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14. ABSTRACT Precise control over the electronic properties of the carbon nanotubes is key to their practical application in plastic electronics. In the present work, we have extended carbon nanotube functionalization via a 2-2 cycloaddition to electron withdrawing non-fluorinated olefins as well. Our results show that this is a fairly general approach, independent of specifics of the addend, to converting the grown mixture of metal and semiconductor tubes into high mobility semiconducting tubes without tedious of separation requirements. Thin film transistors fabricated with functionalized tubes exhibit mobilities of 10-30 cm ² /Vsec and on/off ratios in excess of 10 ⁶ . This simple functionalization approach represents a low cost path to high performance semiconducting inks for printable electronics.					
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High Performance Organic Transistors: Percolating arrays of nanotubes functionalized with an electron deficient olefin

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Abstract

Precise control over the electronic properties of the carbon nanotubes is key to their practical application in plastic electronics. In the present work, we have extended carbon nanotube functionalization via a 2-2 cycloaddition to electron withdrawing non-fluorinated olefins as well. Our results show that this is a fairly general approach, independent of specifics of the addend, to converting the grown mixture of metal and semiconductor tubes into high mobility semiconducting tubes without tedious of separation requirements. Thin film transistors fabricated with functionalized tubes exhibit mobilities of 10-30 cm²/Vsec and on/off ratios in excess of 10⁶. This simple functionalization approach represents a low cost path to high performance semiconducting inks for printable electronics.

Because of their unique structural, mechanical and electronic properties, carbon nanotubes have been the subject of considerable interest¹. Part of the effort has been directed to the use of carbon nanotubes in electronics devices ²⁻⁵. However, one of the serious drawbacks has

been the inability to control electronic structure of carbon nanotubes during their growth. The synthesized carbon nanotubes are a mixture of semiconducting and metallic tubes which hinders many applications, such as thin film transistors, where high mobility and high on-off ratio are necessary. Although various methods have shown some success in the separation of metallic and semiconducting tubes⁶⁻⁸ a suitable commercialization process remained unattainable.

A considerable amount of work focused on separating single wall carbon nanotubes (SWNT) via monovalent side wall functionalization⁹⁻¹⁶, which also provided a route to improve solubility while aiding in purification and exfoliation.¹⁴ The theoretical calculations¹⁷⁻¹⁸ predicted that upon monovalent functionalization, sp³ re-hybridization of the carbon atom at the functionalized site induces a localized impurity state at the Fermi level strongly disrupting the conducting π - π^* states. As a result, the functionalization site acts as a strong scattering center, hampering ballistic transport. Experimental work support these findings, showing that monovalent functionalization has a strong effect in the SWNT electrical properties; disrupting π transitions in visible spectra¹⁹⁻²⁰, with drastic changes in resistance²¹, shifting of Raman spectra²² and even leading to tube fragmentation²³.

In contrast, very few studies have focused on divalent functionalization of SWNT. The theoretical calculations predict that the two neighboring impurity states create strong localized bonding and antibonding states away from the Fermi level and, as a result, the electronic structure near the Fermi level is not strongly affected²⁴⁻²⁶. Experimental studies are few. Menard-Moyon et Al.²⁷ work on cycloaddition of azomethine suggests preferential functionalization of the semiconducting tubes. In contrast, Kamaras et al.²⁸ FIR work shows that a [2+1] cycloaddition with dichlorocarbene largely reduces the density of states at Fermi level. Our recent work²⁹ on [2-2] cycloaddition of fluorinated olefins suggests that cycloaddition suppresses the conductivity of the metallic carbon nanotubes at low addend concentration. However, this limited body of work suggests that divalent functionalization not only offer a suitable path to controlling the electrical properties of carbon nanotubes, but that the method appears to be fairly independently of tube type, size and chirality.

In these work we show that divalent functionalization of SWNT with the non-fluorinated electron withdrawing olefins tetracyanoethylene (TCNE) (C₆N₄) effectively suppressed the conductivity of the metallic tubes without considerable degradation of the semiconducting ones. As with the fluorinated counterpart²⁹, functionalization enables the formation of

percolating semiconducting arrays with high mobilities and on/off ratio of 10^6 without requiring further tube separation. Although severe tube fragmentation is apparent with increasing TCNE functionalization, mobilities of $\sim 1 \text{ cm}^2/\text{Vsec}$ are maintained. Thus, reflecting that the electrical properties of the semiconducting tubes are not drastically degraded as previously observed with F-olefins.

There have been few studies³⁰⁻³² on interactions of carbon nanotubes with electron withdrawing systems such as TCNQ or Tetracyanoethylene (TCNE). Takenobu et al.³³ suggested that as C60, TCNQ and TCNE are encapsulated inside the tubes. The data presented here suggests that, as with the much larger size F-olefins, considerable TCNE functionalization appears to occur on the outside of the SWNT walls.

Commercially purified HiPco SWNTs were functionalized as described in reference 34. The effect of a systematic cycloaddition reaction on the mobility and off current (I_{off}) of a percolating array of functionalized SWNT (FSWNT) as a function of $c_{\text{TCNE}}/c_{\text{SWNT}}$, where c_{TCNE} and c_{SWNT} are the concentrations of TCNE and SWNT, is illustrated in Fig. 1a. The dramatic reduction of the I_{off} with increasing $c_{\text{TCNE}}/c_{\text{SWNT}}$ concentration is key to this work. Devices fabricated from a percolating array of pristine HiPco tubes have high mobilities but also high I_{off} , which indicates that conduction pathways are dominated by metallic tubes²⁹. Increasing TCNE functionalization led to a dramatic decrease in I_{off} , caused by a rapid reduction in the number of metallic percolating pathways. For $c < 0.02$, high mobility was largely preserved while I_{off} was reduced by almost 5 orders of magnitude as compared to pristine SWNTs. As the $c_{\text{TCNE}}/c_{\text{SWNT}}$ concentration is further increased ($c < 0.06$) the mobility slowly decreases to about $1 \text{ cm}^2/\text{Vsec}$, suggesting that the electronic properties of the SC-SWNTs are somewhat retained. The electrical response of TCNE functionalized tubes in the low functionalization regime is similar to what we previously reported for fluorinated olefins. Thus, suggesting that TCNE as perfluoro-2(2-fluorosulfonylethoxy) propyl vinyl ether (PSEPVE) ($\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$) appears to proceed via a cycloaddition reaction also attaching to the outside SWNT walls.

Gate sweep for FSWNT-TCNE under optimum functionalization conditions for $c=0.0035$ are shown in Figure 1b. The field effect mobilities deduced from the linear regime $30 \text{ cm}^2/\text{Vsec}$, with on/off ratios in excess of 10^5 . Due to the high reactivity of TCNE, all thin film transistors were measured in a nitrogen glove box.

The morphology of the arrays studied via atomic force microscopy (AFM) is shown in Figure 2 a-d. The micrograph of pristine Hipco in 2 a shows thick entangled ropes of about 0.6 micron in average length. In contrast, the micrographs b-d suggest that low levels of functionalization not only efficiently exfoliate the ropes, as previously observed with F-olefins, but also leads to chain cleavage. The correlation between average chain length and mobility is illustrated in figure 2 e. We proposed that chain cleavage may occur via the radical mechanism shown in Figure 2f. In this scheme, the cyclobutyl ring undergoes a reverse cycloaddition reaction and the tubes get open up at that site creating more reactant sites and at the same time shortening the tubes. As tube cleaves, open ends become available for TCNE, as does TCNQ, to enter. The extent of TCNE functionalization and tubes reactivity was apparent in thermal gravimetric analysis (TGA) and x-ray photoemission spectroscopy included as references 36 and 37, respectively.

The data presented here suggests that functionalization of SWNT with TCNE, an electron deficient olefin, enables the disruption of the conductivity of the metallic SWNT without degradation of semiconducting ones. These findings, which extend beyond the previous work on fluorinated olefins, are well aligned with theoretical work on SWNT functionalization predicting that metallic tubes are universally more reactive than semiconducting tubes¹⁴. However, unlike F-olefins, the electrical properties of TCNE functionalized semiconducting tubes are partially retained to higher addend content ($c < 0.06$). The work further suggests that the electrical properties of tubes functionalized via 2-2 cycloaddition are fairly insensitive to the difference in binding energy, specific size of the olefin, tube size or chirality. .

The few theoretical studies on divalent functionalization of carbon nanotubes focused on [2+1] cycloaddition reactions, where a carbene or nitrene group saturates a double bond between two carbon atoms forming a *cyclo-propane like three member ring*²⁴⁻²⁶. However, calculations show that whether the sidewall bond at the attachment site is broken or it remains intact plays a fundamental role in the resulting electronic properties of the functionalized SWNT, the open bond predicted as more stable. In the latter configuration, band structure calculations show that two neighboring impurity states create strong localized bonding and anti-bonding states which are located away from the Fermi level. As a result, the overall electronic structure near the Fermi level is not strongly affected and the conductance remains high. In contrast, configurations for which cycloaddition does not break the sidewall bond, can display low conductance (although this is an unstable configuration for 2+1 cycloaddition

where a three member rings is formed). In contrast, this work focus on [2+2] cycloaddition reactions, where an electron deficient olefin saturates a double bond between two carbon atoms forming a *cyclo-butane like four member ring* instead. Within a four-member C-C bond distances remain mostly unchanged and without the strain induced by forming a cyclo propane ring perhaps the sidewall integrity can be retained. Although, theoretical calculations need to be extended to this case, our results suggest the formation of a cyclo-butane ring occurs without sidewall rupture and, as in the closed 3-member ring, it leads to a lowering in conductance^{24,26}. Thus, the electronic structure near the Fermi level is affected. We propose that functionalization via 2-2 cyloaddition; forming a cyclo-butane like four member ring between two sidewall carbons atoms, likely proceeds without bond rupture which leads to the lowering of the conductance of metallic tubes.

In summary, we have developed a simple, high yield method for the functionalization of of as grown Hipco mats with TCNE into preferentially semiconducting tubes with properties that are suitable for device applications. We propose that, in the low concentration regime, cycloaddition provides an effective method to anchor molecules to the carbon nanotube framework and to either eliminate or transform metallic tubes. The dramatic reduction of the off current reflects a decrease of the density of state at the Fermi level, consistent with the opening of a gap at E_f ; perhaps converting metallic tubes into semiconducting tubes via functionalization. The functionalization with TCNE also seem to shorten the tubes extensively even at very low functionalization regime although it appears to preserve the high mobility of the semiconducting tubes to a great extent. We demonstrated the utility of the method by fabricating thin film transistors (TFT) using percolating arrays of functionalized carbon nanotubes as the semiconducting layer with nobilities of $30 \text{ cm}^2/\text{Vsec}$ and on/off ratios of 10^6 .

Fig.1. (A) Plot of off current, on current, and linear mobility of all measured devices (40 total— 8 devices per point?) showing the mean +/- SD values as a function of PSEPVE/ SWNT/ molar concentration ratio c , W and L are 200 and 20 μm , respectively, the source-drain voltage $V_{ds} = -0.1 \text{ V}$. (B) On and off current dependence on channel length for $c = 0.018$ (C) AFM images of pristine and PSEPVE functionalized SWNT at $c = 0.018$ and $c = 0.038$.

Fig. 2. Plot of source-drain current vs. gate voltage for (A) FSWNT- PSEPVE and (B) FSWNT- PFMDE TFTs at $c = 0.018$ and $V_{ds} = -0.1 \text{ V}$ and -0.01 V , respectively.

