Sorting Carbon Nanotubes for Electronics

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Growth processes of single-wall carbon nanotubes (SWNTs) produce a mixture of nanostructures having diameter and helicity distributions that exhibit a broad range of properties. For instance, the laser ablation process produces highly crystalline SWNTs, but the diameter distribution is broad (1.1−1.5 nm) and includes a mixture of metallic and semiconducting species.[1] Although better selectivity has been achieved in commercial sources of SWNTs, such as the CoMoCAT nanotubes[2] from Southwest Nanotechnologies and the HIPCO tubes from Unidym,[3] they also contain SWNTs having a wide diameter distribution (0.6−1.2 nm). As far as applications are concerned, the presence of this mixture is a serious issue. The use of commercial SWNTs thus requires purification and adequate enrichment procedures in order to harvest SWNTs according to their desired properties. Most applications also require robust and reliable techniques that enable transfer, assembly, and/or deposition of the nanotubes on substrates.

In a series of groundbreaking studies, the Hersam group has developed a robust process for sorting SWNTs by both diameter and electronic properties (or helicity).[4,5] The process uses preparative ultracentrifugation in a density gradient and capitalizes on small differences in the buoyant density of SWNT−surfactant mixtures in water. Because of the success of this work, sorting SWNTs by solution processing appears as the most promising route for future research on SWNT materials. Here, we briefly review the steps required to manipulate SWNTs in solution for electronics applications and elaborate further on the impact of the most recent work from Arnold et al. appearing in this issue on the hydrodynamic properties of SWNTs in surfactant solutions.[6]

Processing Nanotubes in Solution. Processing raw nanotube samples generally starts by preparing stable suspensions of carbon nanotubes in solution. SWNTs are, however, typically found in bundles or larger aggregates because they are hydrophobic and their surfaces are smooth, which results in strong van der Waals bonding between them. Many attempts at obtaining individual nanotubes in solution have shown that the nanotubes are insoluble under normal conditions; however, effective methodologies have been developed in order to improve either their solubility or the stability of SWNT suspensions in liquids. These methods can be classified into two groups: noncovalent adsorption and covalent functionalization.

Noncovalent Adsorption. The method involving SWNT encapsulation in a surfactant−water solution is one of the simplest noncovalent methods to enable stable suspensions of individual nanotubes.[7] Fluorescence measurements have shown that the technique is effective in isolating semiconducting SWNTs in water.[8] To improve the encapsulation yield, the method calls for harsh ultrasound treatments and long ultracentrifugal sedimentation. Ultrasound is effective, but it also shortens the nanotubes into small segments.[9] As discussed below, this is problematic for applications requiring large SWNT networks. More gentle approaches have been explored recently,[10,11] but these are a clear departure from the surfactant−water method. For example, the preparation of nanotube salts using charge transfer doping from alkalis appears to be one of the more promising routes to dissolve nanotubes gently in solution without the use of ultrasound.[11] The result is a thermodynamically stable solution of nanotubes in polar aprotic solvents. A disadvantage is that the nanotube solutions are unstable in air, which makes the procedure difficult and costly; however,

ABSTRACT Because of their unique structure and composition, single-wall carbon nanotubes (SWNTs) are at the interface between molecules and crystalline solids. They also present properties that are ideal for making lightweight, inexpensive, and flexible electronics. The raw material is composed of a heterogeneous mixture of SWNTs that differ in helicity and diameter and, therefore, requires purification and separation. In a series of groundbreaking experiments, a robust process serving this purpose was developed based on SWNTs encapsulated in surfactants and water. Ultracentrifugation in a density gradient combined with surfactant mixtures provided buoyant density differences, enabling enrichment for both diameter and electronic properties. A new paper in this issue explores further the process through the hydrodynamic properties of SWNT−surfactant complexes. The study reveals that we have just begun to uncover the dynamics and properties of nanotube−surfactant interactions and highlights the potential that could be gained from a better understanding of their chemistry. The time scale of integration of carbon nanotubes into electronics applications remains unclear, but the recent developments in sorting out SWNTs paves the way for improving on the properties of network-based SWNTs.

See the accompanying Article by Arnold *et al.* on p 2291.

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the method has been largely unexplored for the moment.

Covalent Functionalization. Methods involving sidewall functionalization of nanotubes have also been developed to prepare stable suspensions or solutions of SWNTs in solvents. Processes involving oxidative activation[12] and radical addition[13,14] are common examples. Covalent functionalization of SWNTs is becoming one of the most powerful tools for the processing, biodelivery, and assembly of SWNTs from solution.[15] It also provides an effective path to anchor new groups onto the sidewalls, thus enabling a large variety of covalent functionalities to be subsequently attached to the struc-

ture with the potential for expanding the use of SWNTs in applications. However, the functionalization breaks the π-electron conjugation and introduces disorder on the SWNT sidewalls, which disrupts their electrical and optical properties. Covalent SWNT chemistry has, therefore, severe limitations when applied to make electronics materials. The reversibility of reaction upon thermal cycling at high temperature alleviates some of the problems because it removes side groups and repairs sidewall damages.[16] Toward this end, the reversibility of the diazonium reaction has recently been tested using spectroscopy and conductance measurements.[17] The study revealed that the reaction is partially reversible and leads to accumulation of defects on the nanotube sidewalls.

Thus, procedures have been developed for making stable suspensions and solutions of individualized nanotubes and new ideas are actively being pursued to improve on those procedures. So far, the noncovalent methods based on surfactant complexes have had the largest impact on the field.

The Nanotube Mixture. Figure 1 presents an atomic force microscope (AFM) image of SWNTs produced by laser ablation and deposited as a network on a silicon substrate using a noncovalent method refined in the author's laboratory.[18] Figure 1 also presents an optical absorption spectrum of the same source taken before (black curve) and after (red curve) encapsulation in surfactants and enrichment using the procedure by Arnold *et al.*[5,6] The difference is striking, which explains the rapid integration of encapsulating nanotubes in surfactants as part of the procedure for enrichment and purification of SWNTs. The features in the absorption spectrum after encapsulation (red) contain information

> The process uses preparative ultracentrifugation in a density gradient and capitalizes on small differences in the buoyant density of SWNT−surfactant mixtures in water.

about the structure of the nanotubes, their electronic energy states, and the sensitivity of those states toward environmental changes.

The AFM image confirms what is already known about the source; the nanotubes have different lengths and diameters, almost all in the 1.1−1.5 nm range. Although a few small bundles appear in the image, the statistics reveal that the solution contains mostly individualized nanotubes. However, the experiments also show that the sample is a mixture of nanotubes with differing helicities. The absorption spectrum confirms this point: there are metallic (labeled E^M_{11}) as well as semiconducting (labeled E^S_{11}, E^S_{22}, and E^S_{33}) absorption bands, seen in the spectrum as sharp absorption peaks superimposed over the broad π-plasmon absorption background. A closer look at the spectrum collected for different fractions along the density gradient (not shown) indicates that diameter enrichment has been made, but the sample remains a mixture of SWNTs unless the process is repeated or improved. In this first attempt to repeat the work by Arnold *et al.* in our laboratory, positive results were achieved quickly, indicating the generality of the method.

The Process of Ultracentrifugation of Surfactant-Encapsulated SWNTs. The process of separation discussed above is based on a method introduced in 2002 by O'Connell *et al.*[7] Separation is achieved by taking advantage of the different sedimentation
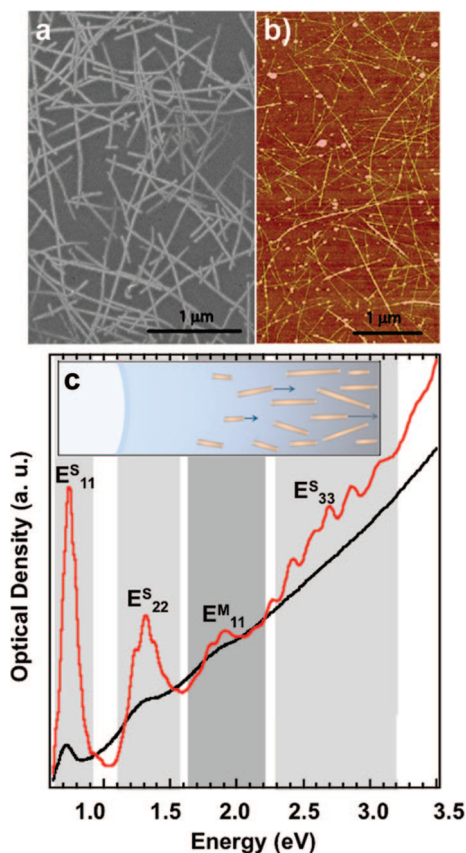

Figure 1. (a) Scanning electron microscope and (b) atomic force microscope images of SWNTs after deposition on a silicon substrate. Although a mixture of SWNTs is present, the layer is semiconducting and serves to make network transistors. (c) Optical absorption spectra of laser ablation SWNTs encapsulated in an aqueous solution of sodium cholate taken before (black line) and after (red line) one cycle of ultracentrifugation in a density gradient. Inset of bottom figure is an illustration of the sedimentation process adapted from the accompanying article from ref 6. Copyright 2008 American Chemical Society.

rates between individual and bundled nanotubes to prepare a measurable quantity of individual SWNTs encapsulated in a surfactant layer. The work by O'Connell *et al.* has stimulated many optical studies on individualized SWNTs and transformed the way we now probe their optical properties.[8,19] A logical extension to the work by O'Connell *et al.* was to include a density gradient profile in the sedimentation path. This approach first resulted in achieving bulk enrichment by diameter of SWNTs wrapped in DNA.[4] Further improvement using bile salts and their mixtures with other surfactants provided even better results and clear signatures of enrichment according to the band gap and electronic properties.[5] These results are remarkable in that the method generated, for the first time, brightly colored solutions of enriched SWNTs, a contrast to the black solutions that characterize heterogeneous mixture of SWNTs.

In retrospect, preparative ultracentrifugation to process and to sort SWNTs on the basis of diameter appears straightforward because differences in the mass-to-volume ratio of nanotubes are expected with differences in diameter. This is certainly what moti-

> SWNTs are, however, typically found in bundles or larger aggregates because they are hydrophobic and their surfaces are smooth, which results in strong van der Waals bonding between them.

vated Arnold *et al.* to pursue investigation along this path, which eventually led to the discovery of true enrichment of SWNTs by electronic properties. Their method is preparative and goes beyond separation by diameter because it also provides significant quantities of highly pure metallic or semiconducting SWNTs. Enrichment by metallic character of SWNTs is achieved since the buoyant density of the surfactant complexes is somehow related to the electronic density of states of a SWNT. The latter is defined by the way π-electrons are confined around the SWNT hollow cylinder. Only the lattice arrangement of carbon atoms (or helicity, as described by the indices *n* and *m*) determines whether small SWNTs are metallic or semiconducting.[20] That is, two SWNTs with the *same* diameter can differ in their electronic properties (*i.e.*, metal or semiconductor). As pointed out by Arnold *et al.*, the density gradient ultracentrifugation fractionation exploits subtle differences in the buoyant densities.[6] A combination of surfactants presents properties that help refine complexes for SWNTs having a specific diameter and specific electronic properties.

The chemistry by which enrichment by electronic properties is possible is still unclear, and understanding the subtleties will require further investigation. The modeling of the hydrodynamic properties presented by Arnold *et al.* in this issue is an important step toward achieving that goal.[6] They fit the redistribution profiles measured on SWNTs in sodium cholate solutions and developed a model to determine the linear packing density and the anhydrous molar volume of the surfactant molecules on the nanotube surface. This method is shown to be effective in gaining *quantitative* insights into the dependence of surfactant structure on the buoyant density. The next step will likely be adapting this method to characterize new surfactant mixtures in different conditions. For this respect,

> [The Arnold *et al.*] method is preparative and goes beyond separation by diameter because it also provides significant quantities of highly pure metallic or semiconducting SWNTs.

there is yet another surfactant mixture that has shown good properties for sorting other sources of SWNTs.[21]

Enrichment or Separation: What is Needed? The electrical performance of individual SWNTs is not an issue for making electronic devices. On the contrary, studies have shown that the characteristics of individual SWNT transistors outperform state-of-the-art silicon transistors, the leading structure in electronics.[22] However, the presence of a mixture of physical and electronic properties found in unsorted SWNTs has been a challenging issue for their integration into electronic circuits. Now that preparative enrichment techniques are available, it is tempting to conclude that the challenges can be addressed, but the reality is more complicated.

The processing of SWNTs for high-performance transistors remains, in fact, an unsolved problem, even with the current capabilities of separation. That is, enriched semiconducting SWNT fractions still contain metallic species (although in small quantities).[5] The assembly of these fractions in single-nanotube transistor channels (contacted at both ends with electrodes) will certainly short-circuit transistors. Although solutions to the problem have been proposed,[23,24]
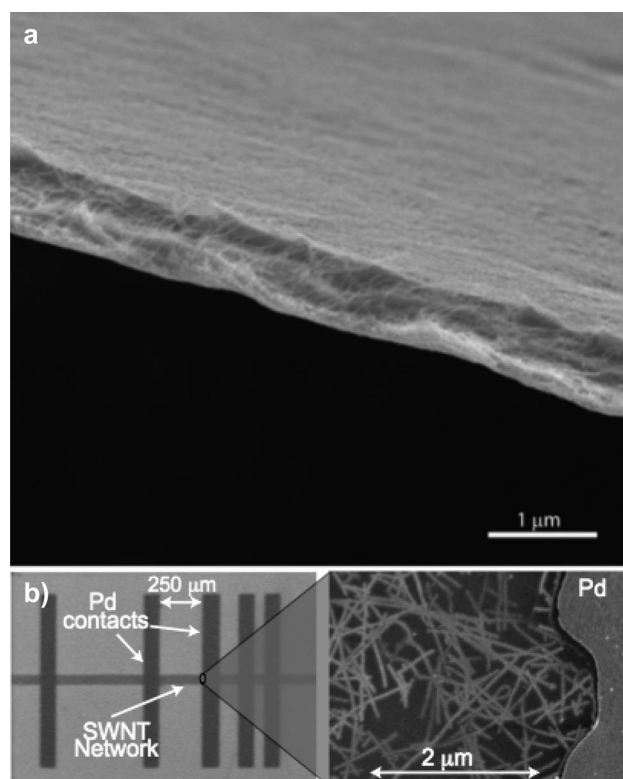
Figure 2. (a) Scanning electron microscope images of a freestanding carbon nanotube film fabricated by filtration method. The film is a highly conductive transparent layer. (b) A network SWNT field-effect transistor device structure. Image adapted from ref 30. Copyright 2008 American Chemical Society.

their use for high-performance logic applications remains unlikely for the moment because the current architecture imposes reliability issues that are well beyond current fabrication technology, even using the purification and enrichment methods described above. Moreover, placement/deposition techniques for making large and ordered arrays of SWNTs have yet to be perfected.[22]

The situation is quite different for SWNT networks. For this class of materials, the electronic and electrical properties are controlled by percolation. Based on simple percolation arguments, it is easy to predict that the enrichment of SWNTs on the basis of their physical and sedimentation properties will open possibilities for making better SWNT networks and significantly improve their bulk properties. Examples of SWNT network materials made in the author's laboratory are shown in Figure 2. Figure 2a presents an

example of a freestanding SWNT film having mainly metallic properties. It can potentially be applied in making transparent conductive thin film layers.[25−27] The other example (Figure 2b) capitalizes on the semiconducting properties of SWNTs deposited as thin film layers onto a silicon substrate[18] for making network transistors.[28,29] In both cases, a complete separation into pure SWNT species is not necessary in order to control the properties of the layer; however, better performance of this inhomogeneous media is expected through the enrichment of either metallic SWNTs in Figure 2a or semiconducting SWNTs in Figure 2b. Moreover, it is important to mention that the tube−tube junctions present high resistance compared to the intrinsic resistance of SWNTs. Improving the performance of SWNT films will, therefore, require the number of tube−tube junctions to be kept as low as possible along the percolation paths.[31] Encapsulation in surfactant solution could offer a logical means for making better films, but the procedure will have to minimize or avoid ultrasound treatments that cut SWNTs.

Conclusions and Challenges. Because of their useful electronic, optical, and physical properties, SWNTs present many advantages over other plastic-like materials for making flexible and lightweight electronics. On one hand, the varying properties arising from a mixture of SWNTs and the dramatic effects of quantum confinement add to the richness of the material's optical and electrical properties. On the other hand, it requires separation methods to be perfected and scaled

up. Until there is an experimental means to grow SWNTs with given (n,m) indices, purification and enrichment procedures will be necessary so that metallic or semiconducting SWNT samples with known band gaps can be prepared at will and in large quantities. The ability to sort SWNTs is now a reality, and it will continue to be an essential part for the future developments in SWNT research and applications.

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