum Research, Santa Barbara, CA) with a cantilever (Arrow NC, Nanoworld) in ac mode. All electrical measurements were carried out in ambient conditions using a Keithley semiconductor parameter analyzer, model 4200-SCS. Scanning electron microscopy (SEM) analysis was performed on a JEOL JSM-6700F Field-Emission Scanning Electron Microscope (FE-SEM) operating at 1 kV. UV−vis−NIR absorption spectra were measured with a Varian Cary 5000 UV−vis−NIR spectrophotometer.
3.4 Results and Discussions

In this chapter, we demonstrate the use of 4-Amino-1,1′-azobenzene-3,4′-disulfonic acid sodium salt (Acid Yellow 9, AY) (Figure 3-1a) to perform in-situ metal-to-semiconductor conversion of individual as-grown SWNTs for application in field effect transistors. This approach is simple, easily scalable to whole wafers, and does not impair the nanotube conductance. Figure 3-1b shows the transfer characteristics (drain current $I_{ds}$ versus gate voltage $V_g$) for a typical device, with a single metallic SWNT as the conducting channel, before and after AY treatment. Scanning electron microscopy (SEM) of the device is also shown in Figure 3-1b inset. The $I_{ds}$-$V_g$ curve (Figure 3-1b) shows there is a little increase in nanotube’s conductance after AY treatment. We observed a considerable increase in the channel current on/off ratio ($I_{on}/I_{off}$) from ~1.21 to ~$1.235 \times 10^3$ after AY treatment. The appearance of a strong gate voltage dependence of the conductance and the corresponding increase of on/off ratio implies the conversion of this nanotube from metallic to semiconducting.
Figure 3-1 (a) Structure of 4-Amino-1,1’-azobenzene-3,4’-disulfonic acid sodium salt (Acid Yellow 9, AY). (b) Transfer characteristics (Vds = 0.5V) of a single metallic SWNT-FET before (black) and after (red) AY treatment. The on/off ratio increased from ~1.21 to ~1.235×10^3. Inset is FESEM image of the single SWNT-FET.

We performed electrical measurements and Raman spectroscopy on the same device to investigate the effect of AY treatment on individual SWNTs in the channels of FET devices. Figures 3-2a and 3-2b show the Raman spectra and I\textsubscript{ds}-V\textsubscript{g} curves of a single metallic nanotube device before and after AY treatment. In general, the tangential mode
(G-band) of M-SWNT is characterized by a broad and asymmetric Breit-Wigner-Fano (BWF) peak around 1552 cm\(^{-1}\), attributed to phonon-plasmon coupling in the presence of conduction electrons.\(^{193, 217, 218}\) The G-band of S-SWNTs show a sharp and symmetric Lorentzian line.\(^{189}\) In Figure 3-2a, after AY treatment, the BWF peak of the nanotube is significantly suppressed, which can be attributed to charge-transfer doping from the SWNT to AY. The significant suppression, with respect to the pre-AY-treatment spectrum, of the BWF intensity implies greatly decreased metallicity in the nanotube after AY treatment.\(^{185, 219, 220}\) For the D band, no obvious change is observed before and after AY treatment. AY is an organic electron-acceptor molecule.\(^{221}\) Electrons near the M-SWNT Fermi level can be transferred to AY, leading to weakening of the phonon-plasmon coupling and considerably diminution of the BWF peak.\(^{217, 220, 222-224}\) In addition, the peak frequency of the G-band was upshifted by about 3.2 cm\(^{-1}\) from 1592.3 cm\(^{-1}\) before to 1595.5 cm\(^{-1}\) after AY treatment (Figure 3-2a inset i). This G band upshift is consistent with the previous reports of the phonon stiffening effect caused by charge-transfer doping from SWNTs to electron-acceptor molecules.\(^{220, 222, 223}\) The current versus gate-voltage (I\(_{ds}\)-V\(_{g}\)) curve (Figure 3-2b) shows a dramatic increase in the gate-voltage dependence after AY treatment. The on/off ratio of this single nanotube device increases from \(\sim 1.05\) before to \(\sim 1.01 \times 10^{3}\) after AY treatment. It appears that electron-acceptor molecule AY interacts with the metallic SWNT, introducing a band gap and causing the M-SWNT to behave like an S-SWNT. We also performed the temperature dependency of a “converted” device in figure 3-2c. With increasing temperature from 80K to 297K, the threshold voltage (V\(_{th}\)) of the “converted” tube is shifted toward more positive, which can
be attributed to enhanced charge-transfer doping from the SWNT to AY at higher temperature.

Figure 3-2 (a) Raman spectra showing D and G bands of a single metallic SWNT in the FET device before (black) and after (red) AY treatment. Inset (i) shows the G peak position upshift.
Inset (ii) is FESEM image of the metallic single-tube device. (b) Current (Ids) versus gate voltage (Vg) characteristics of the device (inset of a) before (black) and after (red) AY treatment, showing $I_{on}/I_{off}$ improvement from ~1.05 to ~1.01×10$^3$. The strong gate bias dependence of the treated device indicates metal-to-semiconductor conversion of the SWNT. (c) Transfer characteristics ($V_{ds} = 0.5$V) of a single metallic SWNT-FET before (black) and after (coloured) AY treatment at different temperature from 80K to 297K. Inset is FESEM image of the “converted” single-tube device.

In order to ensure the single tube is metallic before AY treatment, we extended the gate-voltage range from (-15V to 15V) to (-50V to 50V) (Figure 3-3). The results under extended $V_g$ from -50V to 50V is similar with that under $V_g$ from -15V to 15V. It is implied that if the tube is originally metallic, $V_g$ range from -15V to 15V is enough to demonstrate its metallicity.

![Current (Ids) versus gate voltage (Vg) characteristics of a M-SWNT device before (black), after (red) AY treatment under extended Vg range from -50V to 50V. Inset is FESEM image of the single-tube device. The scale bars are 2µm.](image)

**Figure 3-3** Current ($I_{ds}$) versus gate voltage ($V_g$) characteristics of a M-SWNT device before (black), after (red) AY treatment under extended $V_g$ range from -50V to 50V. Inset is FESEM image of the single-tube device. The scale bars are 2µm.
We treated 43 single-SWNT FET devices, with a range of SWNT diameters, by 1 hour immersion in AY solution. Before AY treatment, the metallic/semiconducting characters of the SWNTs were determined with a semiconductor parameter analyzer. The current versus gate-voltage ($I_{ds}-V_g$) curve of M-SWNT is flat, and on/off ratio is very low ($I_{on}/I_{off} \approx 1$). In contrast, the current through S-SWNT devices shows strong gate bias dependence. More than half of the pre-AY-treatment devices, 26, exhibited metallic conduction; the balances were semiconducting. AFM measurements were performed before and after AY treatment to measure the SWNT diameters. SWNT diameter and morphology, as determined by AFM measurements were unaffected by the AY treatment. Figure 3-4a shows a typical $I_{ds}-V_g$ curve (black curve) of a single M-SWNT with diameter of about 2.10nm. After AY treatment, the $I_{ds}-V_g$ characteristic significantly changed, as shown in the red curve in Figure 3-4a, and the $I_{on}/I_{off}$ increased from ~1.03 before to ~1127.5. The electron-acceptor AY molecules presumably withdraw electrons from the M-SWNT Fermi Level, leading to opening up of the band gap and transforming the M-SWNT to S-SWNT. In contrast, in Figure 3-4b, little change in the $I_{ds}-V_g$ curve before (black curve) and after (red curve) AY treatment is observed for another FET device made of a smaller-diameter (~1.00nm) M-SWNT (Figure 3-4b inset). Figure 3-4c shows a scatterplot of on/off ratios of the 26 M-SWNT-based FETs before and after AY treatment versus the SWNT diameter. The nanotubes are insensitive to AY treatment for diameters less than about 1.4 nm. At diameter ~1.4nm and larger, up to the largest diameter in the sample, i.e. ~2.6nm, AY treatment converts metallic nanotubes to semiconducting, with an increase in on/off ratio of 1 to $\sim 10^3$. There is an obvious diameter dependence to the on/off ratio increase, with a rapid rise form in the range from ~1.4 to ~2.2nm and an apparent plateau or gradual decline with larger diameters.
Figure 3-4 (a and b) $I_{ds}$-$V_g$ curves ($V_{ds}$ = 0.5V) showing (a) large-diameter M-SWNT and (b) small-diameter M-SWNT device behaviours before (black) and after (red) AY treatment. Insets in each diagram are AFM images of the M-SWNT in the device channel and surface height plot showing the tube diameter. The scale bars are 1µm. (c) On/off ratio
(I_{on}/I_{off}) versus SWNT diameter before (black) and after (red) AY treatment. In the small-diameter range (0.60nm<d<1.40nm), I_{on}/I_{off} of metallic SWNTs were nearly unchanged by AY treatment. In contrast, for large-diameter M-SWNTs (1.40nm<d<2.60nm), I_{on}/I_{off} were enhanced by up to ~3 orders of magnitude by AY treatment.

Some reports have proposed that charge-transfer interaction between SWNTs and charge-transfer molecules is strongly dependent on the SWNT reduction potential.\textsuperscript{221, 223, 227, 228} Based on theoretical calculations,\textsuperscript{229} the reduction potential of SWNT has been found to scale inversely with nanotube diameter, which has also been confirmed experimentally via \textit{in-situ} near-IR absorption spectra.\textsuperscript{230} Our observed strong diameter dependence of the effect of AY treatment is compatible with this. For M-SWNT, large-diameter nanotubes have smaller reduction potential than small-diameter ones, implying that large-diameter nanotubes is easier to transfer electron to electron-withdrawing molecules (in our case is AY) than small-diameter ones. The larger-diameter M-SWNTs (1.40nm<d<2.60nm) were converted into S-SWNTs with significantly enhanced on/off ratio (figure 3-4c) after AY treatment due to bandgap opening caused by charge transfer from nanotube to AY. In contrast, smaller-diameter (0.60nm<d<1.40nm in our sample) M-SWNTs (which have higher reduction potential) were little affected by AY treatment, which may be interpreted to be due to the greater difficulty of “losing” electrons to AY treatment.

We also measured the I_{ds}-V_g curves for single S-SWNT devices before and after AY treatment. For both large-diameter (Figure 3-5a) and small-diameter (Figure 3-5b) S-SWNT, the high on/off ratio was preserved after AY treatment.
Figure 3-5 (a and b) Ids-Vg curves (Vds = 0.5V) showing (a) large-diameter S-SWNT and (b) small-diameter S-SWNT device behaviours before (black) and after (red) AY treatment. Insets in each diagram are AFM images of the S-SWNT in the device channel and surface height plot showing the tube diameter. The scale bars are 1µm. The arrow shows the threshold voltage shift to higher positive gate bias after AY treatment.

Figure 3-6 shows on/off ratios for 17 single S-SWNTs with different diameters (from 0.60nm to 2.50nm) before and after AY treatment. Whether small-diameter or large-
diameter, $I_{on}/I_{off}$ ratios of S-SWNTs were nearly unchanged after AY treatment, and their high on/off ratios were maintained. It is worth noting that the threshold voltage ($V_{th}$) for single S-SWNT devices is shifted toward more positive-gate bias after AY treatment. The $V_{th}$ shift to more positive gate bias after AY treatment further demonstrates electron-transfer doping from SWNT to AY. This phenomenon is consistent with previous reports. 227, 231-233

![Figure 3-6 On/off ratio ($I_{on}/I_{off}$) versus SWNT diameter before (black) and after (red) AY treatment with semiconducting SWNTs. For semiconducting SWNTs with high on/off ratio, whether small-diameter or large-diameter, $I_{on}/I_{off}$ of S-SWNTs were nearly unchanged by AY treatment.]

Bekyarova et al. observed the charge transfer effect between poly(m-aminobenzenesulfonic acid) (PABS) oligomer and semiconducting SWNTs when PABS-functionalized SWNTs was exposed to ammonia. 234 The charge transfer from PABS
oligomer to semiconducting SWNT during exposure to ammonia leads to refilling the valence band of SWNTs, and thereby increasing the resistance of PABS-functionalized SWNTs. It is worth noting that our AY treatment is reversible. Long-time (usually several hours) rinsing with DMF can remove AY molecules adsorbed on SWNT sidewalls, and the original behaviour is recovered (see Figure 3-7).

Figure 3-7 Current ($I_{ds}$) versus gate voltage ($V_g$) characteristics of a M-SWNT device before (black), after (red) AY treatment and after long-time rinsing (blue).

We also use AY to treat bulk arc discharge SWNTs (arc-SWNT). The bulk arc-SWNT sample has a mean nanotube diameter of 1.4 nm. Figure 3-8a shows RBM profiles of arc-SWNTs at wavelength of 633nm. Only the semiconducting peaks (mainly 145.2 cm$^{-1}$ and 161.9 cm$^{-1}$) were observed. After AY treatment, the intensities of semiconducting
RBM peaks were significantly decreased due to electron-transfer doping from SWNT to AY. In figure 3-8c, the broad and asymmetric BWF line near 1540 cm\(^{-1}\), a known characteristic of M-SWNTs, was significantly diminished after AY treatment, implying the weakening of phonon-plasmon coupling effect due to charge-transfer doping from SWNT to AY.\(^{217,222-224}\) This diminution is consistent with our Raman characterization of a single M-SWNT after AY treatment in Figure 3-2a. The peak position of the G-band (Figure 3-8c) appearing near 1590 cm\(^{-1}\) was upshifted after AY treatment. This upshift caused by charge-transfer doping is also observed in the previous reports.\(^{222-224}\) It is well known that the intensity of the G'-band is proportional to the metallicity of the SWNT sample.\(^{235}\) Figure 3-8d shows that intensity of the G'-band near 2620 cm\(^{-1}\) was highly decreased after AY treatment, implying the decrease in metallic character of the arc-SWNTs after AY treatment. The upshift of G'-band (Figure 3-8d) further demonstrates charge-transfer doping from SWNT to AY.\(^{223,224,235}\)

![Figure 3-8](image)

**Figure 3-8** (a) RBM, (b) D-band, (c) G-band, and (d) G'-band in the Raman spectra of Arc-SWNTs before and after AY treatment.
To demonstrate the bandgap opening after AY treatment, we prepared the arc-SWNTs film on the quartz substrate for UV-vis-NIR absorbance spectra measurement. In figure 3-9, before treatment, the SWNTs film clearly shows the absorption due to van Hove singularities (vHs) transitions of the semiconducting ($E^{S}_{11}$ and $E^{S}_{22}$) and metallic ($E^{M}_{11}$) nanotubes. After AY treatment, a new absorption peak (near 0.87 eV) between $E^{S}_{11}$ and $E^{S}_{22}$ was significantly observed. This can be attributed to a new transition band gap caused by AY treatment.

![Absorbance spectra of SWNTs film before (black) and after (red) AY treatment.](image)

**Figure 3-9** UV-vis-NIR absorbance spectra of SWNTs film before (black) and after (red) AY treatment.

AY molecules, which contain π systems, can bind to SWNT sidewall via π-π stacking interaction. AY has also been reported to disperse or solubilize carbon nanotubes. We demonstrate here that AY, acting as an electron-acceptor molecule can extract electrons from the Fermi Level of M-SWNTs when it is adsorbed onto nanotube sidewall. Sulfonic groups in AY molecule, which are generally considered to be strong electron-withdrawing groups, are likely to promote electron-transfer doping from SWNT to AY. The electron-transfer effect from SWNT to electron-acceptor
molecules leads to the change of Fermi Level in M-SWNT, and gives rise to opening of the band gap, which effectively convert the M-SWNT to an S-SWNT. This has been confirmed by some theoretical calculations.\textsuperscript{164, 189} In addition, when AY molecule is adsorbed onto the sidewall of nanotube, the negatively charged sulfonic group can induce image charges on the surface of the nanotube, leading to formation of a local electric field, which can break the cylindrical symmetry and also result in bandgap opening.\textsuperscript{189} A combined effect from the electron transfer as well as Coulomb interaction between image charges on surface of nanotube and negative charged sulfonic groups gives rise to a stronger opening of the band gap. Accordingly, M-SWNT exhibits semiconducting property after AY treatment.
3.5 Conclusion

In summary, this work demonstrates a simple and scalable method to improve the switching of SWNT-based FET devices by *in-situ* conversion of metallic SWNTs to SWNT/adsorbed molecule complexes which exhibit semiconducting behaviour using electron-acceptor molecules. This approach, using AY as electron-acceptor, is found to be diameter dependent and is highly effective for M-SWNTs with diameters in the range 1.4nm to 2.6nm. The enhancements of on/off ratio in FET devices after AY treatment generally ranged between 10 and $10^3$. Single SWNT-FET devices used here enable the precise characterization of AY treatment with different nanotube diameters and metallicity. Our work provides a promising approach to realize high-performance SWNT-based electronics.
4.1 Abstract

The key hurdle to the practical use of as-grown single-walled carbon nanotubes (SWNTs) for high performance nanoelectronics is the unavoidable presence of metallic nanotubes with current synthesis methods. We present a simple approach to in situ silence metallic SWNTs to improve device field effect behaviour, using Heptadecafluoro-1-iodooctane (HFI). We show that the reaction between HFI-generated radicals and SWNTs is diameter and metallicity dependent; in the diameter regime between 1.2 and 1.4 nm, the HFI-generated radicals preferentially attack the metallic SWNTs over semiconducting ones, as evidenced by D band rising and conductance loses for metallic SWNTs.
4.2 Introduction

Single-walled carbon nanotubes (SWNTs) have drawn intensive attentions due to their exceptionally electrical, chemical and optical mechanical properties.\textsuperscript{6-9, 45, 46} Promising applications of SWNTs in nanoelectronics\textsuperscript{11, 35, 41} and thin-film flexible electronics\textsuperscript{45, 240-242} have been demonstrated. A major obstacle to practical FET application for SWNTs is the coexistence of both metallic SWNTs (M-SWNT) and semiconducting SWNTs (S-SWNT) in as-grown SWNT samples. Most sorting techniques involve suspension of the nanotubes in solutions\textsuperscript{118, 138, 141, 243} which generally result in nanotube defects, and also cut long grown SWNTs into short ones. As-grown SWNTs typically have far superior conductivity or carrier mobility than solution-suspended SWNTs.\textsuperscript{42} In-situ SWNTs separation on wafer has become an attractively alternative methodology for solution-based sorting methods. In-situ sorting methods can selectively remove or suppress unwanted SWNTs species, and leave desired SWNTs intact, and especially the length of as-grown SWNTs will be preserved.
4.3 Experimental Methods

4.3.1. Materials Preparation and Device Fabrication

SWNTs were grown on the silicon wafer with 400 nm oxide layer using CVD method. Briefly, the catalyst consisted of ferritin (Aldrich; diluted with de-ionized water at a volumetric ratio of 1:2000 for single SWNT device) was deposited onto the SiO$_2$–Si surface. The wafer was then heated to 800 °C in a quartz tube to oxidize ferritin into iron oxide nanoparticles. Growth temperature is 925 °C. Ethanol vapor was released into the quartz tube as a carbon source. Growth time is 5 mins. For SWNT network devices, 2mM CoCl$_2$/poly(vinylpyrrolidone) alcohol solution was employed to deposit catalyst on the wafer, and the growth temperature is 880 °C. After CVD growth, we used microfabrication techniques to pattern source-drain (S-D) electrode pads to contact SWNTs. Ti/Au (10nm/20nm) was deposited as the contact metal electrode.

Heptadecafluoro-1-iodooctane (HFI) was purchased from Sigma-Aldrich. All other chemicals were ultrapure analytical grade reagents and were directly used without further purification. With stirring, HFI (100 mg) was added in Dimethylformamide (DMF, 30ml) in the reaction vessel covered by aluminum foil in order to protect from light. SWNT-based devices were immersed in the HFI/DMF solution. Then remove aluminum foil, and immediately expose the sample to UV light for an hour. When finishing, the wafer was taken out of the solution, and washed with DMF for 10 mins, ethanol for 10 mins, and DI water for 5mins. Then the wafer was dried in the vacuum oven through overnight to completely remove the solvent. For XPS characterization, we used P2-SWNTs purchased
from Carbon Solution, Inc. (CA, USA). P2-SWNTs were dispersed in DMF solution with or without HFI, respectively. After exposed to UV light for an hour, the solution was filtered through a PTFE membrane (0.2 µm), and rinsed with DMF for 10 mins, ethanol for 10 mins, and DI water for 5 mins. This long-time rinse with different solvents can remove excess HFI. Then resulting SWNT film was transferred to XPS substrate holder, and dried in the vacuum oven before XPS characterization.

4.3.2. Characterization

Raman spectra of the samples were measured with a Renishaw Ramanscope in the backscattering configuration, and Stokes spectra of the samples were obtained with 633 nm lasers. Atomic force microscopy (AFM) was conducted using a MFP 3D microscope (Asylum Research, Santa Barbara, CA) with a cantilever (Arrow NC, Nanoworld) in ac mode. All electrical measurements were carried out in ambient conditions using a Keithley semiconductor parameter analyzer, model 4200-SCS. The UV machine is equipped with an in-built UV mercury lamp with wavelength of 365 nm from Honle UV technology in Germany. Scanning electron microscopy (SEM) analysis was performed on a JEOL JSM-6700F Field-Emission Scanning Electron Microscope (FE-SEM) operating at 1 kV. XPS measurements were made using a Kratos Axis-ULTRA X-ray photoelectron spectroscope with monochromatic Al-Kα X-ray source (1486.7 eV) in an ultrahigh-vacuum environment of 10⁻⁹ Torr.
4.4 Results and Discussions

Herein, we present a simple in-situ method using Heptadecafluoro-1-iodooctane (HFI) (Fig 4-1a inset) to selectively “silence” M-SWNTs to improve SWNT-based FET behaviour. By immersing the as-synthesized SWNT (still attached to a wafer) into HFI solution for a while, the metallic nanotubes can be suppressed (illustrated in Figure 4-1a). This approach is easily scale-up. Fig4-1b shows the transfer characteristics (drain current ($I_{ds}$) versus gate voltage ($V_g$)) for a typical FET device, with a single metallic SWNT bridging between source and drain electrodes, before and after HFI treatment. Scanning electron microscopy (SEM) of the device is also shown in the Fig 1b inset. The $I_{ds}$-$V_g$ curve shows a great decrease in drain current after HFI treatment. Raman spectroscopy is a powerful tool to detect electron-phonon coupling and electronic structure in SWNTs.\textsuperscript{245-247} We also employed resonance Raman spectroscopy to investigate the effect of HFI treatment on the same single SWNT. In Fig 4-1c, the broad and asymmetric Breit-Wigner-Fano (BWF) peak is observed for the metallic SWNT, essentially attributed to coupling of discrete phonons to an electronic continuum.\textsuperscript{248, 249} The tangential mode of the single metallic SWNT, also known as the G band, is significantly decreased after HFI treatment. Before treatment, the disorder mode (D band) of the SWNT is not observed from Raman spectra due to perfect structure of originally CVD-grown SWNTs. After HFI treatment, D band at $\sim$1338 cm$^{-1}$ obviously rises as shown in Fig 4-1b. There is a pronounced increase in the ratio between the D and G band intensities ($I_D/I_G$) for the single metallic SWNT after HFI treatment. The increased $I_D/I_G$ after treatment is widely accepted as arising from chemically covalent reaction with SWNT sidewalls, due to increased numbers of sp$^3$
We suggest HFI treatment introduced disorder on the SWNT sidewall by conversion of sp\textsuperscript{2} hybridized carbon structure to sp\textsuperscript{3}, thus increased the D band intensity, and tremendously suppressed the conductivity for the single metallic SWNT as shown in $I_{ds}$-$V_g$ (red) curve in Fig 4-1b. We also performed characterization of the radial breathing mode (RBM) for the single metallic tube. The RBM frequency ($\omega$) is dependent on the diameter ($d$) of the SWNT, and can be empirically expressed by

$$\omega = \frac{A}{d} + B$$

Where A and B are two constants. Here, we use 223.5 for A and 12.5 for B based on values from studies on individual SWNTs.\textsuperscript{253, 254} The RBM originally at 214.7 cm\textsuperscript{-1} (as shown in Fig 4-1d) for the single metallic SWNT, which corresponds to 1.1 nm in diameter, almost disappeared after HFI treatment. RBM peak is attributed to the symmetric oscillatory vibration of the SWNT circumference normal to the growth axis, and RBM disappearing indicates the symmetry of the SWNT was disturbed by covalent bonds after HFI treatment. The change of RBM for the metallic SWNT is consistent with observed D band feature.
**Figure 4-1** (a) Schematic illustration of the treatment process for SWNT-FET in the HFI solution. Inset is structure of Heptadecafluoro-1-iodooctane (HFI). (b) Transfer characteristics of a single metallic SWNT-FETs before (black) and after (red) HFI treatment. Inset is SEM image of The SWNT-FET. (c) Raman spectra showing D band and G band of the corresponding single metallic SWNT in the FET device before (black) and after (red) HFI treatment. (d) RBM peak of the corresponding single metallic SWNT before (black) and after (red) HFI treatment. The feature marked with an asterisk at 303 cm\(^{-1}\) from Si/SiO\(_2\) substrate.
In Fig 4-2a, the $I_{ds}$-$V_g$ curve from a single semiconducting SWNT device is shown, and inset is the corresponding SEM image of the device. The black and red curves almost coincide with each other, and no change in $I_{ds}$-$V_g$ curve is observed before and after HFI treatment. Fig 4-2b shows G band of the semiconducting SWNT remains unchanged after treatment, and D band is not observed after HFI treatment. The RBM peak at 140.2 cm$^{-1}$ for the semiconducting SWNT, which corresponds to 1.7 nm in diameter, is also intact after treatment in Fig 4-2c. The results from Raman spectra (G band and RBM) of the semiconducting SWNT are consistent with observation from its $I_{ds}$-$V_g$ curves, and both indicate this semiconducting tube is inert to the HFI treatment.

**Figure 4-2** (a) Transfer characteristics of a single semiconducting SWNT-FETs before (black) and after (red) HFI treatment. Inset is SEM image of The SWNT-FET. (b) Raman
spectra showing G band of the corresponding single semiconducting SWNT in the FET device before (black) and after (red) HFI treatment. (c) RBM peak of the corresponding single semiconducting SWNT before (black) and after (red) HFI treatment. The feature marked with an asterisk at 303 cm\(^{-1}\) from Si/SiO\(_2\) substrate.

In order to clarify the diameter range in which HFI can suppress metallic SWNTs and preserve semiconducting ones, we treated 31 single-SWNT FET devices with different diameters by immersion in HFI solution. Before HFI treatment, the metallic/semiconducting characters of the SWNTs were determined with a semiconductor parameter analyser (Keithley, model 4200-SCS). The I\(_{ds}\)-V\(_{g}\) curve of M-SWNT is flat, and on/off ratio is very low.\(^{116, 256}\) In contrast, the current through S-SWNT devices shows large on/off ratio (I\(_{on}/I_{off} \geq 10^3\)).\(^ {35, 117}\) Originally, 17 SWNTs exhibited metallic performance; the balance were semiconducting. Atomic force microscopy (AFM) was employed to measure the diameter of the single SWNT. Here, we define a “lost” device is the one with the current lower than 0.1 nA (10\(^{-10}\) A) at V\(_{ds}=0.5\) V. We observed four different device behaviours after HFI treatment, including metallic→lost (becoming electrically nonconductive (Fig 4-3a)), metallic→metallic (metallic conductance is preserved (Fig 4-3b)), semiconducting → lost (Fig 4-3c), and semiconducting→semiconducting (semiconducting performance is immune from the HFI treatment (Fig 4-3d)).
Figure 4-3 (a to d) Ids-Vg curves showing four different device behaviours before (black) and after (red) HFI treatment. Insets in each diagram are AFM images of the SWNT in the device channel and surface height plot showing the tube diameter.

Fig 4-3a reveals an I_{ds}-V_g (black) curve of a single M-SWNT with a diameter of ~1.3 nm (Fig 4-3a inset). After HFI treatment, the device almost lost conductance (I_{ds}< 0.1 nA), as shown in the red curve. We observed that metallic→lost devices were composed of the M-SWNT with the diameter smaller than 1.4 nm (d<1.4 nm, as shown in Fig 4-4a). Fig 4-3b shows a representative I_{ds}-V_g curve for metallic→metallic device with diameter of ~1.5 nm, metallic conductance is preserved after HFI treatment. For the metallic→metallic devices, the M-SWNTs have large diameters (d>1.4 nm, in Fig 4-4a). This indicates large-diameter M-SWNTs (d>1.4 nm) immune from HFI treatment. For the
semiconducting→lost devices (Fig 4-3c), the diameter of the S-SWNTs is smaller than 1.2 nm (d<1.2 nm, as shown in Fig 4-4b). In contrast, in semiconducting→semiconducing devices (Fig 4-3d), the semiconducting tubes were observed to have larger diameter (d>1.2 nm, as shown in Fig 4-4b).

![Figure 4-4](image)

**Figure 4-4** (a) Current versus metallic SWNT diameter before (black) and after (red) HFI treatment. In the diameter smaller than 1.4 nm, metallic SWNTs were silenced after HFI treatment. (b) On-current versus semiconducting SWNT diameter before (black) and after (red) HFI treatment. In the diameter smaller than 1.2 nm, semiconducting SWNTs lost conductance after HFI treatment.

It is well-known that HFI can generate perfluoroalkyl radicals (R_F) when exposing to UV irradiation. The bond energy of F-C, C-C and I-C is 4.533, 3.565 and 2.451 eV, respectively. The I-C bond is the easiest to be broken to generate radicals. Noncovalent interaction between HFI and SWNTs can be ruled out due to the significant rising of D-band (Fig 4-1c) after HFI treatment. Here, we attributed conductance loses of
small-diameter SWNTs to the attack of light-induced perfluoroalkyl radicals toward the sidewall of SWNTs. This aggressive covalent reactions damage the electronic structure of small-diameter SWNTs, thus introducing D-band and greatly decreasing the conductance. Such a reaction process is illustrated in Fig 4-5.

Figure 4-5 (a) Schematic illustration of the proposed radical reaction process.

In order to further confirm perfluoroalkyl radicals covalently binding to SWNTs, we also performed X-ray photoelectron spectroscopy (XPS) measurements of SWNTs before and after HFI treatment. In Fig 4-6, F1s peak at ~687 eV significantly emerges after HFI treatment. It is worth noting that peak related to iodine is not observed in the XPS spectra after treatment.

Figure 4-6 Photoelectron spectra of SWNTs before (black) and after (red) HFI treatment.
It is well-accepted that SWNTs with smaller diameters are preferentially reactive over larger ones due to C-C bonding’s higher strain and the higher radius of curvature.\textsuperscript{152, 167, 261} Our results demonstrate this diameter selectivity. For smaller-diameter SWNTs (d<1.2 nm), both M-SWNT and S-SWNT lost electrical conductance after HFI treatment. When the diameter is large than 1.4 nm (d>1.4 nm), whether metallic or semiconducting, both were immune from HFI treatment, and preserved their device performance. Our results also indicate that only in the medium-diameter range (from 1.2 nm to 1.4 nm), M-SWNTs are selectively suppressed over S-SWNT by HFI treatment. In this diameter regime, the effect of HFI treatment depends on the electronic properties of SWNT. In other words, HFI treatment shows electronic selectivity between 1.2 nm and 1.4 nm. This electronic selectivity is dictated by the intensity of electrons near Fermi level.\textsuperscript{118} Compared with S-SWNT, M-SWNT with the same diameter has higher intensity of electrons near Fermi level, leading M-SWNT to preferentially reacting with perfluoroalkyl radicals over S-SWNT in the range of 1.2 nm and 1.4 nm. We also tried other perfluoroalkyl iodide compounds, such as Nonafluoro-1-didobutane (figure 4-7a), and perfluorodecyl iodide (Figure 4-7b). For Nonafluoro-1-didobutane, only in the diameter range from ~1.5 nm to 1.6 nm, M-SWNTs were selectively destroyed over S-SWNTs. For perfluorodecyl iodide, Metallic tubes were preferentially removed over semiconducting ones in the diameter interval between ~1.2 nm and ~1.3 nm.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structure.png}
\caption{Structure of (a) Nonafluoro-1-didobutane and (b) perfluorodecyl iodide.}
\end{figure}
Our method utilized single SWNT FET devices in the interest of precise characterization of the effects of the HFI treatment. It is also readily applicable to network devices, in which it would greatly reduce the connectivity of the metallic network which limits the on/off ratio and switching ability of devices fabricated from SWNT networks. We also applied HFI treatment to SWNTs network-based FET devices. For SWNT network devices, CoCl2/poly(vinylpyrrolidone) alcohol solution is used as catalyst. According to AFM measurements, the diameter distribution of SWNTs in the networks is predominantly from 0.9nm to 1.7 nm as shown in figure 4-8.

**Figure 4-8** Diameter distributions of SWNTs networks grown by CVD.

In Fig 4-9a, original $I_{ds}$-$V_g$ (black) curve of a CVD-grown SWNTs-network FET (network device 1) was flat ($I_{on}/I_{off}$≈1), which indicated that CVD-grown SWNT networks are mixtures of metallic and semiconducting ones. After HFI treatment, the network device 1 showed significantly enhanced on/off ratio ($I_{on}/I_{off}$≈ $10^2$). In Fig 4-9b, even after HFI treatment, $I_{ds}$-$V_g$ (red) curve of another SWNTs-network device (network device 2)
showed little response to the gate voltage ($V_g$) sweep. This indicated that in network device 2, there existed metallic SWNTs with diameter larger than 1.4 nm, which were immune from HFI treatment. After HFI treatment, we used our previously reported AY (Acid Yellow) method\textsuperscript{210} (in chapter 3) to treat network device 2. The AY method can converse M-SWNTs with $d>1.4$ nm into semiconducting ones.\textsuperscript{210} Finally, the $I_{ds}$-$V_g$ (blue) curve of network device 2 showed increased on/off ratio ($I_{on}/I_{off}>10^2$) after combined HFI and AY treatment, as shown in Fig 4-9b.

**Figure 4-9** (a) Transfer characteristics of CVD-grown SWNTs network device 1 before (black) and after (red) HFI treatment. (b) Transfer characteristics of CVD-grown SWNTs network device 2 before (black), after HFI treatment (red) and after combined HFI and AY treatment (blue).
4.5 Conclusion

In general, we have clearly presented that a UV irradiation induced radical methods can effectively *in situ* silence M-SWNTs with diameter smaller than 1.4 nm. Perfluoroalkyl radicals’ covalent binding to sidewall of SWNTs was monitored by Raman and XPS spectra. This approach was found to be electronic dependent in the diameter range from 1.2 nm to 1.4 nm, in which the intensity of electrons near Fermi level dictates chemical reactivity of SWNTs. This method combined with our previously reported AY method can be applied to SWNTs network-based devices, and the resulting devices shows significantly enhanced on/off ratio. So it provides a promising technique to realize high-performance SWNT-based electronics.
Chapter 5

Summary and Future Research Outlook

In this thesis, we developed three different on-chip separation/conversion methods to obtain SWNT-based FET with high on/off ratio. On-chip based separations are more simple and direct due to not involving purification, surfactant and sonication. Especially this method is more suitable for CVD-grown SWNTs. CVD synthesis technique is highly compatible for the industrial process of electronic devices. All the work, including SWNT growth, device fabrication and separation/conversion, can be finished in the substrate for on-chip methods.

For small-diameter SWNTs with range from 0.8 to 1.0 nm, EAQ method was demonstrated to be highly useful to convert metallic SWNTs to semiconducting ones, and in-situ improve device performance, as evidenced by several orders ($10$ and $10^4$) increase in the on/off ratio. We showed that the reaction between EAQ-generated radicals and SWNTs is diameter and metallicity dependent; in the diameter regime (0.8 to 1.0 nm), the EAQ-generated radicals preferentially attack the metallic SWNTs over semiconducting ones and convert them to semiconducting. Single SWNT-FET devices used here enable the precise characterization of EAQ treatment with different nanotube diameters and metallicity.

Furthermore, we demonstrates a simple and scalable method to improve the switching of SWNT-based FET devices by in-situ conversion of metallic SWNTs to
SWNT/adsorbed molecule complexes which exhibit semiconducting behaviour using electron-acceptor molecules. This approach, using 4-Amino-1,1’-azobenzene-3,4’-disulfonic acid sodium salt (Acid Yellow 9, AY) as electron-acceptor, is found to be diameter dependent and is highly effective for M-SWNTs with diameters in the range 1.4nm to 2.6nm. The enhancements of on/off ratio in FET devices after AY treatment generally ranged between 10 and $10^3$. Also, we showed that a UV irradiation induced radical methods can effectively in situ silence M-SWNTs with diameter smaller than 1.4 nm with Heptadecafluoro-1-iodooctane (HFI). Perfluoroalkyl radicals’ covalent binding to sidewall of SWNTs was monitored by Raman and XPS spectra. This approach was found to be electronic dependent in the diameter range from 1.2 nm to 1.4 nm, in which the intensity of electrons near Fermi level dictates chemical reactivity of SWNTs. This method combined with our previous AY method can be applied to SWNTs network-based devices, and the resulting devices shows significantly enhanced on/off ratio. So it provides a promising technique to realize high-performance SWNT-based electronics.

On the basis of present work in this thesis, there is still much room for improvement in realizing practical application in SWNTs’ nanoelectronics. The future research will address the following directions:

(1) Our on-chip separation/conversion methods are diameter dependent. Obtaining high-quality SWNTs with suitable diameter distribution is keen to utilize our developed on-chip methods. Although various synthesis methods of SWNTs with diameter control have been reported, it is still difficult to obtain SWNT with relatively narrow diameter distribution, such as from 1.2 to 1.4 nm.
(2) More works are needed to further understand the mechanism of conversion from metallic SWNT to semiconducting ones. This understanding is highly helpful to make us to find more compounds which can improve the performance of SWNTs with wider diameter distribution.
Reference


88. Treacy, M.; Ebbesen, T.; Gibson, J., Exceptionally high Young's modulus observed for individual carbon nanotubes. **1996**.


136. Mesgari, S.; Poon, Y. F.; Yan, L. Y.; Chen, Y.; Loo, L. S.; Thong, Y. X.; Chan-Park, M. B., High selectivity cum yield gel electrophoresis separation of single-walled carbon nanotubes


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Appendix

List of publications

