Type-specific Single-wall Carbon Nanotube Growth and Separation

Edward Sosa, *Engineering Research Consultants, Inc.*
Pasha Nikolaev, *Engineering Research Consultants, Inc.*
Peter Boul, *Engineering Research Consultants, Inc.*
William Holmes, *Engineering Research Consultants, Inc.*
Sivaram Arepalli, *Engineering Research Consultants, Inc.*
Leonard Yowell, *Johnson Space Center*

Single-wall carbon nanotubes (SWCNTs) have excellent electronic properties that, as in any nanomaterial, are strongly dependent on their molecular structure and size. Current SWCNT production methods yield polydispersed materials with various diameters and chiralities leading to distribution of types. This distribution of types, in turn, has limited the successful use of SWCNTs in applications in both the commercial sector and the aerospace industry. For many applications, the availability of exclusively metallic or semiconductive SWCNTs would be greatly beneficial. Such applications that would benefit from type-specific SWCNTs include: transistors, photovoltaic and optoelectronic devices, transparent conductive films, chemical and radiation sensors, and mechanically enhanced conductive nanocomposites. NASA scientists are particularly interested in using type-specific SWCNTs to provide electromagnetic interference shielding by transparent conductive films, conductive coatings for electrostatic discharge, radiation dosimeters, and quantum conducting wires (replacing copper). We focused on achieving metallic SWCNTs through both type-specific growth and type-selective separation.

One approach to acquire predominately metallic SWCNTs was to optimize the production parameters in the pulsed laser vaporization (PLV) technique to direct nanotube growth toward the metallic configuration. While this method may prove to be more difficult than the use of metallic tube separations, it is the more desirable method since higher yields and lower costs are to be expected. Even if the production of a single nanotube type is unattainable, the production of material with a narrow-type distribution would be favorable for subsequent separation efforts.

Cobalt/nickel and rhodium/palladium catalysts together with variations in the production temperature were used for SWNC synthesis. We monitored the nanotube-type populations through photoluminescence, ultraviolet-visible-near infrared (UV-Vis-NIR) absorption, and Raman spectroscopy. For both catalysts, lower production temperatures resulted in smaller nanotube diameters and exceptionally narrow type distributions (figure 1), with marked preference toward large chiral angles. The larger nanotube diameters tended to be associated with larger chiral angles. Although no drastic enrichment in metallic SWCNTs was observed, the results demonstrate that SWCNT growth can be directed toward a narrow distribution of particular nanotube types. Such material is highly favorable for separation attempts.

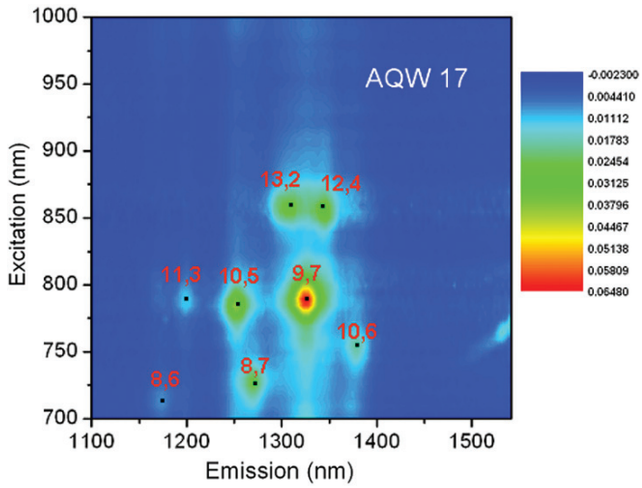

Fig. 1. *Photoluminescent spectral map of SWCNT sample produced at reduced temperature. Only eight semiconducting tubes are detectable, indicating exceptionally narrow type distribution. Regular SWCNT samples typically have 30 or more semiconducting nanotubes.*

The second approach to obtain metallic enriched SWCNTs is through separation techniques. Various separation methods, including electrophoresis, centrifugal density gradients, polymer and DNA [deoxyribonucleic acid] wrapping, and selective chemical functionalization, have been attempted. While these techniques have produced promising results, they still lack the ability to be scaled up toward large quantities. It is proposed that selective chemical functionalization is the most likely method to produce isolated nanotubes in greater than-microgram quantities.

Nanotube separations were performed on the nanotube samples with a narrow-type population produced at lowered temperature. Aryl diazonium salts are known to react preferentially with metallic nanotubes. Dodecyloxybenzenediazonium tetrafluoroborate, which is a special diazonium salt, was synthesized specifically for this task as it renders metallic SWCNTs soluble in tetrahydrofuran after reaction. Unreacted semiconducting tubes remained insoluble, and were separated from the

soluble metallic tubes by filtration. The metallic tubes were subsequently precipitated out by the addition of sodium chloride and methanol. Both materials were then heated in a furnace to remove the dodecyl functional groups and characterized by Raman and UV-Vis-NIR absorption spectroscopy. The suspended material showed increases in both the Raman and the absorption spectral features (figures 2(a) and 2(b)) associated with metallic nanotubes, indicating that the metallic types had been enriched. It is expected that further refinement of this technique will lead to more dramatic separations of types and diameters.

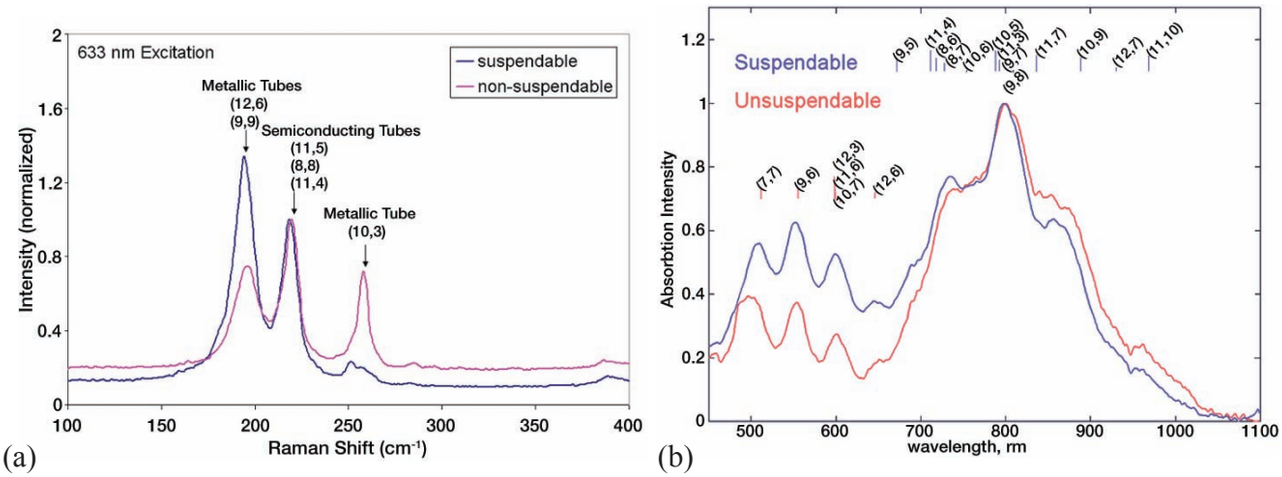

Fig. 2. *Raman (a) and absorption spectra (b) of SWCNT samples acquired after separation. Soluble (suspendable) sample shows increase in spectral features associated with metallic nanotubes, indicating enrichment in metallic types.*

Click here for next report