User Proposal #2484

Nondestructive Carbon Nanotube Modification for Tailored Functionality

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Project Summary:

Controlled chemical modification of carbon nanotubes and other graphitic structures is highly desirable for the processing and use of these materials in practical devices. Chemical means for modifying nanotubes have existed for some time, but most involve pre-treating the tubes in strong acids to induce oxidized defects in the tube surfaces and ends at which to perform chemistry. Sidewall functionalization methods, such as those employed by James Tour and his group at Rice University, have been developed to attach desired chemical groups to nanotubes without first damaging the tubes by oxidation. This approach, however, also results in an interruption of the conjugated backbone of the carbon nanotube with a corresponding loss in mechanical and electronic properties. One strategy to limit this drawback is the use of such chemistry on multi wall carbon nanotubes. In the case of multi wall nanotubes only the outer wall might be damaged in the process, leaving the inner walls intact. Unfortunately for this strategy, the larger diameter of multi wall carbon nanotubes leads to a lower strain in the carbon-carbon bonds of the tubes and a much lower reactivity compared to single wall carbon nanotubes. Chemical modification of multi wall nanotubes is thus difficult to accomplish without cutting, opening, and oxidatively damaging the tubes to provide reaction sites.

The utilization of noncovalent means for carbon nanotube modification is preferable for applications in which the properties resulting from the conjugated backbone of the nanotubes need to be maintained. In addition, noncovalent approaches such as the use of molecular anchors for chemical functionalization are generally applicable to all types of graphitic surfaces. The use of organic molecular anchors is a viable way to chemically modify multi wall carbon nanotubes, which are less difficult to synthesize and less expensive to purchase than single wall nanotubes, while keeping attractive carbon nanotube properties intact.

We have developed a facile and effective method for depositing molecular anchors onto multi wall carbon nanotubes using supercritical fluids. Characterization of the degree of loading in these nanotube-anchor structures is achieved with the use of thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). It is our contention that employment of the described method will facilitate the use of carbon nanotubes in a variety of applications including chemical separations and chemical sensors.

Publications, Presentations, and Proposals:

"Nanostructured materials for efficient carbon dioxide separation " Leonard S. Fifield, Glen E. Fryxell, Thomas S. Zemanian, R. Shane Addleman, Feng Zheng, Larry R. Dalton, and Christopher L. Aardahl. 225th ACS National Meeting, New Orleans, LA, March 23, 2003.

"Development of Active Nanomaterials based on Carbon Nanotubes" Leonard S. Fifield, Larry R. Dalton, Rosemary A. Golhotra, R. Shane Addleman, Glen E. Fryxell, and Christopher L. Aardahl. JINN Nano Workshop, University of Washington, Seattle, WA, September, 2003.

Proposals Submitted as a Result of this Work:

"CO_2 Capture from Submarine Atmospheres" NAVSEA Philladelphia—in process

"Signature Collection" Coastal Security, United States Navy—in process

Selected Figures:

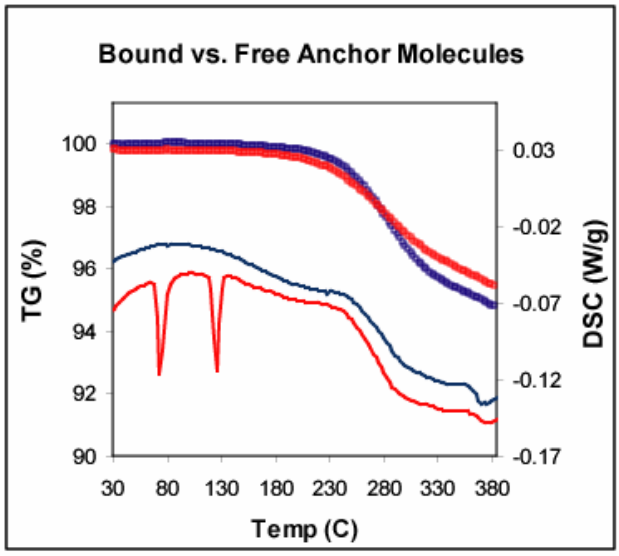

Figure 1 Plot of TGA/DSC data for anchor compound reacted (blue line) and merely mixed (red line) with MWNTs. Melting points of the unreacted anchor (dips on the red DSC curve) indicate that the molecules are not in close association with surface, while absence of melting points for the reacted anchor indicate a close association with the nanotube surface.

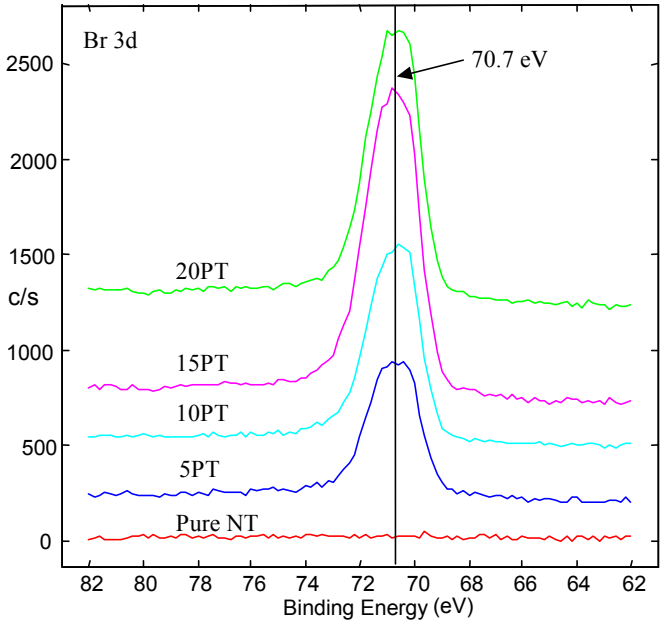

Figure 2 X-ray Photoelectron Spectroscopy results indicate an increasing Br content of carbon nanotubes modified with increasing amounts of 1-bromoacetyl pyrene (BAP) molecular anchor (XPS results and figure credit: Mark Engelhard).