Simplifying Carbon Nanotube Identification

Carbon nanotubes belong to the fullerene family, a molecular form of carbon quite distinct from diamond and graphite. These cylindrical structures of carbon atoms take two forms: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs), each of which has its advantages and disadvantages for different applications. SWNTs are essentially single layers of pure-carbon atoms rolled into a seamless tube capped at each end by half-spherical fullerene structures. They measure about 1 nm or 10^{-9} m in diameter, and differ from MWNTs in that all of their atoms form a single covalently bound network. This gives SWNTs more distinctive electronic and optical properties.

Sumio Iijima of NEC Laboratories in Japan discovered carbon nanotubes in 1991, and the pace of research into their intriguing properties has accelerated ever since. Typically, carbon nanotube deposits contain both SWNTs and MWNTs. However, a team led by Richard E. Smalley at Rice University has developed a high-pressure process (HiPco) that produces only SWNTs in multigram batches.

Applications

Researchers anticipate nanotube applications in several important areas. One use is as field emitters in flat-panel display technologies—an application that will probably become available as products sooner than any other. Samsung demonstrated a working nanotube display prototype in 1999, and the company may introduce a product during 2004. In Samsung's display, the small, rod-shaped nanotubes provide sharp conductive points that allow a field-emission display to work more efficiently than today's TV screens and computer monitors. SWNT displays could eventually displace liquid-crystal and plasma displays in large flat panels because the carbon

Armchair (α = 30°)
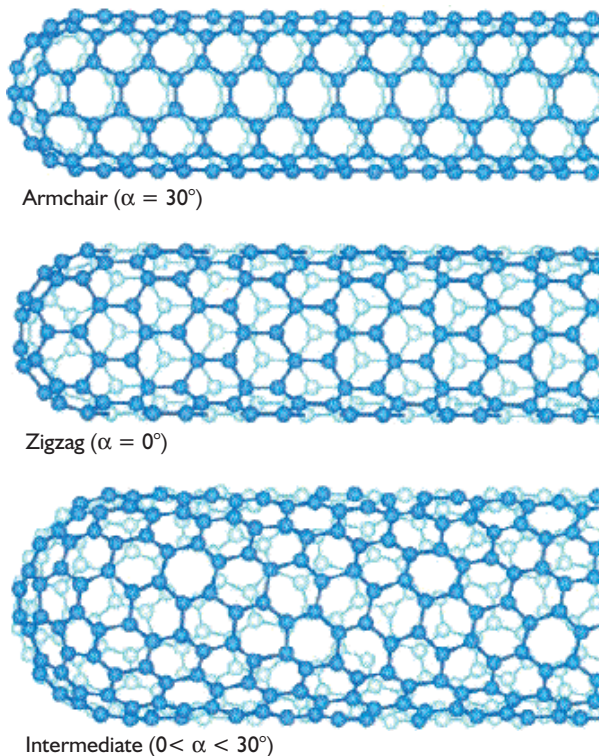
Zigzag (α = 0°)

Intermediate (0< α < 30°)

Figure 1. Single-walled carbon nanotubes exist in a variety of structures corresponding to the many ways a sheet of graphite can be wrapped into a seamless tube. Each structure has a specific diameter and chirality, or wrapping angle (α). The "armchair" structures, with α = 30°, have metallic character. The "zigzag" tubes, for which α = 0°, can be either semimetallic or semiconducting, depending on the specific diameter. Nanotubes with chiral angles intermediate between 0 and 30° include both semimetals and semiconductors. ("Armchair" and "zigzag" refer to the pattern of carbon–carbon bonds along a tube's circumference.)

nanotube panels should be less complex and less expensive to manufacture.

Because carbon nanotubes are very strong, there is also interest in them for their mechanical properties—about 100 times stronger than steel at one-sixth the weight. Thus, SWNTs may provide reinforcing elements for composite materials that would have exceptional mechanical and, possibly, superior thermal characteristics. Another potential application lies in ultraminiaturized electronics. Companies such as IBM have active research programs investigating how they could use carbon nanotubes for future gener-

ations of nonsilicon microchip circuitry, which could be 0.01% the size of today's most advanced versions, or even smaller.

Researchers have just started to explore possible biomedical applications. Using proteins, starches, and DNA as outer wrappings, they have produced several varieties of soluble nanotubes. It is not yet certain where this work might lead, but the possibilities include some applications in medical diagnostics.

Identification

SWNTs come in many structural forms, and their electronic properties vary with differences in their structures. Each batch that is produced by Smalley's HiPco process contains about 50 different species of nanotubes, each with a characteristic diameter and chiral angle—the angle at which it is rolled.

Figure 1 illustrates the structures of three SWNTs that differ in chiral angle and diameter. Armchair SWNTs are always metallic in electronic character. The zigzag and intermediate forms, however, will be either semimetallic or semiconducting, depending on their structure. One factor delaying practical applications of SWNTs has been the inability of researchers to easily measure and interpret the molecules' detailed optical absorption and emission spectra. As a result, it has been difficult to tell which structural types are present in a given sample, and in what quantities. Common identification techniques include Raman spectroscopy and microscopic methods.

Using Raman spectroscopy, researchers can observe metallic and semiconductor SWNTs. But obtaining a full analysis to identify all of the different structures in the sample requires a large set of spectra using different laser wavelengths. Only a small number of laboratories are equipped for such comprehensive measurements. Raman spectroscopy also has limitations, because inves-

tigators have not yet determined the calibration factors that relate signal strengths to relative concentrations of separate SWNT species. That means researchers recording the same signal strength for two different nanotube structures cannot tell whether the two species are actually present in the same amounts.

Microscopic methods require observing many different tubes—one at a time—and building a statistical histogram, which makes the approach time-consuming. Scanning tunneling microscopy can produce images similar to or at least suggestive of those in Figure 1, and with skill and considerable care, the actual structure (chiral angle and diameter) of tubes in a sample can be determined. However, this tedious process requires special expertise to perform. It is also unsuitable for in situ analyses of bulk samples. Transmission microscopy can provide an idea of tube diameters but not chiralities. In general, obtaining accurate chirality data is particularly difficult, especially for bulk experiments, yet it is a key factor in determining the properties of the SWNTs in a sample.

SWNTs tend to aggregate in bundles that are bound by van der Waals attraction. These tube–tube perturbations cause optical spectra of bundles to be excessively broadened and blurred, preventing detailed spectral analysis. Thus, researchers have a difficult time characterizing such samples, which, in turn, leads to problems in comparing results between different laboratories. Accurate sample characterization remains a serious obstacle to SWNT research.

Spectrofluorimetry

Improved sample-processing methods developed at Rice during the last few years now allow researchers to separate some nanotubes from their bundles using ultrasonic agitation, and to obtain distinct spectral features from bulk samples. Using spectrofluorimetry—the absorption of one wavelength of light and the emission of a different wavelength—to study individual semiconductor SWNTs in aqueous micelle-like suspensions, researchers have measured many distinct nanotube structures. They also have mapped structural indices to the various spectral patterns. This correlation between the structure of a nanotube and the wavelengths at which it absorbs

and emits light is valuable for basic science and for future nanotube applications. These findings have provided a tool for the detailed analysis of bulk nanotube samples, and they are the first optical observations clear enough to associate spectral features with nanotube structures. To date, distinct optical absorptions and emissions have been identified for 33 different semiconducting SWNT structures. Each of these species corresponds to a specific nanotube diameter and chiral angle.

This experimental approach has allowed a much clearer view of the absorption and emission characteristics of SWNTs. Each one of the peaks shown in the three-dimensional color graph in Figure 2a arises from a different nanotube structure. Instead of blurring together, the features form a distinct pattern. Once the resolved data were observed, it was necessary to assign the spectrum, that is, identify which nanotube structure gives each spectral feature. A detailed description of this process appeared in *Science* in 2002 (see Further reading).

The three-dimensional plot in Figure 2a reveals the big picture—how the mountains and peaks are separated from each other—but it is hard to determine coordinates from this plot. A detailed analysis requires another view. The contour plot of the same data, shown in Figure 2b, lets one find the precise excitation and emission wavelengths of any peak from the x and y coordinates of the spot's center. Figure 2b shows a plot of the intensity of light coming out of a nanotube sample as a function of two variables. The light intensity is color-coded, with the reds indicating the highest intensity. At each of these spots, the sample was excited at a wavelength given by the coordinate on the vertical scale; the coordinate on the horizontal scale gives the wave-
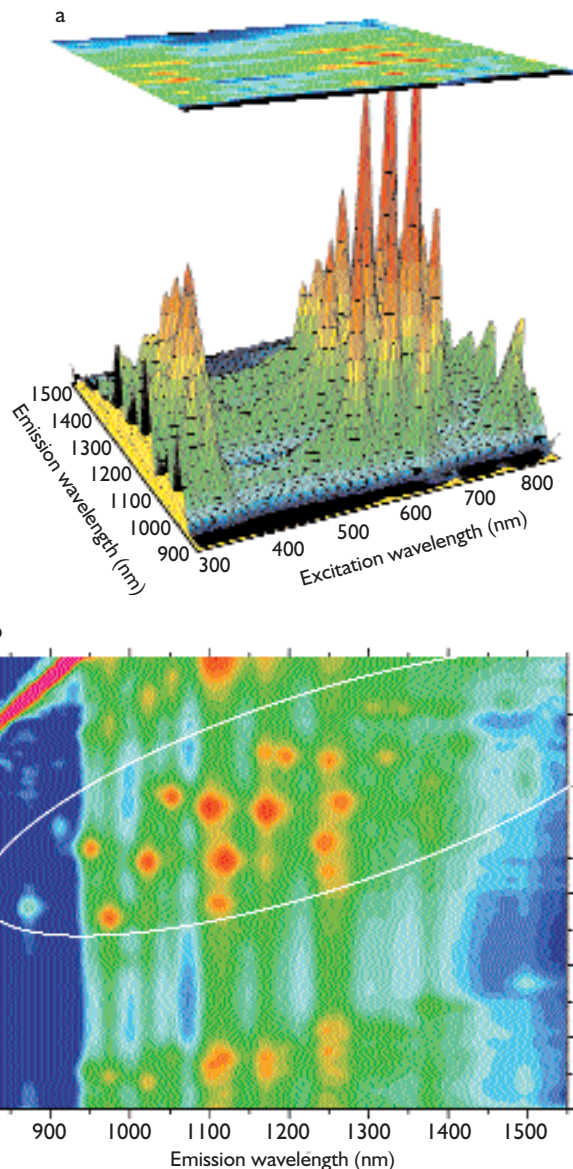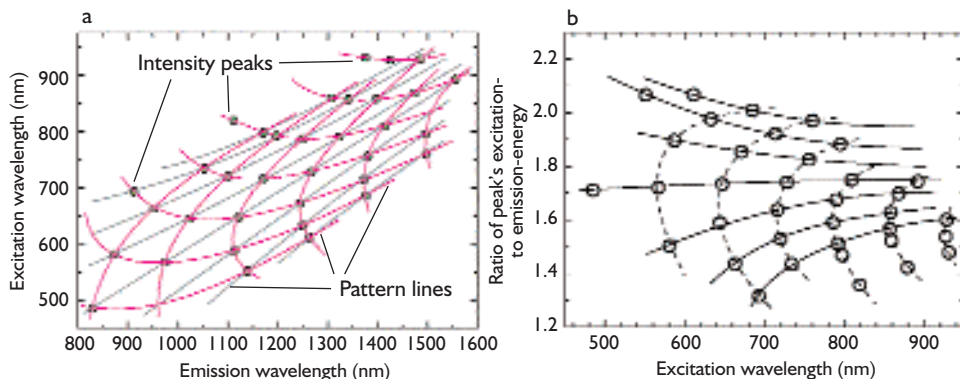

Figure 2. When a sample of single-walled nanotubes is examined by spectro-fluorimetry, emission intensity can be plotted as a function of excitation and emission wavelengths to give a surface plot, where each peak corresponds to a different semiconducting nanotube structure (a). A color-coded contour plot of the same data shows the precise wavelengths for each peak (b).

Figure 3. The data from the oval area of Fig. 2b may be further analyzed and interpreted by drawing pattern curves through the peaks (a) and by plotting the ratio of excitation- to emission-energy for each peak against the peak's excitation energy (b).

length of the resulting emitted light.

We generated the graphs in Figures 2a and 2b by importing 52,000 measurements from a J-Y Spex spectrofluorimeter into a desktop computer for graphing and data analysis using Origin, a versatile scientific graphing and analysis software package. This software served as the central tool to display and analyze large files of data and search for underlying patterns using dozens of work sheets in project files, some of which totaled several megabytes.

Figures 3a and b display additional analyses and interpretation of the data. The circles in Figure 3a plot experimental spectral peak positions of excitation versus emission wavelengths from the oval area in Figure 2b. Solid curves through the data points illustrate the patterns. Figure 3b shows the ratio of optical excitation to emission energy for each peak versus the peak's excitation energy. The patterns helped to assign the spectral features to specific nanotube structures. Figure 4 shows how the measured intensities for the sample studied are related to nanotube diameter and chiral angle.

This plot reveals the nanotube structures most abundant in the mixed sample. The colors code for height, which represents fluorescence intensity.

Future directions

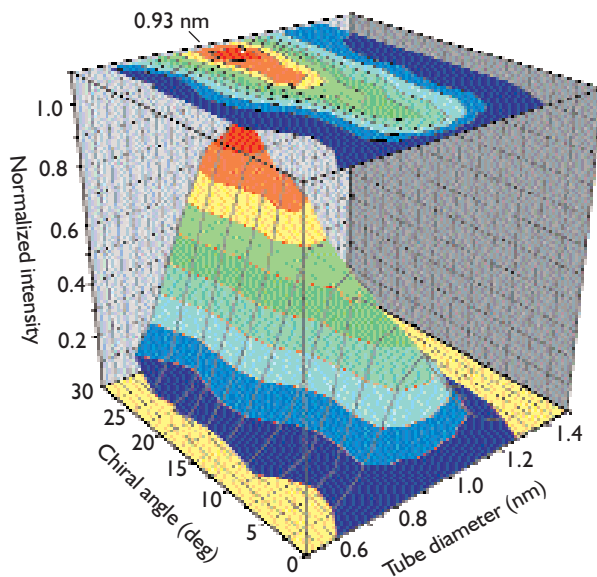Work in my laboratory currently focuses on three goals, one in basic research and

Figure 4. The nanotube structures most abundant in the mixed sample are revealed by plotting fluorescence intensity against chiral angle and tube diameter.

two in applied areas. The basic challenge is to refine and extend nanotube spectroscopy to learn more about the transitions and the electronic structure of nanotubes. In the area of applications, one goal is to convert this type of spectroscopy into a routine analytical tool for use in nanotechnology. Doing so would give researchers who make, separate, purify, and/or use nanotubes in their own experiments a convenient and reliable way to learn the composition of their samples.

Laboratories that produce SWNTs for research have already begun to use optical spectroscopy to get a clearer picture of what a specific sample contains and to obtain valuable feedback to fine-tune the production process. Spectroscopy techniques will also provide an important tool for investigators who want to separate mixtures of nanotubes into their component species (see box "Sorting nanotubes" below). Because nanotubes have electronic and optical properties that depend on their structure, this is a goal of great interest, especially in nanoelectronics laboratories.

Another application might be in biomedicine, where the near-infrared emission characteristics of these tubes may provide advantages over other materials now used in noninvasive diagnostic-imaging applications. Eventually, it may become possible to induce nanotubes to concentrate in a patient's diseased or cancerous cells and kill them by noninva-

SORTING NANOTUBES Sorting single-walled carbon nanotubes by their different structures—and thus, their physical properties—remains an enormous challenge to the commercial application of the molecules. However, a collaboration by scientists at DuPont Co., the University of Illinois at Urbana-Champaign, and the Massachusetts Institute of Technology has tapped the self-assembly powers of DNA to sort SWNTs by their diameters and electronic properties.

Ming Zheng of DuPont and his colleagues found that a specific single-stranded DNA, called DNA-d $(GT)_n$—where n (the integer number of nucleotide (GT) units in the DNA polymers) equals 10 to 15—formed a helical structure around individual SWNTs (*Science* **2003**, *302* (5650), 1545–1548). This self-assembly resulted in hybrid molecules whose electrostatic properties depended on the diameter and electronic properties of the nanotube. Using anion-exchange chromatography, the team sorted the SWNTs by their size and electronic properties. Early fractions separated by the process contained smaller-diameter and metallic nanotubes; later fractions yielded larger-diameter and semiconducting SWNTs. In this research, structure-resolved optical absorption spectroscopy provided a primary tool for monitoring and assessing the separation of different nanotube structures.

sively irradiating the nanotubes with laser light tuned to specific absorption wavelengths. However, determining the range of nanotube spectroscopy applications will require many more studies.

Conclusion

Optical spectroscopy has been used to analyze the composition of bulk SWNT samples and provide semiquantitative distributions of tube diameter and chiral angle. With the deciphering of SWNT spectra, a powerful new analytical tool has become available to nanotube investigators. Spectroscopy can take the characterization of SWNTs out of the specialty realm and make it routine. This should significantly assist efforts to capitalize on the remarkable properties of carbon nanotubes and help find new applications.

Further reading

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B I O G R A P H Y

R. Bruce Weisman is a professor of chemistry and a member of the Center for Nanoscale Science and Technology and the Center for Biological and Environmental Nanotechnology at Rice University in Houston, Texas (weisman@rice.edu).