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Rectifying Diodes from Asymmetrically Functionalized Single-Wall Carbon Nanotubes

Zhong Wei,[†] Mykola Kondratenko,[†,‡] Lê H. Dao,[†] and Dmitrii F. Perepichka*,[†,‡]

Centre Energie, Materiaux et Telecommunications, Institut National de la Recherche Scientifique,
1650 Bd. Lionel-Boulet, Varennes, Qc, Canada J3X 1S2, and Department of Chemistry, McGill University,
801 Sherbrooke Street West, Montreal, Qc, Canada H3A 2K6

Received June 15, 2005; Revised Manuscript Received February 7, 2006; E-mail: dmitrii.perepichka@mcgill.ca

Single-wall carbon nanotubes (SWNTs) are promising materials for future nanoelectronics technologies, with specific applications as nanowires,[1] semiconductors for field-effect transistors[2] and (bio)-chemical sensors,[3] memory elements,[4] etc. Chemical functionalization of carbon nanotubes by attaching various substituents to side walls and oxidized ends has been extensively investigated, mostly with the aim to improve the solubility and processability of SWNTs.[5] Except for chemical doping effects[6] and suppressing the conductance via destruction of the conjugation by fluorination[7] or side-wall oxidation,[8] little is known about substituent-induced tuning of the electronic properties of SWNTs (although significant modulation of the SWNT conductance, including rectifying behavior, by naturally occurring defects has been demonstrated[9]). On the other hand, an asymmetric functionalization (AF) of a highly polarizable SWNT with electron donor substituents at one end and electron acceptors at the other should yield a highly dipolar molecule for which interesting electronic properties, including current rectification, can be expected. Most recently, an AF of *multiwall* carbon nanotubes (in aligned films immobilized at a solvent−air interface) was reported by Dai et al., but the resulting electronic properties have not been investigated.[10]

Here we describe the first AF of SWNTs and demonstrate modulation of the current rectification by the modified nanotubes. Our synthetic strategy is based on a surface-confined reaction at one end of the tubes (yielding a film of SWNTs covalently linked to the surface), followed by functionalization of the other end via solution chemistry. Specifically, purified SWNTs (produced by HipCO method) were cut by sonication in a mixture H_2O_2/H_2SO_4, according to the modified literature procedure.[11] The resulting short SWNT cylinders, which are terminated on both ends with carboxylic groups (see Supporting Information), were isolated by membrane filtration, dried, and redispersed in dry dimethylformamide (DMF). A substrate covered with a gold film modified with a SAM of 11-mercaptoundecanol was introduced into the SWNT solution along with an excess of a coupling reagent (dicyclohexylcarbodiimide). The surface-confined reaction between the OH group of $AuSC_{11}H_{22}$-OH and CO_2H groups of SWNT forms an ester bond, linking one end of the tube to the surface. This surface-confined reaction leads to formation of SWNT “forest” films (Figure 1a), as demonstrated earlier by several groups.[12] At this point, further modifications should be selective for the CO_2H groups at the “top” end of SWNT because the CO_2H groups at the “bottom” were protected by esterification.

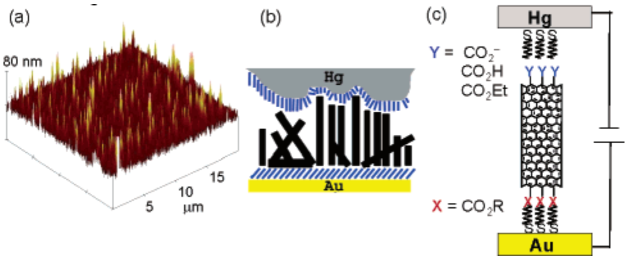

Figure 1. (a) Tapping mode AFM image of SWNT film on Au; (b) scheme of the Au/SWNT/Hg contact; (c) scheme of the studied junctions.

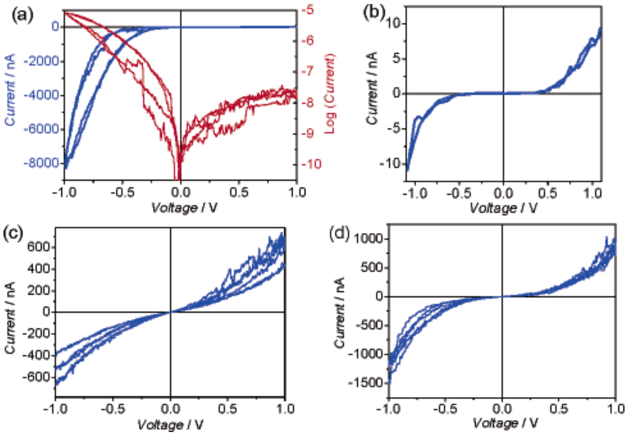

Figure 2. *IV* characteristics of junctions (a) $AuSC_{11}H_{22}O_2C-SWNT-CO_2^-//H_{25}C_{12}SHg$; (b) $AuSC_{12}H_{25}//H_{25}C_{12}SHg$; (b) $AuSC_{11}H_{22}OH//$ physisorbed SWNT $//H_{25}C_{12}SHg$; (d) $AuSC_{11}H_{22}O_2C-SWNT-CO_2Et//H_{25}C_{12}SHg$. The bias voltage was applied to the Au electrode; the sweep rate was 50 mV/s.

To address the induced asymmetry of SWNTs, the conductance of the prepared film was studied in mercury drop junction experiments.[13] A $C_{12}H_{25}SH$-protected mercury drop electrode ($d \sim 0.5$ mm) was brought into contact with the SWNT film under hexadecane solvent (using a micromanipulator), to form an $Au-SC_{11}H_{22}O-SWNT\backslash\backslash C_{12}H_{25}S-Hg$ junction (Figure 1). A similar setup was successfully applied in our group to interrogate a donor−acceptor molecular rectifier.[14] The current−voltage (*IV*) characteristics were measured with a potentiostat in a two-electrode scheme in a cycling mode. The sweep direction or the sweeping rate (50−1000 mV/s) showed no significant effect on the junction conductance. The measurements were repeated on different spots of a slide and on different slides.

Although the AFM image in itself does not allow us to claim a vertical alignment of all SWNTs in the film (i.e., some tubes can well be randomly oriented or lay flat on the surface), the transport characteristics of the junction should be determined by “outstanding”, vertically oriented tubes, connecting both electrodes (Figure 1b).

The typical *IV* characteristics of the studied junctions are presented in Figure 2. The conductance of the $Au-SC_{11}H_{22}O-SWNT\backslash\backslash C_{12}H_{25}S-Hg$ sandwich described above was highly asymmetric, with typical rectification ratio (RR) of $\geq 10^3$ (Figure 2a).

[†] Institut National de la Recherche Scientifique.
[‡] McGill University.

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Such a high RR has never been observed in Hg junctions before. Rather, symmetric *IV* curves are normally produced from alkylthiol/alkylthiol bilayer junctions (Figure 2b), although a weak rectification (RR $\leq$ 10) was reported for junctions with two different monolayers.[13b,c] Furthermore, a similar junction prepared with a physisorbed layer of SWNT (laying flat on the substrate, with no covalent binding) also shows very symmetric *IV* curves (Figure 2c). The current values of SWNT-containing junctions were up to 3 orders of magnitude higher than that for junctions containing only aliphatic monolayers. This is surprising since larger or at least the same tunneling barriers are expected for such junctions. Yet, such an increase of the electron transfer rate by attaching SWNTs to an electrode surface has already been observed.[12c,15]

The high RR observed can hardly be attributed only to a different coupling with two electrodes (covalent bonding vs van der Waals contact) and suggests an electronic asymmetry of the SWNT. Indeed, performing the reaction in basic media of DMF (which also contains traces of Me_2NH) should reasonably result in ionization of carboxylic groups (CO_2^-). In the given monolayer, such ionization should occur preferentially on the upper (not esterified) ends of the tubes, affording a $CO_2R-SWNT-CO_2^-$ structure, with electron-withdrawing alkoxycarbonyl substituents at one end (CO_2R, Hammet parameter $\sigma = +0.37$) and electron-releasing carboxyl anion groups (CO_2^-, $\sigma = -0.10$) at the other end. The resulting electronically asymmetric structure, with electron-rich (CO_2^- end) and electron-deficient (CO_2R end) parts, can be viewed as an Aviram−Ratner molecular diode, and the observed preferential current flow in the acceptor → donor direction (Au → Hg) fits well with this mechanism.[16]

We also performed chemical transformations on the upper end of the tubes and measured their conductance in the same junction experiments. While treating SWNT films with a basic solution (K_2CO_3) shows no effect on the *IV* characteristics (as the upper carboxylic groups were already ionized in DMF), acidification with 1 M aqueous HCl (for 1−2 min) is expected to suppress the ionization of the upper end of the tube and was found to result in dramatically reduced RR (~10−50). A more pronounced effect was observed upon esterification of the upper end groups with ethanol (transforming CO_2^- into CO_2Et), which completely rules out the possible ionization (providing all groups are esterified) and renders electrically symmetric junctions (Figure 2d).

A significant dispersion of the current values (and rectification ratios) was observed from different experiments. A poor reproducibility (or working device yield) is a general feature of most reported monolayer junctions (particularly with quasi-stable mercury contacts). We found it even more pronounced for less ordered (as compared to aliphatic SAMs) SWNT films, which consist of intrinsically polydisperse material (nanotubes of different length, band gap, orientation, carboxylic group density, etc.). At the same time, the analysis of all junctions[17] clearly supports the described trend, with the CO_2^--terminated SWNT showing highly asymmetric *IV* curves and the CO_2Et-terminated SWNT being symmetric for the vast majority of junctions (Figure 3). A particularly broad distribution of RR for the CO_2^--terminated SWNTs (Figure 3b) reflects the unstable character of these junctions and, possibly, a varied ionization level.

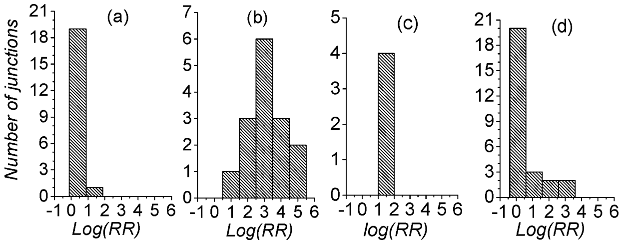

Figure 3. Statistic distribution of rectification ratios measured in the first *IV* cycle for different junctions:[17] (a) $AuSC_{12}H_{25}//H_{25}C_{12}SHg$; (b) $AuSC_{11}H_{22}O_2C-SWNT-CO_2^-//H_{25}C_{12}SHg$; (c) $AuSC_{11}H_{22}O_2C-SWNT-CO_2H//H_{25}C_{12}SHg$; (d) $AuSC_{11}H_{22}O_2C-SWNT-CO_2Et//H_{25}C_{12}SHg$.

In summary, we have shown that asymmetrically functionalized SWNTs can be prepared via surface-confined reactions. The conductance of the nanotube junctions, prepared with the acceptor−donor $CO_2R-SWNT-CO_2^-$ structure, is highly asymmetric (with RR over 10^3), whereas the rectification is suppressed for symmetric (top-end esterified or acidified) tubes. However, at this point, we can only speculate on the mechanism of the observed behavior. The rectification direction (acceptor → donor) is in agreement with the Aviram−Ratner molecular rectification ansatz, although other effects, such as a different coupling to two electrodes or Schottky barrier created by the ionic CO_2^- group, could also contribute to the observed *IV* asymmetry.

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Supporting Information Available: Experimental details, SWNTs characterization data, details of *IV* measurements and analysis; full ref 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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