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High performance organic transistors: Percolating arrays of nanotubes functionalized with an electron deficient olefin

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Precise control over the electronic properties of carbon nanotubes is key to their application in plastic electronics. In the present work, we have functionalized carbon nanotubes with an electron withdrawing nonfluorinated olefins via a 2–2 cycloaddition reaction. Our results suggest that the formation of cyclobutanelike four-member ring at the functionalization site 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 separation requirements. Thin film transistors fabricated from such functionalized tubes exhibit mobilities of ~ 30 cm²/V s and on/off ratios in excess of 10⁶. This simple functionalization represents a low cost path to high performance semiconducting inks for printable electronics. © 2010 American Institute of Physics. [doi:10.1063/1.3457171]

A serious challenge of carbon nanotube for application in electronic devices such as thin film transistors (TFT) is separating semiconducting from metallic tubes from as-synthesized carbon nanotubes. Although various methods have shown some success in separating semiconducting from metallic tubes,^{1–3} a suitable commercialization method remains unattainable.

A considerable amount of work focused on separating single wall carbon nanotubes (SWNT) via monovalent side wall functionalization,^{4–9} which also provided a route to improve solubility while aiding in purification and exfoliation.⁸ Theoretical calculations^{10,11} and supporting experimental work show that monovalent functionalization has a strong effect on the electrical properties of SWNT. It disrupts π transitions in the visible spectra,^{12,13} drastically changes the resistance,¹⁴ shifts the Raman spectra,¹⁵ and can even lead to tube fragmentation.¹⁶ In contrast, very few studies have focused on divalent functionalization of SWNT which creates two neighboring impurity states. Theoretical calculations show that such bonding results in pair of strongly localized bonding-antibonding states far away from the Fermi level. As a result, electronic transport is not strongly affected.^{17–19} Experimental studies are few. The work of Menard-Moyon *et al.*²⁰ on [2+1] cycloaddition of azomethine suggests preferential functionalization of the semiconducting tubes. The far-infrared work of Kamaras *et al.*²¹ shows that a [2+1] cycloaddition with dichlorocarbene largely reduces the density of states at Fermi level; thus preferentially affecting the metallic tubes. Our recent work²² shows that [2–2] cycloaddition of fluorinated olefins suppresses the conductivity of the metallic carbon nanotubes at low addend concentration regime. However, while limited, this body of work suggests that divalent functionalization of

carbon nanotubes may offer a path for controlling the electrical properties fairly independently of tube type, size, and chirality.

In this letter, we show that divalent functionalization of SWNT with nonfluorinated electron withdrawing olefin tetracyanoethylene (TCNE) (C₆N₄) effectively suppresses the conductivity of the metallic tubes without considerable degrading the semiconducting ones. This is consistent with our previous work on fluorinated olefins²² and studies^{23–25} proposing that SWNT interactions with electron donor and acceptor molecules cause significant changes in their electronic and optical properties. As with the fluorinated counterpart,²² functionalization enables the fabrication of percolating semiconducting arrays with high mobilities of 30 cm²/V s and high on/off ratio of 10⁶ without requiring tube separation. Although increasing tube fragmentation is apparent with increasing TCNE functionalization, mobilities of ~ 1 cm²/V s are maintained. This deviates from our studies using F-olefins, where the electrical properties of the semiconducting tubes more rapidly degraded at high functionalization levels. Furthermore, the similarity of the results suggest that, as with the much larger size F-olefins, considerable TCNE functionalization must occur on the outside SWNT walls. This contrasts a previous study²⁶ on the interactions of tetracyanoquinodimethane (TCNQ) and TCNE with carbon nanotubes, which suggests that as with C₆₀, TCNQ and TCNE are rather encapsulated inside the tubes.

As for our experiments, commercially purified high pressure CO SWNTs were functionalized with TCNE and the extent of TCNE functionalization and tubes reactivity was measured via thermal gravimetric analysis (TGA) and x-ray photoemission spectroscopy as detailed in the supporting information.²⁷ Figure 1(a) illustrates our systematic study of the effect of a 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 molar concentrations of TCNE and SWNT. The dramatic reduction in I_{off} with increasing

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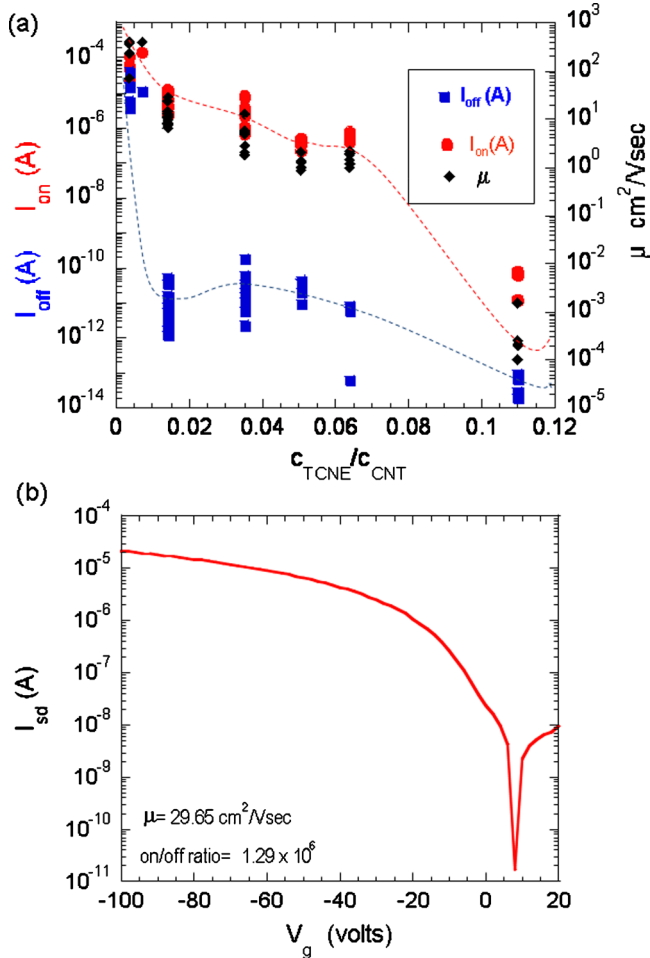


FIG. 1. (Color online) (a) Plot of off current, on current, and linear mobility of all measured devices as a function of TCNE/SWNT/molar concentration ratio c . W and L are $200 \mu\text{m}$ and $20 \mu\text{m}$, respectively, the source-drain voltage $V_{\text{ds}} = -0.1 \text{ V}$. (b) Plot of source-drain current vs gate voltage for FSWNT-TCNE TFT at $c=0.014$.

$c_{\text{TCNE}}/c_{\text{SWNT}}$ concentration represents the key observation of this work. Standard devices, fabricated from a percolating array of pristine HiPco tubes, show high mobilities but are also plagued with high I_{off} , indicating the dominance of conduction pathways due to an abundance of metallic tubes.²² In contrast, TCNE functionalization leads to a dramatic decrease in I_{off} , caused as we will show by a precipitous reduction in the number of metallically conducting tubes. For $c < 0.02$, high mobility was largely preserved while I_{off} was reduced by almost five orders of magnitude as compared to arrays of pristine SWNTs. With increasing $c_{\text{TCNE}}/c_{\text{SWNT}}$ concentration ($0.02 < c < 0.06$) the mobility slowly decreases to about $1 \text{ cm}^2/\text{V s}$ revealing the impact of the chemical treatment on the semiconducting tubes as well. The electrical response of TCNE functionalized tubes in the low functionalization regime is similar to what we reported for fluorinated olefins.²² It suggests that TCNE similar to perfluoro-2-(2-fluorosulfonylethoxy) propyl vinyl ether [$\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$] proceed via cycloaddition, rather than the molecule simply entering the nanotube and acting as a scattering center.

Gate sweep for FSWNT-TCNE under optimum functionalization conditions ($c=0.014$) are shown in Fig. 1(b). The field effect mobilities deduced from the linear regime are $30 \text{ cm}^2/\text{V s}$ with on/off ratios in excess of 10^5 . Due to the

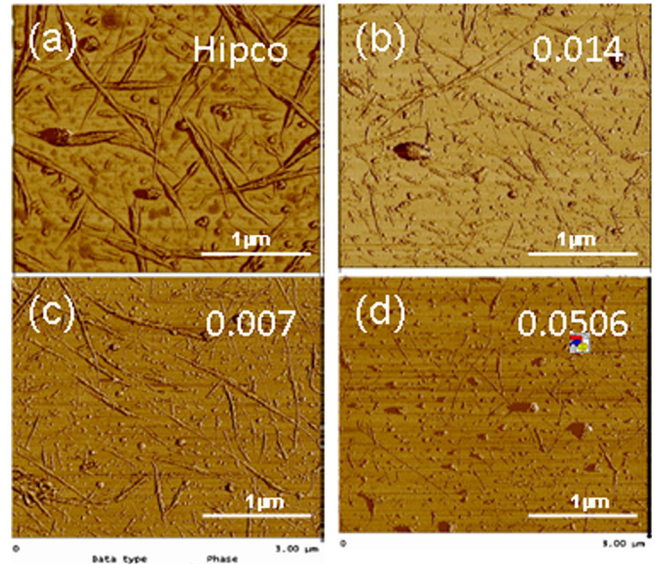


FIG. 2. (Color online) [(a)–(d)] AFM images of (a) pristine and [(b)–(d)] functionalized SWNTs at $c=0.007$, 0.014 , and 0.055 .

high reactivity of TCNE, all TFTs were measured and stored in a nitrogen glove box.

Figures 2(a)–2(d) show the morphology of the arrays measured via atomic force microscopy (AFM). The micrograph of pristine HiPco in Fig. 2(a) shows thick entangled ropes of about $0.6 \mu\text{m}$ in average length. In contrast, micrographs in Figs. 2(b)–2(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, probably caused by a radical mechanism, resulting in shortening of the tubes and also perhaps entering the tubes. The schematic of the possible radical mechanism is shown in the supplementary material.²⁷

The UV-visible, IR, and Raman spectra are shown in Figs. 3(a)–3(d). Figure 3(a) shows optical spectra (UV-visible-near IR) for mats of carbon nanotubes functionalized at $c=0$, 0.0035 , 0.014 , and 0.11 . The broad features at 0.9 to 1.6 eV , associated with the E_{11}^S and E_{22}^S semiconducting transitions, are observed in both pristine and functionalized tubes. It is interesting that such semiconducting transitions persist at $c=0.11$ in spite of the fact that there the tubes of $\sim 200 \text{ nm}$ in length have coiled into nearly spherical entities of $\sim 25 \text{ nm}$ diameter. Figure 3(b) shows that at ($c=0.014$) an IR peak appears at 2200 cm^{-1} associated with the $\text{C}\equiv\text{N}$ IR stretching mode of TCNE (C_6N_4). This indicates that a considerable fraction of the TCNE molecule has not fragmented supporting that the reaction constitutes a cycloaddition.

Figures 3(c) and 3(d) show the Raman radial breathing modes (RBMs) and tangential G bands²⁸ for pristine and FSWNT-TCNE at $c=0$, 0.0035 , 0.014 , and 0.11 at an excitation wavelength of 514 nm . As expected, increasing functionalization strongly reduces the intensity of the bands above 230 cm^{-1} , generally associated with the presence of metallic tubes. The behavior of the bands below 230 cm^{-1} , generally associated with the presence of semiconducting tubes, is less clear. While the intensity of the 180 cm^{-1} band decreases, the intensity of the 220 cm^{-1} band increases with increasing TCNE concentration. This dependence, which was also observed for SWNT functionalization with F-olefins, may reflect a functionalization induced change in

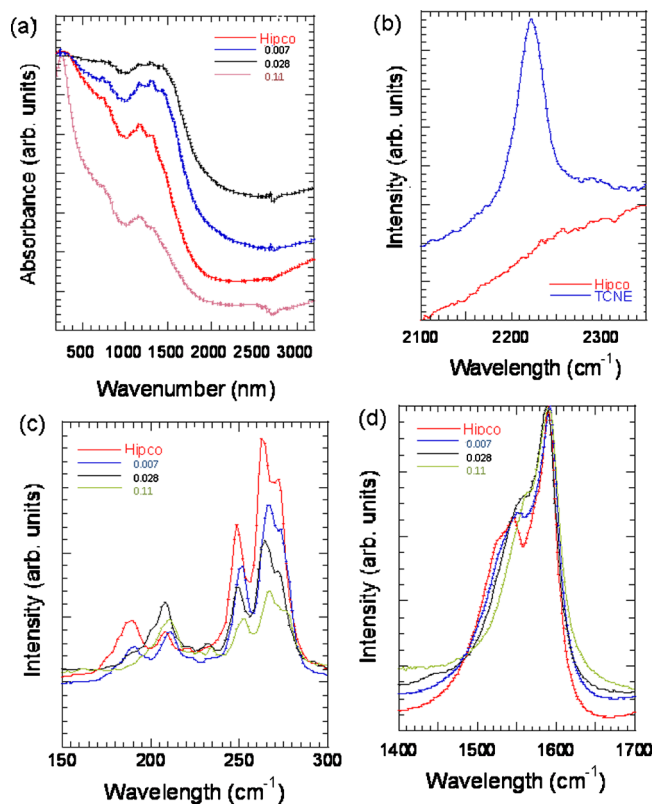


FIG. 3. (Color online) (a) Optical spectra of pristine HiPco tubes and the TCNE functionalized tubes. (b) IR spectra of pristine and functionalized TCNE at $c=0.014$ showing the $C\equiv N$ IR stretching mode of TCNE at 2200 cm^{-1} . [(c) and (d)] Raman spectra of pristine and TCNE functionalized tubes; (c) RBM (d) and tangential and disorder mode region at 514 nm excitation wavelength. Spectra are normalized to the 1591 cm^{-1} band.

the electronic structure of the tube, which moves the resonance condition for the Raman effect. Thus, the 180 cm^{-1} mode is shifting out of resonance while a population of tubes at 230 cm^{-1} is coming into resonance.

The G band of semiconducting tubes consists of two peaks at 1568 cm^{-1} (radial) and at 1591 cm^{-1} (longitudinal), whereas the G band spectrum of the metallic tubes shows bands at 1589 cm^{-1} (radial) and at 1544 cm^{-1} (longitudinal), the latter broadened into a Breit–Wigner Fano line shape caused by a strong coupling to the electronic density of states. The spectra of Fig. 3(d) show that the G band due to metallic tubes is strongly affected by functionalization, whereas the bands due to semiconducting tubes are largely preserved. Therefore, the combined visible and Raman data, combined with the decrease in I_{off} of Fig. 1, indicates that cycloaddition with TCNE in the low reactant regime primarily affects the metallic tubes.

The data presented here suggests that functionalization of SWNT with TCNE, an electron deficient olefin, disrupts the conductivity of the metallic SWNT without degradation of semiconducting ones in the low addend regime. 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 tubes.⁸ Unlike F-olefins, the favorable electrical properties of TCNE functionalized semiconducting tubes are partially retained to

addend concentration beyond $c < 0.06$, whereas they drop off much more rapidly in the F-olefin case. The work further suggests that the electrical properties of tubes functionalized via 2–2 cycloaddition, whether olefins or F-olefins, are fairly insensitive to the difference in binding energy, specific size of the olefin, tube size, or chirality.

In summary, we have developed a simple, high yield method for the functionalization 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.

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²⁷See supplementary material at <http://dx.doi.org/10.1063/1.3457171> for materials and methods and characterization of functionalized tubes.

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