Supporting Online Material for

Suppression of Metallic Conductivity of Single-Walled Carbon Nanotubes by Cycloaddition Reactions

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Supporting Information:

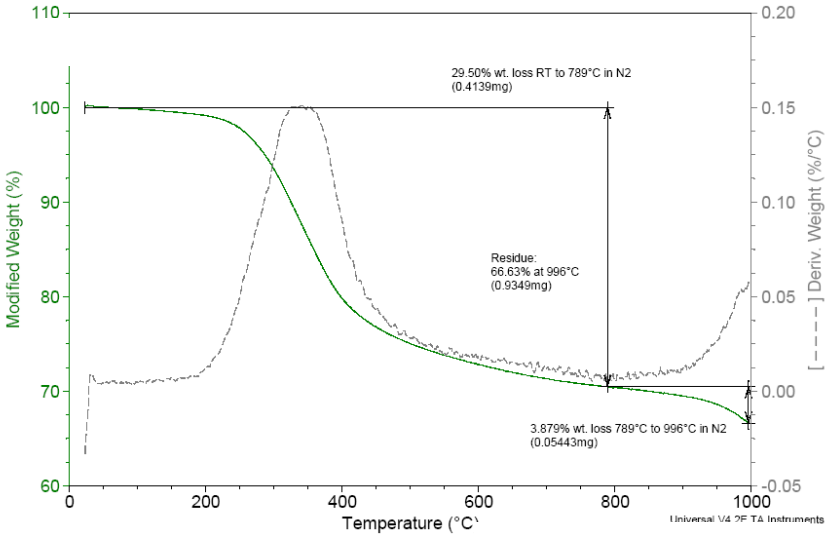
Reagents and Chemicals: Purified High-pressure CO decomposition (HiPco) single-walled nanotubes (SWNTs) were obtained from Carbon Nanotechnologies. PSEPVE, a precursor to Nafion®, was synthesized at DuPont's Fayetteville Works facility.

Synthesis of SWNT-adduct: Commercially purified HiPco SWNTs was dried at 250 ºC, P< 1 mbar overnight. The dried carbon nanotubes were charged into a 10 mL shaker tube in a nitrogen glove box and the required amount of PSEPVE added. The shaker tube was then closed under nitrogen, chilled in dry ice for 30 minutes, and evacuated. The reaction was performed at DuPont's high pressure laboratory where the tube was heated at 215 ºC for 24 hours with constant shaking. The tube was then evacuated through a cold trap, first at ambient temperature and then with gentle heating. The carbon nanotubes were then washed repeatedly with acetone and the fluorinated solvent Vertel-x to remove the residual PSEPVE. The washed tubes were filtered through a 0.2 micron PTFE membrane. The recovered functionalized carbon nanotubes were dried at 175 ^{o}C under vacuum for 2 hours, prior to their dispersion in o-dichlorobenzene (ODCB) at a concentration of 300 mg/L. Tubes in ODCB were horn sonicated for 10 minutes.

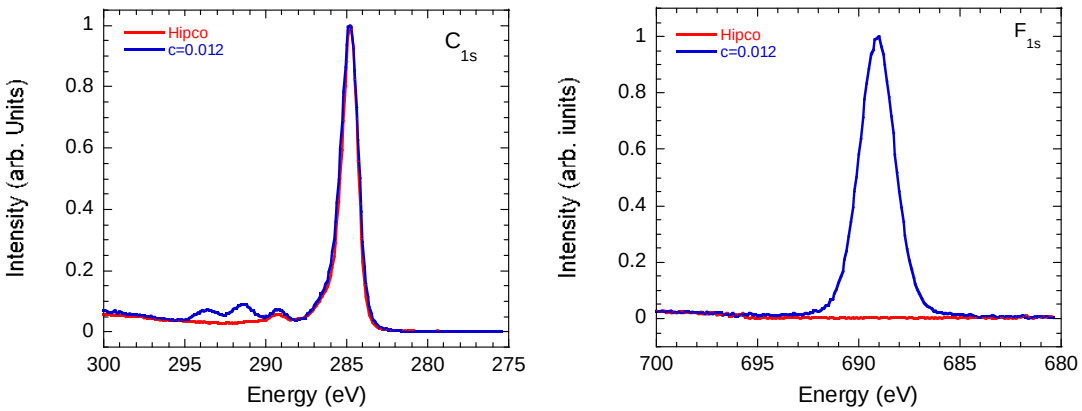
TFT Fabrication: TFTs were fabricated on heavily doped silicon wafers with a 3000 Å wafer thermal oxide. Gold source and drain electrodes were lithographically patterned. The channel dimensions used were W= 200 μm, L=20 μm. A few drops of dispersed carbon nanotubes were allowed to settle on the pattered silicon wafer and then spun coated at a spin speed of 500, 1000 and 2000 rpm.. Electrical properties were measured using a standard Agilent unit. A voltage of 0.01 V to 1 V was applied between source and drain electrodes. The gate voltage was swept from 50 V to -100 V while measuring the drain current.

AFM Characterization: AFM height and phase images of the purified and functionalized SWNTs were obtained in tapping mode. The AFM images were obtained using conventional Si tip with a Veeco Metrology Nanoscope IV (Digital instruments, Santa Barbara, CA).

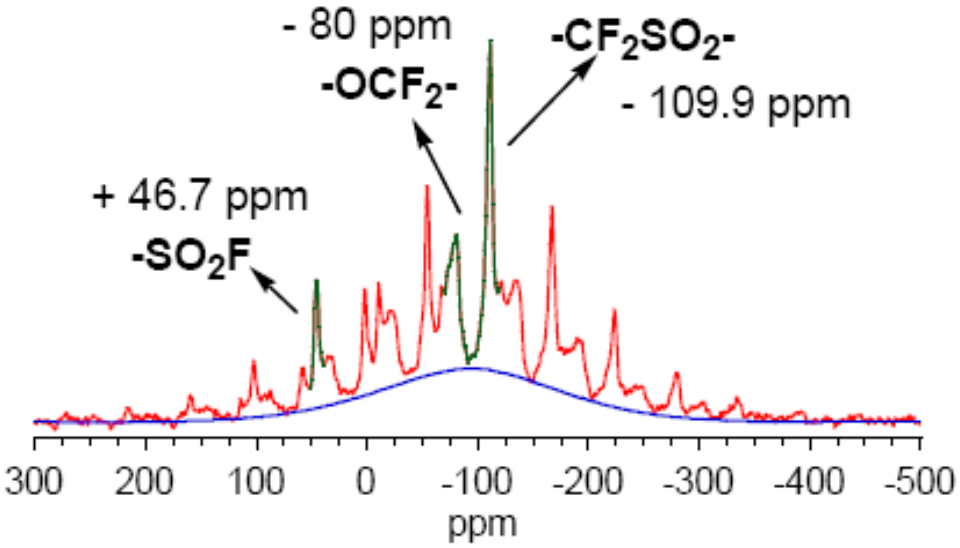
Separation of the reactants on carbon nanotube sidewalls: The average distance between reactant molecules on the carbon nanotube walls was estimated from thermal gravitometric analysis (TGA) and X-ray Photoelectron Spectroscopy (XPS) data. The TGA spectra were measured in a TGA Q500 v6.6 Build 197 instrument after purging the samples under Nitrogen for 2 hours. The samples were heated from room temperature to 1000C at 10C/min in a nitrogen atmosphere. The mass loss below 750C was associated to the reactant and while the mass loss above 750C was associated to the unreacted CNT. From the loss masses and molecular weights of PSEPVE= 472.12 and of C=12 we estimate the relative concentration of reactant to C=C bonds, estimating 1 PSEPVE molecule per 49 C=C (~68A) for c=0.012. While the addend separation remained quite constant below c~0.02, we were not able to determined addend separation at high fluorination level via this method.



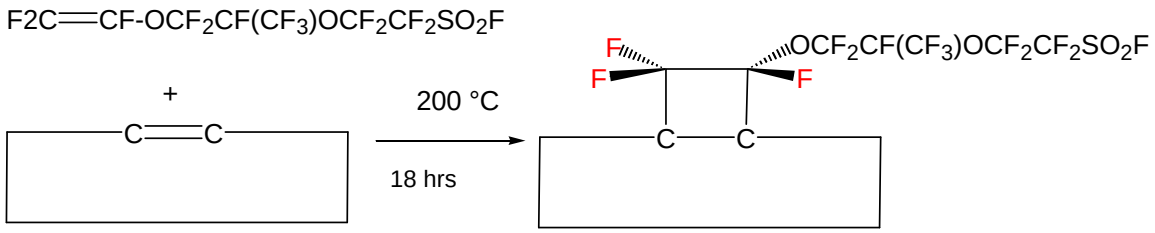
The separation between reactants molecules on the SWNT walls was also estimated from XPS data. For the XPS analysis the pristine and functionalized carbon nanotubes were drop casted onto a clean Si wafer. The experiments were carried out with a Physical Electronics Quantera Scanning ESCA Microprobe, using a focused (100 um) monochromatic Al X-ray (1486.6 eV) beam operated at 18 kV and 100 W. Acquisition times were kept under 30 min. to minimize any F degradation (<10%). The C1s bands (left) and the F1s (right) for Hipco (red) and c= 0.012 (blue) are shown below. From the 0.11 ratio of the integrated F1s and C1s bands we estimate the reactant separation on the SWNT walls to be about 44.5 C=C or ~62.3 Å in good agreement with the TGA data.



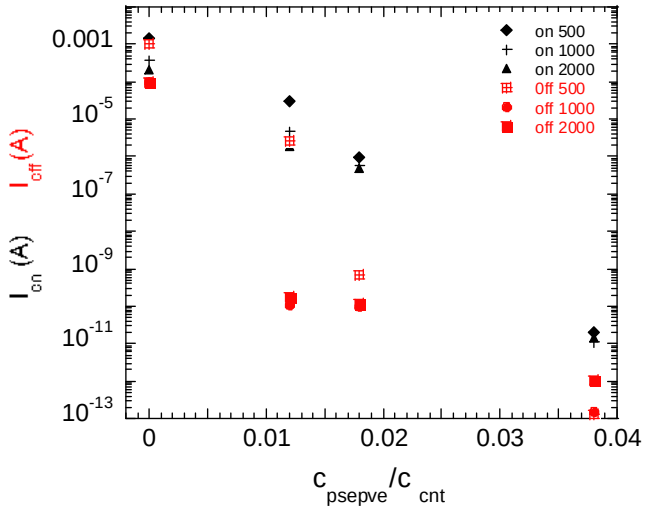
NMR: Solid state magic angle spinning fluorine NMR clearly shows three resonances expected for the fluorines of the pendant groups. The underlying broad absorption is assigned to the cyclobutane fluorines. The broadening of the absorption reflects the various types of nanotubes: armchair, zigzag and chiral, with different chemical shifts for these fluorines so close to the SWNT surface.



Proposed Cycloaddition reactions for PSEPVE:



Effect of network density on the off and off currents: The effect of network density on the on and off currents was also used to estimate the presence of metallic tubes. Network densities ranging from 8-40 CNT/μ^2 were achieved by changing the spin coating speed. Kumar et al. *(App. Phys. Lett.* ***90****, 233509 (2007))* estimated the percolation threshold of 7 CNT/μ^2 for Hipco tubes.



500 RPM ~35-40 CNT/μ2
100 RPM ~ 17 CNT//μ2
2000 RPM ~ 8 CNT//μ2

The figure above shows that while some metallic tubes remain at c~ 0.012 dopant concentrations, they have been eliminated at c~0.018. In the former case, denser network (35 CNT/μ^2) show I_{off} comparable to bare Hipco (~10^{-4}A). However, as the network density is reduced the off current drops by almost seven orders of magnitude (~ 10^{-11}A). Thus, suggesting that although metallic tubes have not been fully eliminated and that conducting percolating pathways still be formed at very high SWNT densities. In contrast, slightly higher dopant concentration, c=0.018, is sufficient to eliminate the remaining metallic tubes and the off current remains in the 10^{-10} A regime independent of the array density.