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Abstract:

Metallic single-wall carbon nanotubes were selectively solubilized in THF and separated from semiconducting nanotubes. Once separated, the functionalized metallic tubes were de-functionalized to restore their metallic band structure. Absorption and Raman spectroscopy of the enriched samples support conclusions of the enrichment of nanotube samples by metallic type.

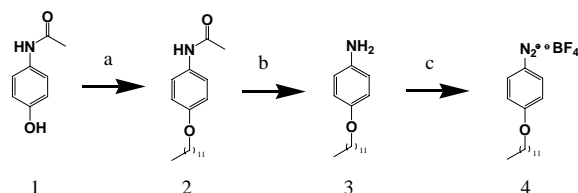
Motivation:

Over the past five years, a number of methods for type-based separation or enrichment of nanotubes have been both proposed and achieved. Methods include electrophoretic techniques, centrifugal density gradients, polymer and DNA wrapping and techniques in selective functionalization. A principal difficulty with all of these procedures is their scalability. It is proposed that selective chemical functionalization is the most likely method to produce isolated nanotube in greater than a microgram quantities. The method that was used to separate single wall carbon nanotubes (SWCNTs) by their conductive type was that involving aryl diazonium salts [1].

1. Shouhei Toyoda, Yoshifumi Yamaguchi, Masataka Hiwatashi, Yasuhiko Tomonari, Hiroto Murakami, and Naotoshi Nakashima, *Chem. Asian. J.* **2007** (145-149);

Experimental:

I. Synthesis of the diazonium salt:

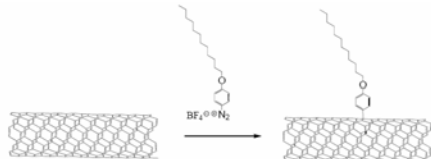


Rxn A: Acetaminophen was reacted with bromododecane in acetone followed by reaction with K_2CO_3 to produce product **2**.

Rxn B: Product **2** was refluxed 24 hr in THF and concentrated HCl producing product **3**.

Rxn C: Nitrosonium tetrafluoroborate was dissolved in acetonitrile and reacted with dodecyloxyaniline under $-40^\circ C$ bath. The product **4** was crystallized from diethyl ether.

II. Selective reaction of the aryl diazonium with metallic SWCNTs:



The diazonium salt was dispersed in SDBS solution and was added in μL aliquots to a dispersed solution of laser produced SWCNTs. Both the diazonium concentration and the reaction temperature were varied. The reaction with SWCNTs was monitored in-situ through changes in the metallic and semiconducting optical transitions in UV-Vis spectroscopy utilizing a flow cell configuration.



Flow cell configuration used monitor the SWCNT/diazonium reactivity

III. Separation of reacted and unreacted SWCNTs:

After selective reactivity at $30^\circ C$ the solution was cooled to $0^\circ C$ in order to flocculate the nanotubes from suspension. Filtered material was then dispersed in THF from which highly functionalized tubes stay in suspension. After filtering unsuspended tubes, the suspended tubes were precipitated out of solution with NaCl and addition of methanol and are believed to be metallic enriched. After the separation materials the functional groups were removed by heating in inert gas and characterized.

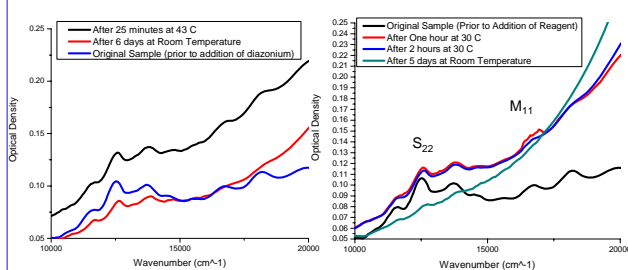
Results:

I. In-Situ Characterization

In-situ optical absorption experiments indicated SWCNTs showed both kinetic and thermodynamic dependence.

The optimal reaction temperature was determined to be $30^\circ C$.

Three different concentrations of 0.004, 0.02 and 0.08 g/L were used for which 0.02 was the optimal concentration.

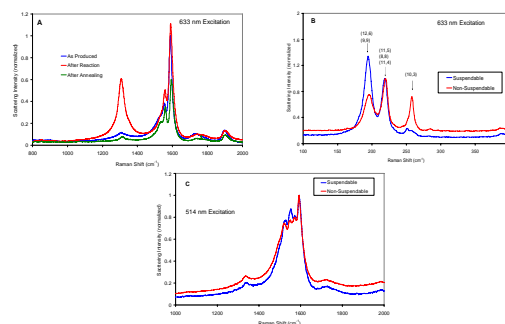


II. Post reaction Characterization:

A. Addition and removal of functional group was monitored by D/G band ratios

B. Suspended material (more highly reacted with dodecylbenzenediazonium) shows increases in RBM intensities associated with metallic type tubes and appears more selective towards larger diameter tubes.

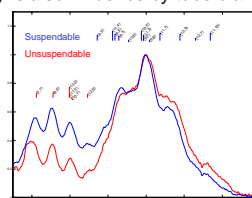
C. Increase in the Fano line shape of the G-band for suspendable material supports metallic enrichment observed with RBM bands.



UV-Vis absorption of annealed materials shows an increase in the intensity of the metallic optical transitions.

Chiral assignments for UV-Vis optical bands are more difficult because of overlapping transitions, still similar chiralities are observed.

UV-Vis data supports Raman data in that metallic enrichment is observed and that selectively is also influence by tube diameters.



Conclusions:

A scalable method for enriching nanotube conductive type has been developed.

Raman and UV-Vis data indicate SWCNT reaction with dodecylbenzenediazonium results in metallic enrichment.

It is expected that further refinement of this techniques will lead to more dramatic separations of types and diameters.