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ABSTRACT
In this Account, we summarize some of our recent studies on the materials properties of the carbon nanotubes (CNTs). The focus is on single-wall carbon nanotubes (SWNTs). We describe experiments on synthesis of SWNTs with controlled molecular structures and assembly of functional macroscopic structures. In addition, we present results on the electron field emission properties of macroscopic CNT cathodes.

1. Introduction
The last 10 years has been an exciting time for the field of carbon materials. The discoveries of fullerenes and carbon nanotubes (CNTs) have attracted the attention and imagination of many researchers worldwide. Tremendous amounts of research and development efforts have been devoted to the studies of these new carbon allotropes. The findings have significantly extended our understanding of the fundamental science at the nanometer scale and created the opportunities for future technologies. The research in fullerences chemistry has led to the discovery of molecular superconductors with a record transition temperature. Potential applications of these nanoscale materials properties of the carbon nanotubes (CNTs). The focus is on single-wall carbon nanotubes (SWNTs). We describe experiments on synthesis of SWNTs with controlled molecular structures and assembly of functional macroscopic structures. In addition, we present results on the electron field emission properties of macroscopic CNT cathodes.

2. Fabrication and Processing of SWNTs
2.1. Synthesis. Carbon nanotubes with different structure and morphology can now be produced in laboratory
Here we present results showing that the diameter and the electronic properties of the SWNTs can be varied by choosing different catalysts used in the laser ablation process.

We synthesized SWNTs using Rh and Pd catalysts instead of the common Ni/Co system. Rh and Pd have higher melting temperatures compared to Ni and Co and have finite solubility of C. In addition, they are nonmagnetic, making the materials easier to characterize. The synthesis procedure is similar to that previously described. All of the samples are 10% 13C-enriched. The percentage of the metallic tubes increases to one-third metallic and two-thirds semiconducting SWNTs, consistent with a random chirality distribution. The purity of the final product can reach over 95%.

2.2. Purification. As-synthesized carbon nanotube materials contain significant amounts of impurities, including amorphous carbon (α-C), graphitic particles, and metal catalysts. The purification schemes that have been developed usually take advantage of the differences in the aspect ratio and oxidation rate between the nanotubes and the impurities. Although the majority of the impurity phases can be eliminated by a combination of filtration and oxidation treatments, these processes also damage the structural integrity of the nanotubes by creating defects on the graphene shells.

A combination of hydrogen peroxide (H2O2) reflux and filtration is an effective way to remove most of the impurities without causing much damage to the nanotube compared to, for example, sonication in more potent acid such as nitric acid. In this process, raw materials (Figure 3A) are first refluxed in H2O2, followed by filtering through 0.8–2μm pore-size membranes. A significant fraction of the nanoparticles and magnetic catalysts can be removed by repeating the filtration process several times until the liquid passing through the filter is clear. The purity of the final product can reach over 95% (Figure 3C,D), although the precise value is difficult to

![Figure 2](image-url)

**Figure 2.** (Left) Experimental and simulated X-ray diffraction patterns of SWNTs made using different catalysts. The average tube diameters of samples A and B are 1.40 and 1.32 nm, respectively. (Right) The Raman spectra from the same samples collected using 514-nm laser light. The average peak positions of the SWNT breathing mode are 172, 175, and 258 cm⁻¹ for samples A, B, and C, respectively. Breathing mode at 258 cm⁻¹ in sample C corresponds to an average tube diameter of 0.85 nm.
determine. After purification, the SWNT bundles can be recrystallized by annealing in a vacuum at 800–1000 °C for a short time. The end product is no longer magnetic: the bundles cannot be moved by a magnet and no Ni/Co Bragg peaks are present in the X-ray diffraction pattern (Figure 3E). The purified materials show a strong electron spin resonance (ESR) signal from the conduction electrons and a narrow $^{13}$C NMR peak of the SWNTs.

2.3. Opening and Closing the SWNTs Tips. Pristine SWNTs have large aspect ratios ($10^3$–$10^4$) and closed ends, which prevents the diffusion of the guest species into the interior spaces of the nanotubes. It has been shown, mostly through TEM measurements, that the nanotubes can be fractured and shortened by techniques such as ball-milling, mechanical cutting, and chemical etching. For macroscopic measurements of the open-end nanotubes, most of the nanotubes need to be opened and have similar lengths. These characteristics have not been demonstrated by the ball-milling and mechanical cutting processes. Here we present results from both local and macroscopic experiments to demonstrate that the SWNTs can be opened and shortened uniformly by chemical etching. Furthermore, the opened SWNTs can again be closed.

Upon sonication in strong acid, oxidation of the nanotubes is believed to initiate from the sidewall defects on the bundle surfaces and the tips, where the reactivity is higher. The reaction then propagates throughout the bundles. This defect-assisted mechanism is supported by the structure of the etched tubes and the overall weight change. TEM micrographs show that the tips of the shortened SWNT bundles are mostly tapered (Figure 4A), which is distinctly different from the case with those made by mechanical cutting and ball-milling. Experimentally, we found a weight loss of 70% when the purified SWNTs ($L > 10 \mu m$) were etched to $0.5 \mu m$ average length. This is significantly higher than what is expected if reaction occurs only at the ends. In addition, the effectiveness and the rate of the etching process depend highly on how the starting materials are synthesized. For SWNTs synthesized by the laser ablation method in our laboratory, the averaged bundle length can be reduced to $0.5 \mu m$ with a narrow distribution after 30 h of sonication in strong acid (Figure 4B 4C). After etching, the nanotubes are still in the form of bundles.

Careful examinations by HRTEM reveal that the SWNT tips are open after etching (Figure 5A). In some cases, disordered structures are observed at the tips which are attributed to functional groups that terminate the broken carbon bonds (Figure 5B). No closed ends were observed in all the shortened SWNTs that we could clearly image, even when the samples were vacuum-annealed below 400 °C. The open ends can be again closed by vacuum annealing at temperatures above 500 °C. Figure 5C shows a HRTEM image of the tips of the individual SWNTs after annealing at 800 °C under $10^{-6}$ Torr dynamic vacuum. All the observed tips are closed and apparently well graphitized. However, instead of the ideal hemispherical geometry, they are closer to polygons, as often observed in the MWNTs.
Electrochemistry and NMR studies\textsuperscript{36} show a drastic enhancement of the specific storage capacity of Li in the open-end SWNTs. Figure 5D compares the reversible Li storage capacity in the closed and opened SWNTs measured under otherwise the same conditions. For close-end SWNTs, a reversible capacity of LiC\textsubscript{6} is observed which is similar to the value for graphite and consistent with Li occupying only the interstitial sites within the SWNT bundles.\textsuperscript{37,38} For open-end SWNTs, the specific Li storage capacity increases to LiC\textsubscript{3.36}.\textsuperscript{39} The increase in capacity is explained by diffusion of Li\textsuperscript{+} into the interior spaces of the SWNTs which are inaccessible in the close-end tubes.

2.4. Tuning the Electronic Properties. Charge transfer is an effective method to modify the electronic properties of the carbon nanotubes. Similar to graphite, both electron donors and acceptors can be readily inserted into the interstitial sites of the SWNT bundles or the interlayer spacing of the MWNTs via redox reactions. Charge transfer leads to significant changes in the properties of the host materials.\textsuperscript{36,40–43} \textsuperscript{13}C nuclear spin–lattice relaxation experiments show that all the SWNTs become metallic upon lithium intercalation. As shown in Figure 6A, the saturation recovery curve of the pristine SWNT sample can be fit with a double-exponential function.\textsuperscript{19} The fast-relaxing component is attributed to the metallic SWNTs, while the slow-relaxing component is attributed to the semiconducting SWNTs. The lithium-intercalated samples can be fitted with a single-exponential function, indicating that all the SWNTs in the sample have the same average electronic properties. The relaxation time decreases with increasing Li/C ratio, indicating an increase of the density of states at the Fermi level.\textsuperscript{36}

Furthermore, in situ photoemission spectroscopy experiments\textsuperscript{44,45} show that the electron work function of the CNTs can be substantially reduced by intercalation of electron donors such as cesium (Figure 6B). The pristine SWNT bundles have a work function of 4.8 eV, similar to that of graphite. Upon exposure to Cs vapor in a controlled environment, the work function decreases with increasing exposure time. A distinct Fermi edge is observed in the Cs-intercalated SWNTs.\textsuperscript{44} Electron field emission measurement of the intercalated SWNTs shows that the threshold field for emission decreases with increasing Cs exposure time,\textsuperscript{46} consistent with reduction of the electronic work function due to Cs intercalation.

3. Integration

3.1. Self-Assembly. Self-assembly is often a preferred process to assemble micro- and nanoscale objects into ordered macroscopic structures.\textsuperscript{47} It has been utilized to produce functional materials such as photonic crystals, nanocomposites, and ordered DNA structures. We have recently shown that functional hierarchical structures of CNTs with long-range ordering can be readily fabricated at room temperature via self-assembly.\textsuperscript{48} This process has several advantages over the CVD and other postprocessing methods.

In this process, SWNT bundles are first rendered hydrophilic and are dispersed in deionized water at a

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\includegraphics[width=\textwidth]{figure5}
\caption{High-resolution TEM micrographs showing that the tips of the etched SWNTs are either (A) open or (B) terminated by large chemical groups. (C) After annealing in a vacuum at 800 °C, the ends are closed again. (D) Second cycle charge–discharge data (cell voltage versus Li concentration) obtained from purified SWNTs and samples after chemical etching. The data were collected at 50 mA/g rate.}
\end{figure}
concentration of 0.5–1 g/L. A clean hydrophilic substrate such as glass is immersed vertically into the suspension (Figure 7). The nanotubes deposit on the substrate along the air/liquid/substrate triple line. A continuous SWNT film forms on the substrate as the triple line progresses downward. The films are smooth and have stepwise sharp edges that are straight at the substrate/film interface. Electron microscopy studies reveal that the SWNT bundles are orientationally ordered, with their longitudinal axes lying on the substrate surface and along the air/water/substrate triple line direction (Figure 8). Similar to the structure of nematic liquid crystals, there is no translational ordering. Under a cross-polarized optical microscope, the SWNT films show birefringence, with extinction at 0° (nanotube alignment direction parallel to the polarization direction) and 90° (Figure 8B) and maximum transparency at 45° over the entire surface area (Figure 8C).

The hydrophilic nanotubes deposit only on the hydrophilic, not on the hydrophobic, surface. This selectivity enables the fabrication of patterned structures by controlling the functionality of the supporting surface. As demonstrated in Figure 8D, periodic structures with a characteristic dimension of 100 μm or lower can be readily deposited on glass substrates at room temperature. The well-defined structures can be utilized as, for example, the basic emission pixels for field emission display (FED). The efficient room-temperature deposition process is attractive compared to the CVD method, especially for the low-melting-temperature glass substrates preferred for display applications.

3.2. Electrophoretic Deposition. Electrophoretic deposition (EPD) is a high-throughput process for production of films/coating with good homogeneity and packing density. It can be applied to essentially any solid with small particle sizes or a colloidal suspension. We have shown recently that preformed CNTs can be deposited on various surfaces with controlled thickness and morphology via EPD.

The first step in this process is to stabilize a suspension of CNTs in a suitable solvent, which is challenging for CNTs. Although surfactants can be used, they are difficult to remove completely after deposition. The residual surfactants can seriously affect the performances of the nanotubes. DMF, a commonly used surfactant, interacts strongly with the CNTs. IR spectroscopy studies of SWNT films deposited from a SWNT/DMF suspension show strong DMF signals even after vacuum annealing. A very dilute suspension of SWNTs in alcohol (i.e., 1 mg of SWNT in 200 mL of ethanol) is typically used. A small amount of “charger” such as MgCl₂ is added to the suspension. Upon application of a direct current electrical field between the substrate and a counter electrode, the SWNTs migrate toward the substrate. The migration direction is controlled by the charger added. The film of long SWNTs is porous, with clearly resolved SWNT bundles, while the...
film of short SWNTs has a much higher packing density. The deposition rate depended on several factors, including the concentration of the SWNT suspension, the charger concentration, and the current. Beyond fabrication of uniform CNT films/coating, the EPD technique can be used to deposit CNTs onto more complicated structures. This can be realized by either using a mask or taking advantage of the fact that deposition occurs only on the conducting surfaces.

4. Electron Field Emission Properties

Electron field emission is a quantum process where, under a sufficiently high external electrical field, electrons can escape from the metal surface to the vacuum level by tunneling.\textsuperscript{52} Compared to thermionic emission, this is a preferred mechanism to extract electrons because no heating is required and the emission current can be controlled by the external field. The basic physics of field emission is summarized by the Fowler–Nordheim equation, which states that the emission current increases exponentially with increasing electrical field.\textsuperscript{53} For a metal with a flat surface, the threshold field is typically around $10^4 \text{ V/\mu m}$, which is impractically high. All the field emission materials rely on field enhancement at the sharp tips/protrusions. The typical threshold fields are in the order of $10$–$100 \text{ V/\mu m}$ for $10 \text{ mA/cm}^2$ current density (Table 1).

Carbon nanotubes have atomically sharp tips and large aspect ratios ($> 10^3$) and, as a result, much larger field enhancement factors than the conventional emitters, such as the Spindt-type tips. Experiments have shown that the emission turn-on field of CNTs is $1$–$2 \text{ V/\mu m}$, significantly lower than the values reported for other electron-emissive materials (Table 1). Compared to diamond emitters, the CNTs are much more stable at high currents. A stable emission current of $> 1 \mu A$ has been observed from an individual SWNT.\textsuperscript{58} These properties make the CNTs attractive for technological applications. Indeed, the potential of using CNTs as cold cathodes has been demonstrated in devices such as field emission flat panel displays (FEDs),\textsuperscript{59} lighting elements,\textsuperscript{60} and discharge tubes for over-voltage protection.\textsuperscript{61}

Most of the cold-cathode applications require a significantly higher emission current than that which can be delivered from a single CNT. For example, FED requires a current density of $1$–$10 \text{ mA/cm}^2$,\textsuperscript{62} while other applications, such as microwave amplifiers, demand a much higher output.\textsuperscript{63} For these applications, macroscopic CNT
cathodes are required. Although an individual CNT can deliver an extremely high and stable emission current, the current density and stability decrease drastically as the cathode area increases. For macroscopic cathodes, the emission characteristics depend not only on the structure of individual nanotubes/bundles but also on their higher level architectures. For example, the emission site density is closely related to the uniformity and density of CNTs. A low emission site density of $10^3 - 10^4$ site/cm$^2$ means that, even at 1 mA/cm$^2$, the current extracted from each CNT is close to the limit. In the ideal case, one would like to have a cathode with well-spaced CNTs aligned in the electrical field direction (Figure 9A). Although aligned MWNT-like structures can now be fabricated by a variety of CVD methods, these materials are highly defective. In most cases, the spacing between the individual MWNTs cannot be controlled. We compared the emission properties of CNTs with different structure and morphology. The results (Figure 9B) show that the emission threshold fields of all the CNT materials are comparable within a factor of 2–3, regardless of the orientation and structure. However, SWNTs fabricated by the laser ablation method are more stable at the high current densities.

Here we show the emission characteristics of macroscopic SWNT cathodes after optimizing the CNT density, uniformity, and adhesion. The data were collected using the parallel-plate geometry. Figure 10A shows the emission stability of a SWNT cathode. Under a constant voltage without feedback, no overall decay in the emission current is observed over a 10-h period at a total current of 1.8 mA(14 mA/cm$^2$). The standard deviation of current fluctuation is $2-3\%$. By incorporation of a simple feedback loop, the fluctuation can be further reduced to below 1%. Figure 10B shows the pulse emission currents triggered by various pulsed voltages. The emission current can be readily controlled by the input voltage signal. No delay between the applied voltage and the onset of the emission current was observed. A total emission current of 16 mA was obtained from a 4-mm-diameter cathode at an 11.3 V/μm electric field (the current output is presently limited by the power supply used). The high emission current and current density of these cathodes make them attractive for a variety of vacuum electronic devices.

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