Spectroscopy of Individual Single-Walled Carbon Nanotubes

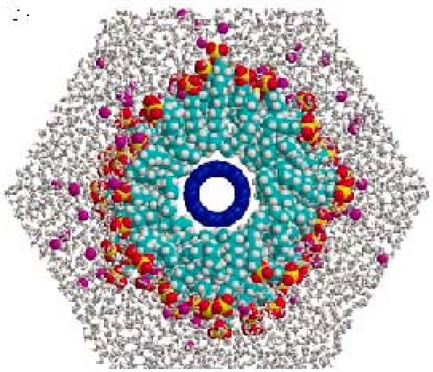
Richard E. Smalley, CNL, Rice University

DMR-0073046, "The Molecular Science of Fullerene Nanotubes", R. E. Smalley, PI

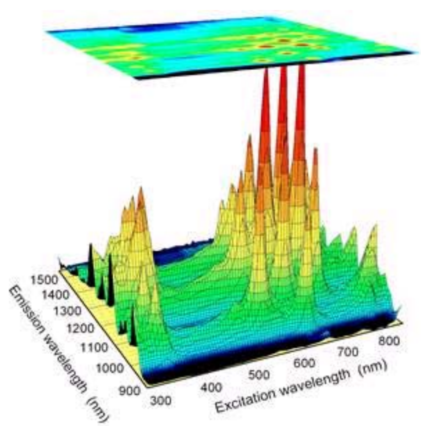
Societal Impact: Single-walled carbon nanotubes are elongated members of the fullerene family that are currently the focus of intense multidisciplinary study because of their unique physical and chemical properties and their prospects for practical applications. A major obstacle to such efforts has been the diversity of tube diameters, chiral angles, and aggregation states. Aggregation is particularly problematic because the highly polarizable, smooth-sided fullerene tubes readily form parallel bundles or ropes; this bundling perturbs the electronic structure of the tubes, and it confounds all attempts to separate the tubes by size or type or to use them as individual macromolecular species.

We developed a surfactant separation method based on vigorous sonication followed by centrifugation that primarily yields individual fullerene nanotubes in aqueous micellar suspensions. Freed from the perturbation of surrounding tubes and surfaces, the tubes in these suspensions show much better resolved optical absorption spectra. Most importantly, the one-dimensional direct band gap semiconducting tubes in these samples are now found to fluoresce brightly in the 800- to 1600-nm wavelength range of the near infrared, a region important in fiber optic xommunications and bioimaging.

Educational Activty: Graduate and undergraduate students contributed to this research, including Michael J. O'Connell, Sergei M. Bachilo, Chad B. Huffman, Valerie C. Moore, Michael S. Strano, Erik H. Haroz, Kristy L. Rialon, Peter J. Boul. This work was published in Science (**297**) 593 and Science (**298**) 2361.



A Cross-sectional model of an individual fullerene nanotube in a cylindrical SDS micelle.



Fluorescence-excitation profile of a mixture of nanotubes, including tubes with metallic and semiconducting properties.

Cutting Single-Wall Carbon Nanotubes through Fluorination

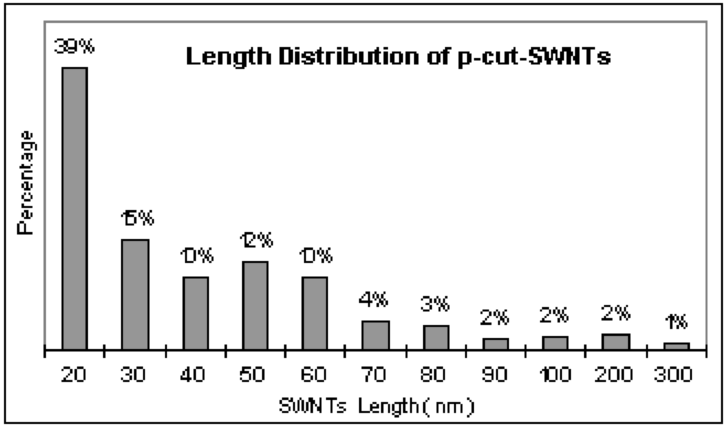
Richard E. Smalley, CNL, Rice University

DMR-0073046, “The Molecular Science of Fullerene Nanotubes”, R. E. Smalley, PI

Societal Impact: Single-wall carbon nanotubes (SWNTs) have become one of the research focuses in current nanoscience and nanotechnology. Their particular nanoscale structure and one-dimensional (1-D) geometry make them not only a perfect model for studying nanoscale phenomena and quantum effects but also promising nanomaterials with many potential applications. Although there have been many methods developed to synthesize and purify single-wall carbon nanotubes on a large scale, the chemical manipulation of single-wall carbon nanotubes is still a big challenge.

We have developed a process that cuts the single-wall carbon nanotubes to an average length <50 nm. The fluorination of purified HiPco single-wall carbon nanotubes to a stoichiometry CF*x* (*x* E 0.2) followed by pyrolysis of the partially fluorinated nanotubes up to 1000 °C was found to have “cut” the nanotubes to a range of short lengths. These chemically “cut” nanotubes have been characterized by Raman, ATR-IR, EDAX, and AFM measurements. The short lengths and specific reactivities should lead to novel applications for these nanotubes.

Educational Activty: Graduate students Z. Gu and H. Peng performed the research. This work was published in Nano Letters, Vol. 2, No. 9, pp 1009 – 1013.



The new fluorine-based process chemically”cuts” carbon nanotubes into distribution of nanometer scale segments

Scanning probe techniques show that carbon nanotubes flourinate in a banded fashion.

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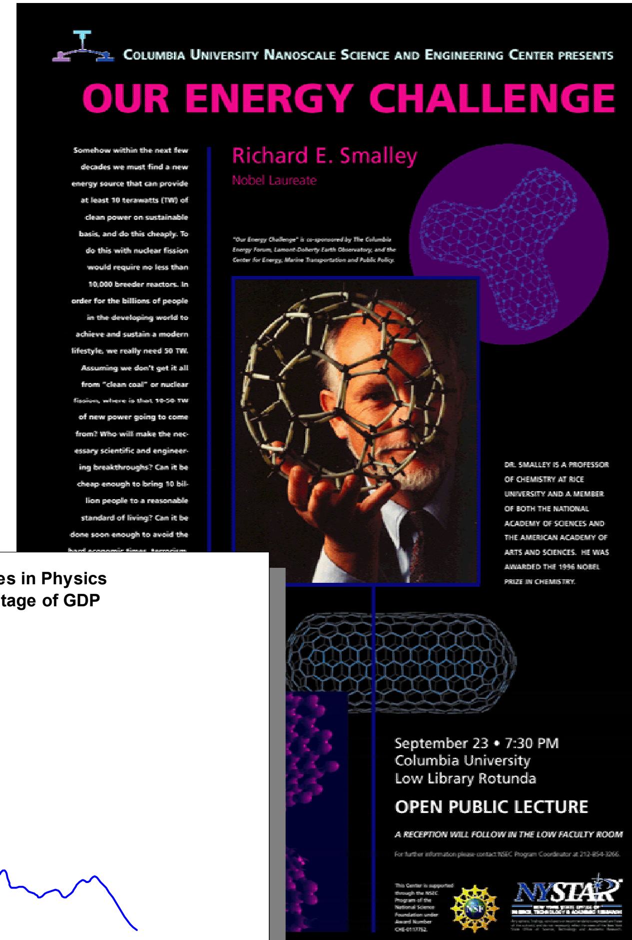
Be A Scientist, Save The World / Our Energy Challenge

Richard E. Smalley, CNL, Rice University

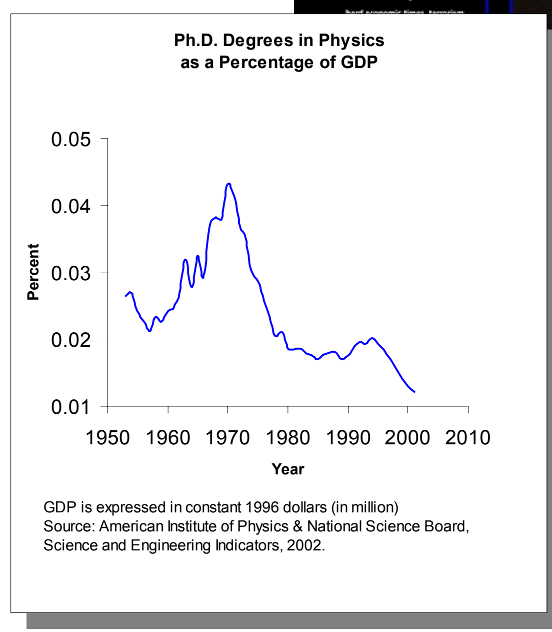
DMR-0073046, "The Molecular Science of Fullerene Nanotubes", R. E. Smalley, PI

Community Outreach: Professor Smalley has delivered a large number of public speeches about the critical need for educating more American scientists and engineers. Our view is that the nation needs a new 'Sputnik Event" to rally a surge in the sciences, and that we have such an issue readily at hand: developing new technologies and infrastructures for global energy needs over the next fifty years.

This message is reaching students directly via presentations at local middle and high schools. Smalley has also presented this educational challenge before the MIT Enterprise Forum, Columbia University (right), the United States Congress and the President's Council of Advisors for Science and Technology.



"*But the key problem in all of this is people. We just don't have enough American boys and girls going into the physical sciences. This is the history of people going into the physical sciences in physics (chemistry, and engineering all look very much the same as this slide for physics)… If the United States were a company and you saw this plot, the comparison of our workforce trend and what the competition is doing, you would short this company.*"



Educational Activty: Post-doctoral associate E. Schuler performed the research supporting the key conclusions regarding science education and energy issues presented in these talks.

Noncovalent Functionalization of Single-Walled Carbon Nanotubes

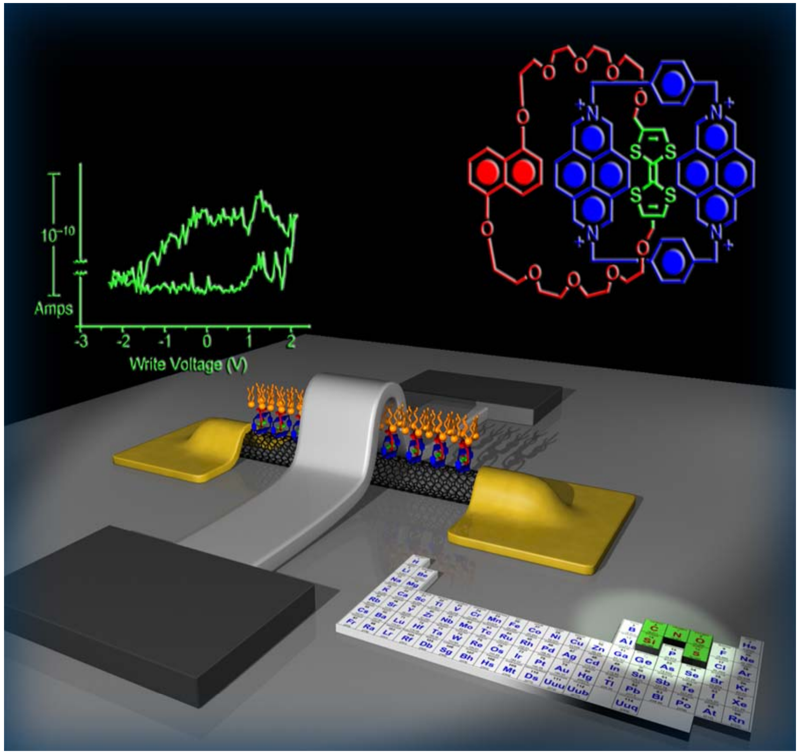
James R Heath & J Fraser Stoddart, CNSI, UCLA, Caltech

DMR-0073046, "The Molecular Science of Fullerene Nanotubes", R. E. Smalley, PI

Educational/Outreach Activity:

The viewgraph, which was designed and produced by **graduate student Scott Vignon**, captures a two-terminal molecular switch tunnel junction (MSTJ) which incorporates a semiconducting, single-walled carbon nanotube (SWNT) as the bottom electrode, interacting noncovalently with a monolayer of bistable, non-degenerate [2]catenane tetracations, self-organized by their supporting amphiphilic dimyristoylphosphatidyl anions which shield the mechanically switchable tetracations from a two-micrometer wide titanium top electrode coated with aluminum. The resulting 0.002 □m^2 area tunnel junction addresses a nanometer-wide row of ~2000 molecules. Active and remnant current-voltage measurements demonstrate that these devices can be reconfigurably switched and repeatedly cycled between high and low current states under ambient conditions.

This work raises the prospect of the **molecular nanoelectronics** in which the **molecules really matter**. **The goal of the project** is to train young scientists for the rapidly approaching age of nanotechnology. This result has been submitted and recently accepted in *ChemPhysChem*.



Noncovalent Functionalization of Single-Walled Carbon Nanotubes

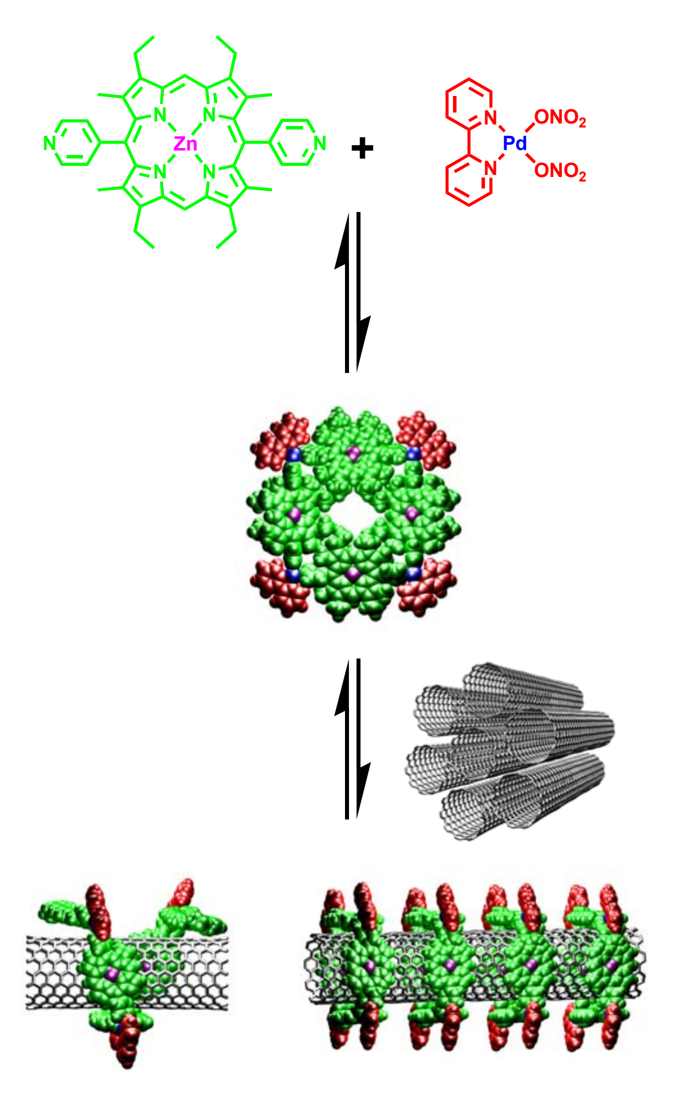
J Fraser Stoddart, CNSI, UCLA

DMR-0073046, "The Molecular Science of Fullerene Nanotubes", R. E. Smalley, PI

Educational/Outreach Activity:

The viewgraph, which was designed and produced by **postdoctoral fellow Kelly Chichak**, highlights some recent advances in the noncovalent functionalization and sorting of individual single-walled carbon nanotubes (SWNTs). The approach utilizes a metal template-directed clipping of transition metal-based cyclophanes (TMCs), whereby SWNTs act as templates for the encircling entity. The components used in the encirclement can be designed to target a range of SWNT diameters by taking advantage of the expected π-π stacking and van der Waals interactions that will occur between TMCs and the surfaces of the SWNTs. Remarkably, mild ultrasonication of the TMCs in a suspension of SWNTs in aqueous acetonitrile resulted, within minutes after addition, in the formation of a stable SWNT suspensions which are resilient toward heating.

This novel approach to solubilizing SWNTs may **transform the current methods used for SWNT purification** and it will inspire and **train young scientists to think big** while gaining **knowledge for rational bottom-up designs of the small world of nanotechnology**.



Noncovalent Functionalization of Single-Walled Carbon Nanotubes

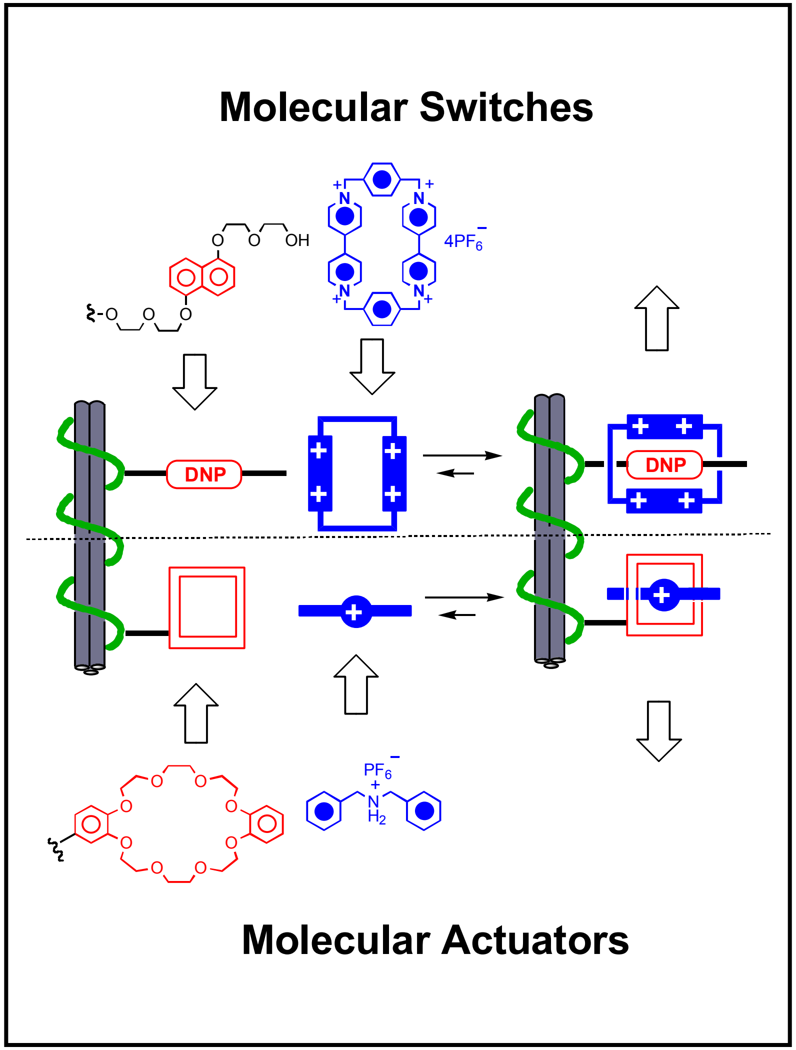
J Fraser Stoddart, CNSI, UCLA

DMR-0073046, "The Molecular Science of Fullerene Nanotubes", R. E. Smalley, PI

Educational/Outreach Activity:

The viewgraph, which was designed and produced by **graduate student Yi Liu**, illustrates the successful appendage of molecular machines onto the sidewall of single-walled carbon nanotubes (SWNTs) using a noncovalent functionalization strategy, namely, a polymer wrapping protocol. Poly{(5-alkoxy-*m*-phenylenevinylene)-*co*-[(2,5-dioctyloxy-*p*-phenylene)vinylene]} (PA*m*PV) derivatives have been shown previously to solubilize SWNT bundles in organic solvents by wrapping themselves around the nanotube bundles. In this research work, molecular recognition units such as rings (crown ether) and threads (1,5-dioxynathphalene, DNP) have been introduced onto the sidechains of the polymers, which form polypseudorotaxanes with threads (dibenzylammonium ions) and rings (cyclobis(paraquat-*p*-phenylene, CBPQT·$4PF_6$), respectively. The formation of the polypseudorotaxanes in the presence of SWNTs on the silicon oxide wafers has been characterized by atomic force microscopy and surface potential microscopy.

Wrapping of these functionalized PA*m*PV polymers around SWNTs results in the **grafting of pseudorotaxanes along the walls of the nanotubes in a periodic fashion**. Those results hold out the prospect of being able to construct **arrays of molecular switches and actuators**.



Functionalization of Carbon Nanotubes

James M. Tour, Rice University

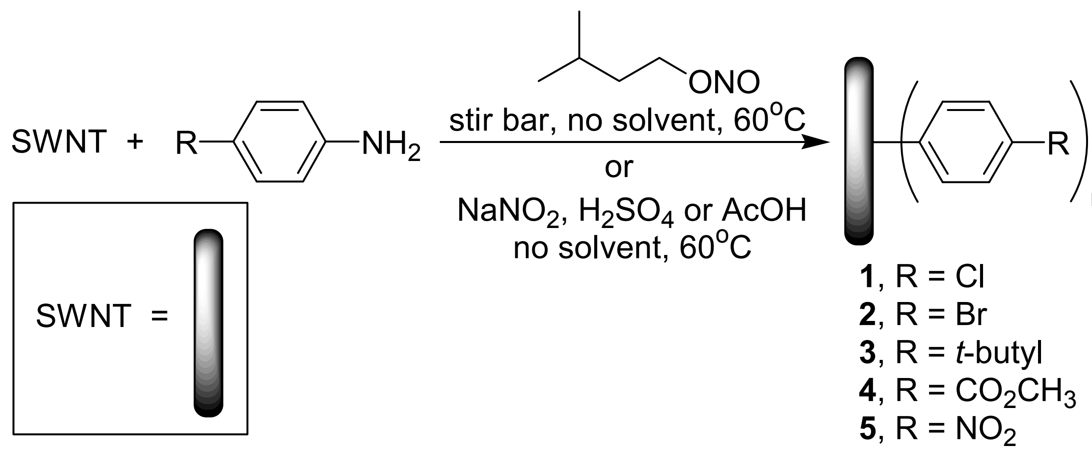
DMR-0073046, “The Molecular Science of Fullerene Nanotubes”, R. E. Smalley, PI

Educational/Outreach Activity:

We have functionalized carbon nanotubes (CNT) without solvent, which lends itself to large-scale processes in structural materials applications. Typical solution-based routes use ~2 L/g of CNTs, whereas this protocol used no solvent at all, and has been successfully done on the 5g scale.

Societal Impact: an industrially viable “green” process where environmentally harmful solvents are excluded.

Postdoctoral associate Christopher Dyke performed this research.



Dyke, C. A.; Tour, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 1156.

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Functionalization of CNTs Dispersed in Water

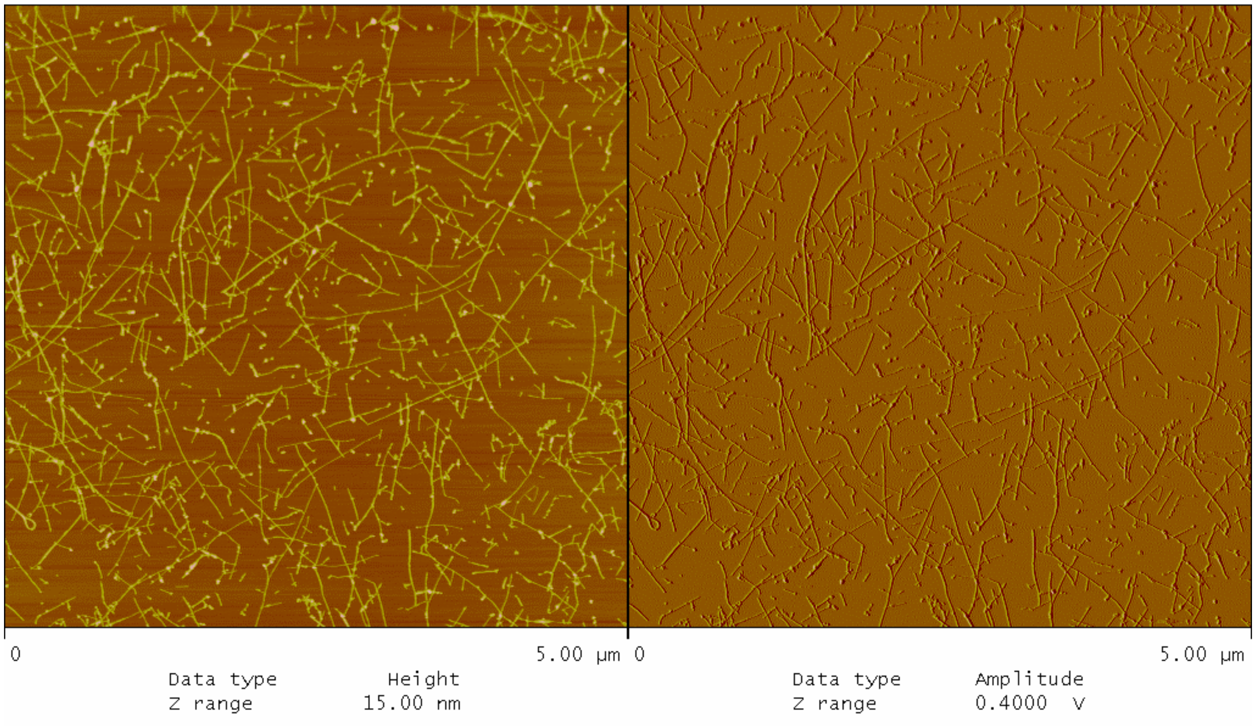
James M. Tour, Rice University

DMR-0073046, "The Molecular Science of Fullerene Nanotubes", R. E. Smalley, PI.

We are also able to functionalize CNTs individually dispersed in water with surfactants. This gives CNTs that do not bundle and are highly functionalized, greatly increasing their solubility.

Societal Impact: the ability to handle individual CNTs is key to their further use in electronics and other applications.

Post Docs Christopher Dyke and Michael Casavant performed this research.



Height (left) and amplitude (right) AFM image of functionalized CNTs dispersed on mica.

Dyke, C. A.; Tour, J. M. *Nano. Lett.* **2003**, *3*, 1215.

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Separation of CNT Types by Functionalization

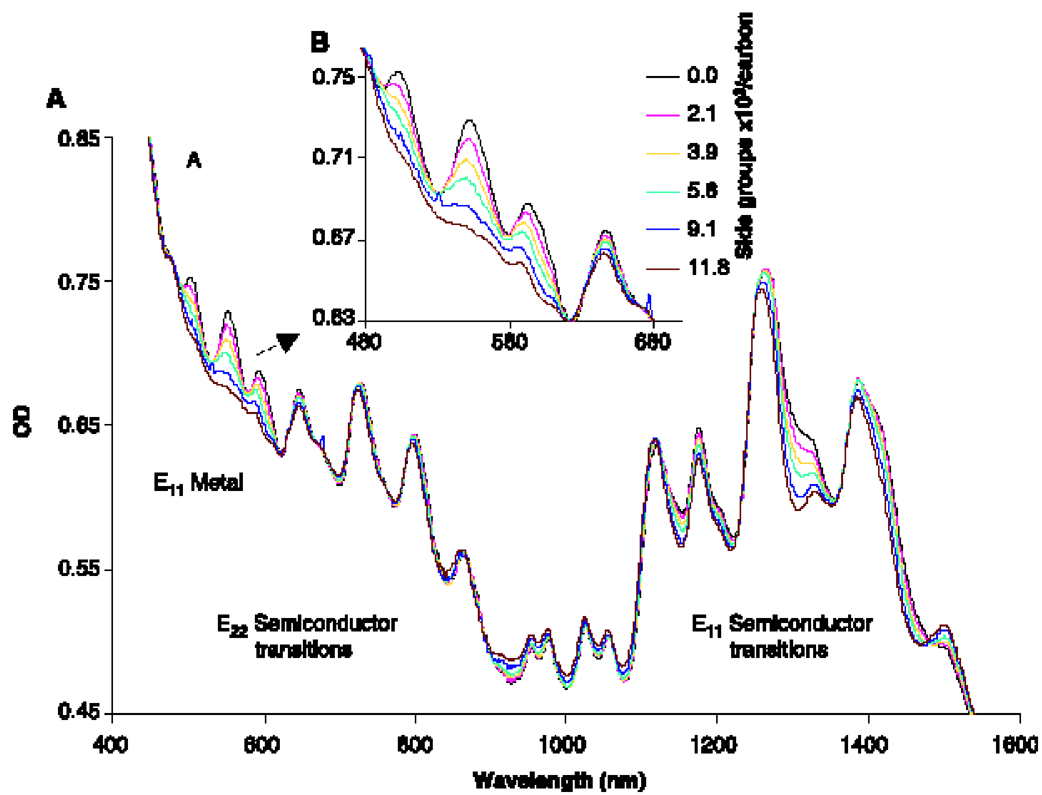
James M. Tour, Rice University

DMR-0073046, “The Molecular Science of Fullerene Nanotubes”, R. E. Smalley, PI

This CNT functionalization methodology gives selective functionalization of metallic CNTs to the exclusion of the semiconductor CNTs when using very low concentrations of the diazonium salt.

Societal Impact: Selectively functionalizing the metals should ultimately lead to bulk separation of CNTs by type, enabling their use in electronics, sensors, and other applications.

Post-Doc Christopher Dyke performed this research.



UV/vis shows the metallic v1 → c1 transitions (440nm-645nm) disappearing whereas the semiconducting v2 → c2 transitions (600nm-800nm) and v1 → c2 transitions (830nm-1600nm) are unaffected.

Strano, M. S.; Dyke, C. A.; Usrey, M. L.; Baron, P. W.; Allen, M. J.; Shan, H.; Kittrell, C.; Hauge, R. H.; Tour, J. M.; Smalley, R. E. *Science* **2003**, *301*, 1519.

Doping of Block Copolymers by Functionalized CNTs

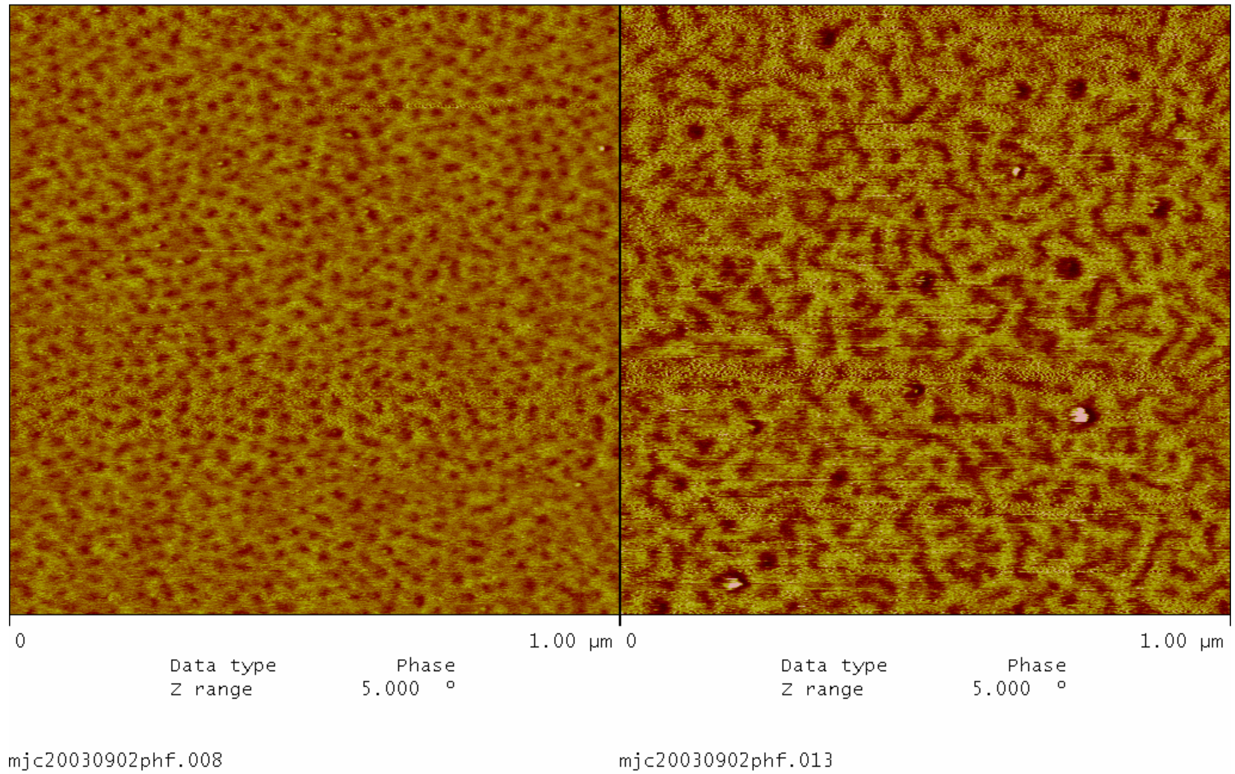
James M. Tour, Rice University

DMR-0073046, "The Molecular Science of Fullerene Nanotubes", R. E. Smalley, PI

We have begun to explore doping of block copolymers with functionalized nanotubes, with the goal of achieving improvements in mechanical, electrical, and/or thermal properties. This may also elucidate the percolation properties of these systems as various property changes manifest.

Societal impact: include the polymer industry, where improvements in strength and other properties are important to advances in technology.

Graduate student Jared Hudson, Post Doc Michael Casavant performed this research.



The change in the morphology of a thin film of polymer (left) when doped with styrene-functionalized nanotubes (styrene chains ~10 monomers long, right).

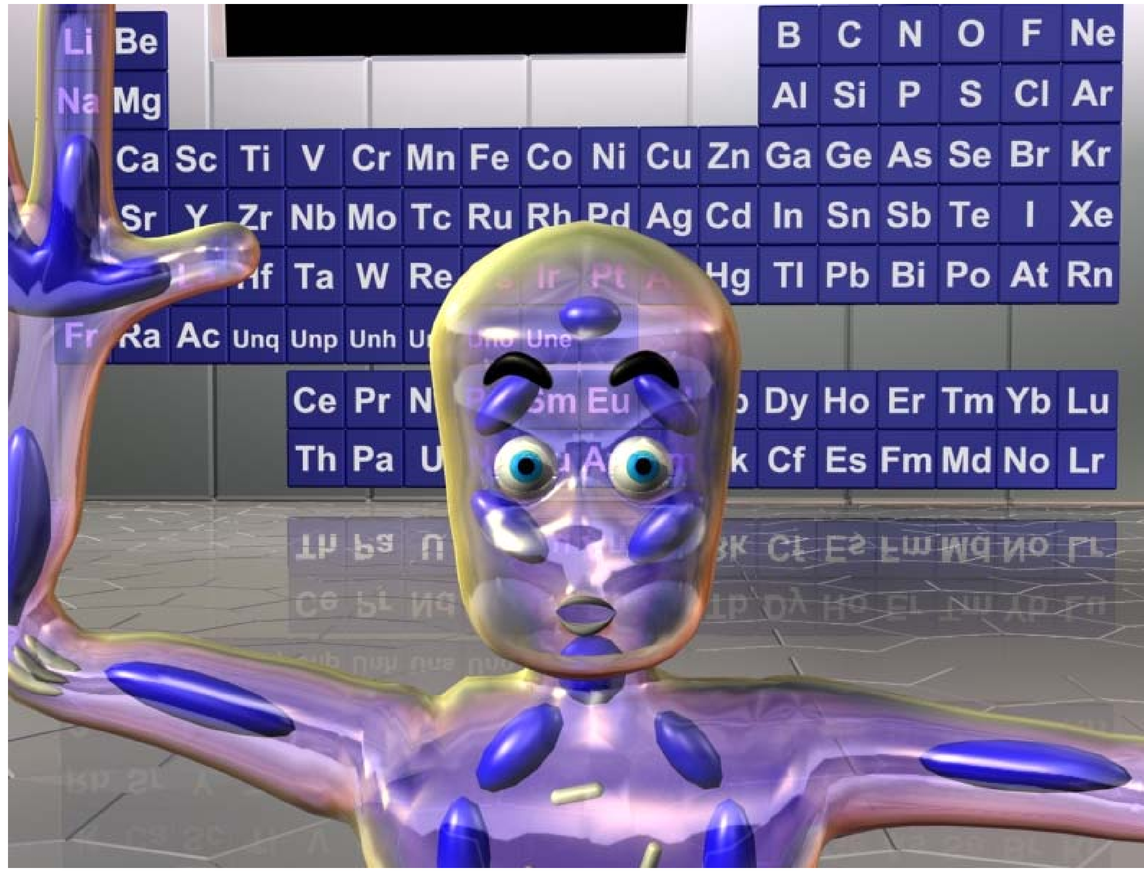
Leveraging of Funds for Educational Outreach

James M. Tour, Rice University

DMR-0073046, “The Molecular Science of Fullerene Nanotubes”, R. E. Smalley, PI

In our educational outreach activities, we have leveraged NSF funds (SGER, CBEN) to develop the NanoKids DVD for introducing students in grades 6-8 to the chemistry, physics, and biological concepts encapsulated by “Nanotechnology.” This approach to teaching using animation to illustrate concepts at the nanometer level is being beta tested in Houston Independent School District middle schools, where more than 50% of the population is from underrepresented groups, and more than 50% are “at risk” by Texas’ literacy standards.

Societal Impact: this will bring more students, including under-represented minorities, into the sciences.



A screen shot from the NanoKids DVD showing one of the characters and the periodic table located in the NanoLoft, where the NanoKids “hang out.” **Students involved in this project include high school student Troy Ruths; undergraduates Justin Ruths and Steve Nebel; graduate students Stephanie Chanteau and Francisco Maya; and post doc Dmitry Kosynkin.**

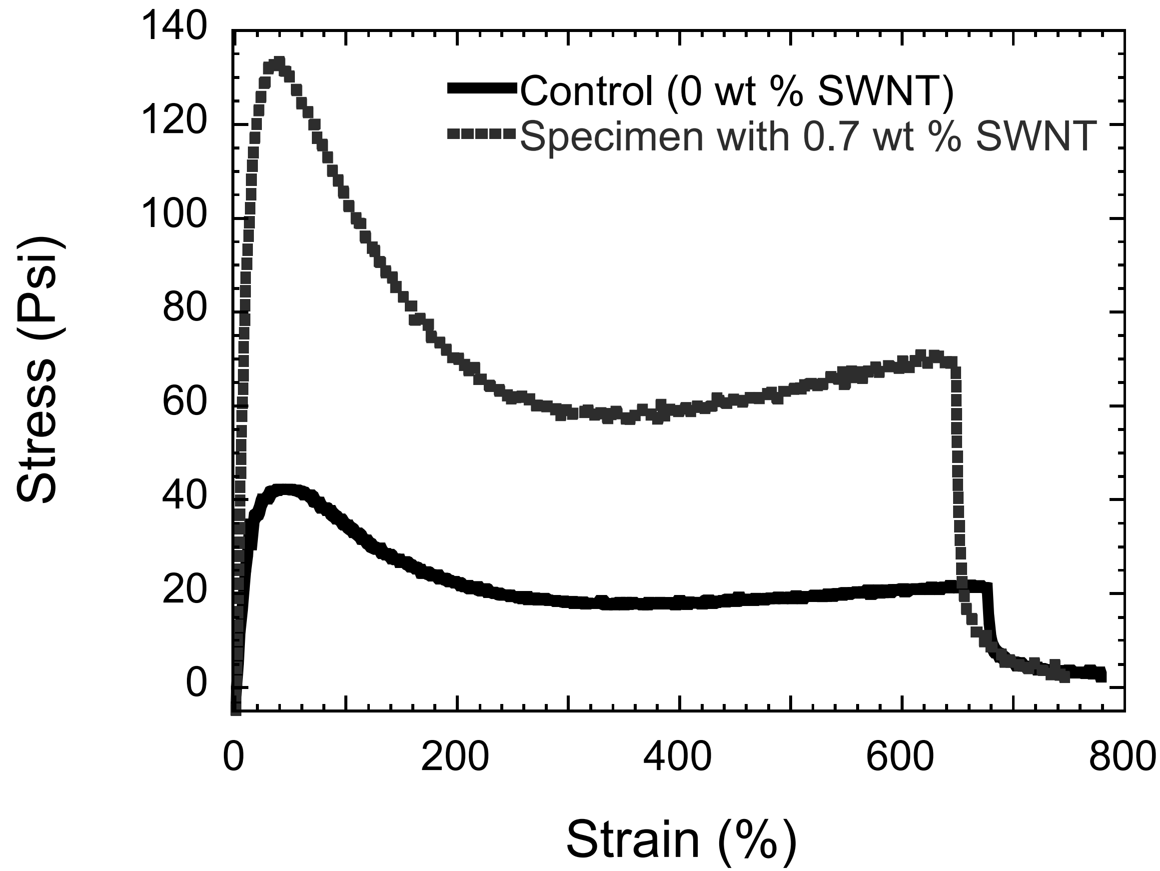
New Elastomer Blends

James M. Tour, Rice University

DMR-0073046, "The Molecular Science of Fullerene Nanotubes", R. E. Smalley, PI

Societal Impact: In one "real world" application of our work, a new generation of high performance functionalized CNT/elastomer blends will be tested initially for high-end applications in oil and gas services industries followed by trials in the commodity elastomers and rubber market. The North American synthetic rubber industry had a volume of 2.2 million metric tons in 2002. The global market for fluoroelastomers, an important category of high-performance elastomer used in extreme environments in aerospace, automotive, chemical processing, oil and gas, and semiconductor applications, was 40,000 metric tons in 2000 with a value of \$450 million in 2002.

Graduate students Jared Hudson and Jason Stephenson, and post doc Christopher Dyke performed this research.



Observed elastomeric reinforcement due to blending 0.7 wt % of functionalized SWNT into polysiloxane.