Carbon Nanotubes

by R. Bruce Weisman and Shekhar Subramoney

The discovery more than two decades ago of the allotrope of carbon referred to as buckminsterfullerene (more commonly called fullerene or C_{60}) was a seminal event in the genesis of nanotechnology. This key discovery[1] showed how intense energy sources may be used to vaporize ordinary carbon and convert it into nanomaterials such as fullerenes and carbon nanotubes. Of the carbon nanotubes, the multiwalled variant was synthesized initially in 1991,[2] although it is now evident that the simultaneous discovery of single-walled nanotubes at NEC[3] and IBM[4] in 1993 was even more revolutionary from a materials science/physics/chemistry viewpoint.

This article focuses on properties of the single-walled form of carbon nanotubes, hereafter referred to as SWNTs. SWNTs are unique materials for several reasons: they are prototypical quasi one-dimensional quantum wires composed of a single element (carbon), with walls only one atom thick and tens of atoms in circumference. Every carbon atom lies on the surface of the nanotube and forms part of a strong covalently bonded structure. SWNTs are typically about 1 nm in diameter but have lengths from hundreds of nanometers to several centimeters, with long-range crystalline periodicity retained along the tube axis. Studies indicate that SWNTs possess remarkable mechanical properties, including an elastic modulus near 1000 GPa and tensile strength of several tens of gigapascals, that are comparable to those predicted for single sheets of graphite.

Perhaps the most exciting characteristics of carbon nanotubes are their unusual electronic properties. As described below, research on SWNTs clearly shows that these materials have the potential to be key players in the arena of molecular electronics, in which the active part of a device is composed of either a single or a few molecules. The electronic structures of nanotubes also lead to unusual and potentially useful optical characteristics. This article briefly discusses SWNT electronic and optical properties and some related potential applications.

Physical and Electronic Structure

Study of electronic characteristics of carbon nanotubes has been an active area of research since their discovery in the early 1990s. Initial theoretical research in this field employed band structure calculations based on planar graphene sheets rolled up to form one of a discrete set of seamless cylindrical structures.[5,6] The electronic character of a SWNT is essentially independent of length but strongly dependent on its transverse physical structure, which is denoted by a pair of integers (n, m) that uniquely specify tube diameter and the chiral angle at which the parent graphene sheet can be rolled to form that structure. Figure 1 shows a model of a (7, 5) nanotube. This species has a diameter of 0.829 nm and a chiral angle of 24.5°. SWNTs for which $n - m = 0$ (the armchair structures) are metallic; those with $n - m = 3p$ (where p is an integer) are semimetals; and those for which $n - m \neq 3p$ are semiconductors. Among the two-thirds of possible SWNT structures that are semiconductors, the bandgap shows an approximate inverse dependence on tube diameter. It is also significant that several theoretical studies have demonstrated that defect structures on the tubes lead to metal-semiconductor, semiconductor-semiconductor, and metal-metal junctions at the defect sites, which may themselves behave as nanoscale device elements, as demonstrated by Chico *et al.*[7] Topological defects and atomic impurities in the tubes alter the local electronic density of states near the Fermi level, leading to localized variations in the dominant conductivity associated with an individual tube. To date, all methods for growing SWNTs produce mixtures containing different structural forms and therefore diverse electronic properties.

Several research groups have explored the electrical properties of carbon nanotubes experimentally. The development of scanning tunneling microscopy (STM) and spectroscopy-based techniques has been particularly helpful in these efforts. The initial step of the experimental approach may involve dispersing dilute suspensions of nanotubes onto patterned electrical contacts with the intention of contacting single nanotubes to two adjacent electrodes for electrical transport measurements. Considering that electrons in π-states control the electrical transport of nanotubes, the low-bias resistance of the nanotube for ballistic transport would be h / 4e^2, which is about 6 kΩ. However, the two-point resistance of single nanotube samples draped over platinum electrodes (or gold electrodes in other cases), was initially measured to be closer to 1 MΩ at room temperature, as reported by Tans *et al.*[8] The key finding was that the contact resistance between the carbon nanotube and metal electrode, as well as other factors such as local re-hybridization of carbon bonds from sp^2 to sp^3-like when the nanotube is draped over the metal electrodes, may lead to substantial resistivity enhancement. Other experiments have also demonstrated that the conductivity of an individual SWNT depends significantly on adsorbed species such as oxygen.[9] This finding suggests the use of SWNTs as sensitive chemical sensors, an important applications area that we do not have space to discuss here.

Growth and Processing

Currently, SWNTs are synthesized by one of three different techniques: pulsed laser vaporization, arc discharge growth, or chemical vapor deposition (CVD) on supported or gas phase catalysts. Nanoscale particles of

transition metals catalyze the growth processes. Because pristine (chemically unaltered) carbon nanotubes are highly polarizable, smooth-sided structures, they tend to aggregate into parallel bundles that are held together by non-covalent interactions of approximately 0.5 eV per nanometer. These substantial van der Waals cohesive forces are sufficient to bundle the nanotubes in raw samples and also make it difficult to exfoliate individual tubes for further study, manipulation, or device construction. One of the greatest current needs in nanotube research and commercialization is the development of effective methods for obtaining samples of disaggregated SWNTs with uniform electronic character.

Ultrasonic agitation in surfactant solution followed by ultracentrifugation can often give stable suspensions that are rich in individual nanotubes.[10] Physical separation of the semiconducting and metallic species is much more challenging, however, particularly for larger batch sizes. Obtaining SWNT samples of specific (n, m) types is the most difficult goal. There are two complementary stages to this task. The first involves developing growth processes that are as selective as possible, so that the as-grown material contains only a limited distribution of SWNT species.[11] The second is to use chemical or physical separation methods to sort the selectively grown material into fractions that are highly enriched in specific (n, m) species.[12] The most promising results in both stages of this effort have been reported for SWNTs of small diameter (below ca. 0.8 nm) because in this regime the set of possible nanotube structures is relatively sparse and distinguishable. However, at present the (n, m) sorting of larger diameter SWNTs appears to be far more problematic. All separation attempts must rely on characterization methods that can reliably reveal changes in the composition of mixed nanotube samples.

Research into the chemical functionalization of SWNTs is a large and active area[13] that falls outside the scope of this article. However, note that the main goals of such research are often to provide solubility of the nanotubes, or to link them to chemical moieties that have specific functions in materials or biological applications. Sidewall functionalization reactions may also disaggregate bundled nanotubes. However, covalent bonding to sidewall carbon atoms perturbs the nanotube π-electron system, often to the extent that its characteristic electronic and optical properties are destroyed. Non-covalent interactions form the basis of SWNT solubilization by surfactants, polymers, or nuclei acids. These agents generally preserve the essential aspects of nanotube electronic and optical character.

Electronic Devices

Of the various existing and potential applications involving carbon nanotubes, none appears to evoke as much interest or excitement as the use of single nanotubes, particularly single semiconducting SWNTs, to make room temperature field-effect transistors (FETs).[14] This interest is driven by the recognition that conventional lithographic techniques for semiconductor manufacturing are approaching their theoretical, practical, and possibly economic limits. The demand/value for continued shrinkage of scale will probably continue to grow even after conventional approaches have reached these limits. From a technological standpoint, this underscores the need for n-type SWNTs, where transport through the semiconducting SWNT is dominated by electrons rather than by holes and allows the fabrication of nanotube-based complementary logic devices and circuits. This can be achieved by converting the predominantly p-type SWNT to n-type SWNT material either by alkali-metal doping or by annealing the device in vacuum or an inert atmosphere, which results in oxygen removal that alters the relative energies of the valence bands at the electrode-nanotube junction.[15] Other advances toward this technology include lowering the contact resistance of the nanotube-electrode junction by end-bonding the nanotube to metals such as titanium,[16] and altering the configuration of the gate electrodes to improve the overall electrical characteristics.[17] Recently, researchers have successfully demonstrated the fabrication and operation of a sub-20 nm FET based on SWNTs using electron-beam lithography with select e-beam resists.[18] Judging by many parameters, including high on/off current ratios, SWNT-based FETs outperform larger state-of-the-art silicon-based devices. The development of single nanotube electronic devices is advancing rapidly.

Optical Properties and Applications

The optical characteristics of single-walled carbon nanotubes reflect their unusual electronic structures.[19] Figure 2 schematically shows the electronic density of states expected for the π-electrons in a semiconducting SWNT. The spikes in state density, called van Hove singularities, arise from the quasi one-dimensional character of electronic motions in systems with very high aspect ratios. Each van Hove singularity is labeled with the index of the subband to which it belongs. Semiconducting SWNTs have direct bandgaps, and optical selection rules allow light polarized parallel to the tube axis to excite intense transitions between corresponding subbands in the valence and conduction bands. Therefore each semiconducting (n, m) species (representing a specific diameter and chiral angle) shows a set of well-defined absorptions. Typically, one of these absorptions lies in the near-infrared, one in the visible, and another in the near-UV. As is the case for molecules,
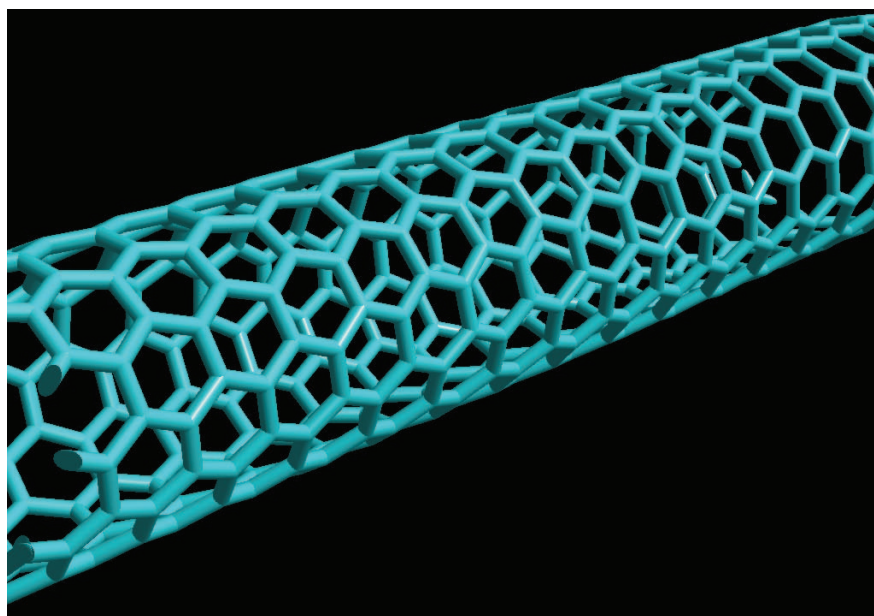
Fig. 1. *Model of a (7, 5) single-walled carbon nanotube.*

Weisman and Subramoney

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rapid internal relaxation suppresses emission except from the lowest energy (near-infrared) transition, which is labeled E_{11}. The metallic and semimetallic SWNT species (collectively termed metallic) also show intense absorption features associated with transitions between matching van Hove singularities in conduction and valence bands. However, the lowest energy optical transition in metallic nanotubes lies at shorter wavelength than the first two transitions of semiconducting tubes having similar diameter.

Many areas of basic and applied nanotube research have an essential need to analyze mixed SWNT samples to determine the structural species that are present. The first optical method found capable of giving this kind of detailed structural information was Raman spectroscopy.[20] When the wavelength of the incident laser is close to a strong optical absorption feature of a nanotube species, relatively intense resonance Raman scattering is generated. This Raman spectrum shows the G-band vibrational mode, which arises from tangential and longitudinal C-C stretching motions, and the radial breathing mode, which represents totally symmetric expansion and contraction of the nanotube cylinder. Although the G-band frequency is not sensitive to nanotube structure, its shape differs significantly for metallic and semiconducting species. The radial breathing mode frequency varies inversely with nanotube diameter and thus provides valuable structural information for SWNTs of either metallic or semiconducting type. A limitation of Raman analysis, however, is that it reveals the spectra only of those species having electronic transitions close to the incident laser wavelength. To perform a full analysis, one may therefore need to collect Raman spectra using numerous lasers.

Another spectroscopic characterization method has emerged from the more recent discovery of near-infrared (near-IR) nanotube photoluminescence (E_{11} fluorescence) from samples containing disaggregated semiconducting SWNTs suspended in water by common surfactants.[10] Subsequent spectrofluorometric research revealed distinct spectral absorption and emission transitions of many different structural species and then assigned those spectral features to specific nanotube structures.[21] Figure 3 shows a surface plot of measured emission intensity as a function of excitation wavelength and emission wavelength for a mixed sample of SWNTs in aqueous suspension. Each peak corresponds to a different semiconducting (n, m) species. (The metallic nanotubes do not photoluminesce because they have no bandgaps.) These results, which give precise E_{11} and E_{22} optical transition energies for a wide range of identified SWNTs, have challenged theoretical models of nanotube electronic structure and have led to more refined treatments and improved understanding. Clearly, nanotube optical absorptions create excitons with substantial binding energies, rather than independently mobile electrons and holes. Nevertheless, there is a one-to-one correlation between each of the simple band-picture transitions shown in Fig. 2 and an intense excitonic transition, so the original E_{ii} spectroscopic indexing scheme remains valid. It is well known in analytical chemistry that fluorescence spectroscopy is among
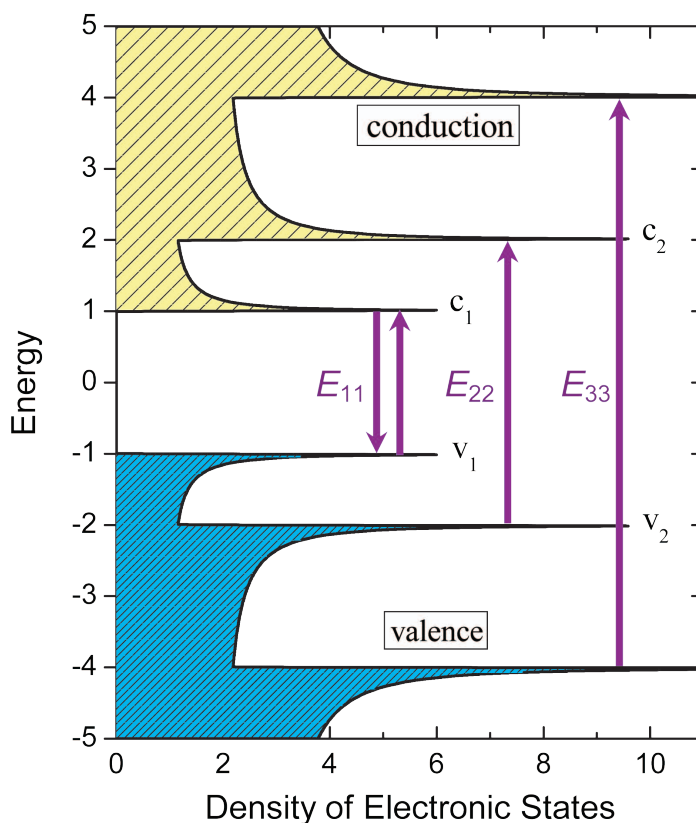

FIG. 2. *Schematic density of electronic states pattern in a semiconducting single-walled carbon nanotube. The sharp maxima are van Hove singularities. Arrows show the dominant optical absorption and emission transitions (in a one-electron model).*
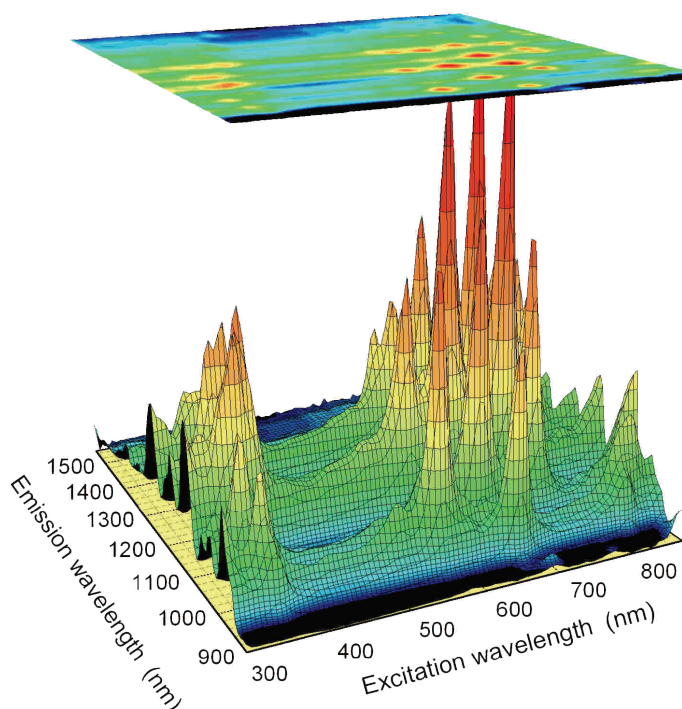

FIG. 3. *Surface plot showing emission intensity measured from an aqueous suspension of single-walled carbon nanotubes as a function of excitation and emission wavelengths. Each peak corresponds to a specific semiconducting (n, m) species.*
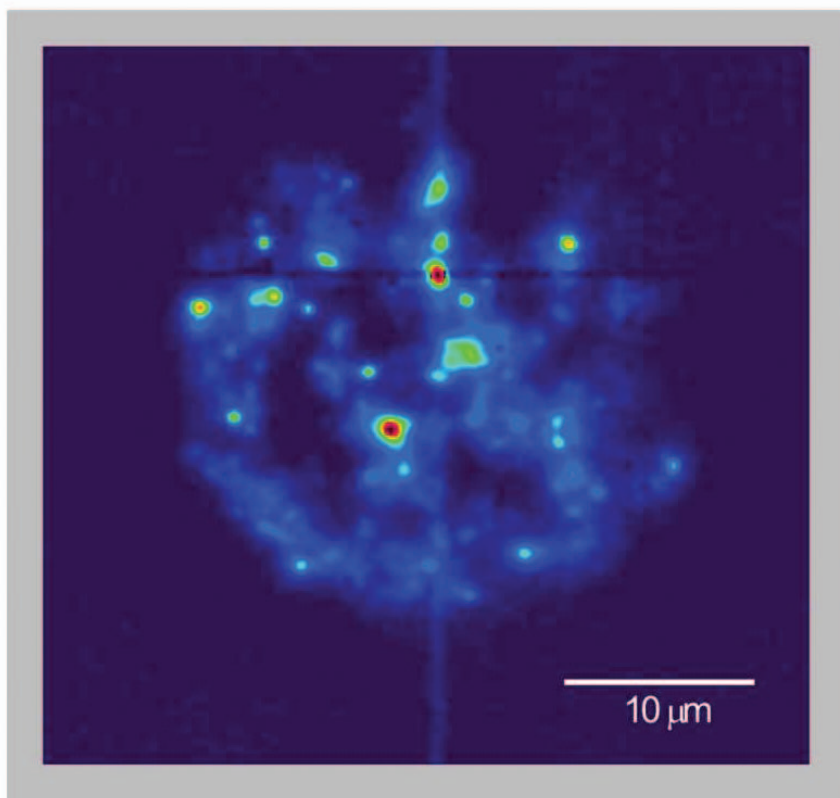
Fɪɢ. 4. *False-colored near-infrared fluorescence micrograph of a single macrophage cell that had been exposed to SWNTs in its growth medium. Nearly all of the emission is from ingested nanotubes, which appear to be concentrated in intracellular structures called phagosomes.*

the most sensitive and selective tools for detecting emissive molecules. The spectral assignments therefore also provide an important foundation for practical methods to analyze the compositions of SWNT samples in detail, to study structure-dependent physical and chemical processes, and to observe single nanotubes in various environments using optical microscopy.[22]

In contrast to Raman analyses, which require intense laser sources, spectrofluorimetric measurements can be performed on bulk nanotube samples using the weaker but widely tunable excitation light generated from an incoherent source and monochromator. This allows simple excitation of the full range of (*n, m*) structures in a sample, although only the semiconducting species are detectable by monitoring near-IR (E_{11}) fluorescence. However, it is relatively tedious to measure fluorescence intensity as a function of both excitation and emission wavelengths and acquire data such as those plotted in Fig. 3. One may extract nearly equivalent analytical information from only two or three spectral slices obtained by exciting samples at appropriate fixed wavelengths

(using diode lasers) and detecting their emission spectra with a spectrograph and multichannel detector array. This efficient experimental approach reduces data acquisition time to a few seconds. It can be combined with automated data interpretation software to generate a detailed (*n, m*)-level sample analysis in less than 1 min. This type of streamlined spectroscopic analysis likely will become a practical and widely used sample characterization tool for SWNT producers, users, and researchers.

The average fluorescence quantum yield of SWNTs is estimated to be only approximately 10^{-3}. Although this value may appear too low to allow fluorescence experiments on individual nanotubes, such studies are feasible. Two factors aid these efforts. First, unlike conventional organic fluorophores, carbon nanotubes are robust and resistant to photobleaching by intense irradiation. In many environments they do not show the blinking behavior that is observed for semiconductor quantum dots. Nanotube emission therefore may be collected steadily for extended periods under strong optical excitation. Second, the fluorescence of SWNTs occurs in the near-IR at wavelengths that are not only quite shifted from the

E_{22} excitation wavelengths, but at which there is normally little background emission from other materials that may surround the nanotubes. This allows the SWNT fluorescence to be detected with high selectivity and optical contrast.

When two-dimensional InGaAs arrays are used as detectors in SWNT near-IR fluorescence microscopy, emission from many thousands of image pixels may be captured simultaneously. This makes it possible to record image sequences with millisecond time resolution to track the translational, rotational, and bending motions of single SWNTs in fluid media.[23] Because their spectroscopic transitions are strongly polarized, nanotube orientations are also easily determined with optical methods. The spatial resolution of far field optical microscopy in this spectral range is limited to hardly less than 1 µm, which is much coarser than attained with scanning probe or electron microscopies. However, the versatility provided by time-resolved selective imaging in complex media makes this method a valuable probe of some important SWNT properties and processes.

A most promising emerging application area for SWNTs is in biomedical sensors, diagnostics, and therapeutics.[24] These applications require careful prior studies of the effects of SWNTs on cells, tissues, and organisms and measurements of nanotube retention, clearance, and biodistributions with different forms of administration. Clearly, these studies must use robust analytical methods that can detect, quantify, and image nanotubes in complex biological specimens. It was demonstrated several years ago that resonance Raman spectroscopy of individual nanotubes in controlled environments is feasible and can provide valuable structural insight through the radial breathing mode frequency.[25] For nanotubes that are present in low concentrations in complex surroundings such as biological media, however, Raman observation becomes much more challenging because of significant fluorescence, nonresonant Raman, and resonant Raman background signals arising from the surroundings. Fortunately, near-IR fluorescence often remains capable of selectively detecting nanotubes even under these challenging circumstances. Figure 4 illustrates the high-contrast imaging of SWNTs inside a macrophage cell through near-IR fluorescence microscopy.[26] These cells had actively ingested nanotubes from their growth medium and concentrated them into vesicles called

Weisman and Subramoney
(continued from previous page)

phagosomes. Ongoing research shows that even single nanotubes can be imaged in biological tissues using this technique. Therefore, although near-IR fluorescence is unsuitable for studying metallic, aggregated, or most chemically derivatized SWNTs, it appears to be the method of choice for tracking pristine semiconducting nanotubes in biological systems. This may become one of the most important applications exploiting the remarkable electronic and optical properties of single-walled carbon nanotubes. ■

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