Chemically Induced Conductance Switching in Carbon Nanotube Circuits

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The chemical reactivity of carbon nanotubes in H_2SO_4 is investigated using individual, single-walled carbon nanotubes (SWNTs) incorporated into electronic devices. Exploiting the device conductance as a sensitive indicator of chemical reactions, discrete oxidation and reduction events can be clearly observed. During oxidation, a SWNT opens circuits to a nanometer-scale tunnel junction with residual conduction similar to Frenkel-Poole charge emission. When electrochemically reduced, a SWNT returns to its original conductance. This redox cycle can be repeated many times, suggesting a novel chemical method of reversibly switching SWNT conductivity.

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The reversible switching of carbon nanotube electrical conductance is being extensively researched, in part due to the tremendous commercial importance of high density memory and logic circuitry. Traditional field-effect transistor (FET) architectures applied to single-walled carbon nanotubes (SWNTs) have demonstrated prototype devices with very competitive electronic properties [1]. While FETs may achieve the highest possible switching rates and most readily integrate with traditional electronics, SWNT conductivity can also be modulated by less conventional means. Polymer coatings [2,3], electrochemical potentials [4,5], adsorbed gases [6], localized charge trapping [7,8], and mechanical deformations [9,10] have all been observed to lead to reversible SWNT conductance changes, and these techniques are currently investigated as the means to building chemical sensors, nonvolatile memory, and other potential products [11].

The success of so many varied methods is due to the extreme sensitivity of SWNT electronic properties to the immediate local environment. With one exception, all of these switching mechanisms work because external electric fields change a SWNT's free carrier concentration and thus its conductivity. The exception is mechanical deformation, in which a rearrangement of the SWNT carbon bonds modulates conductance.

Here, we demonstrate a novel switching mechanism based on reduction-oxidation (redox) cycles at the SWNT sidewall. Using electrochemistry, a SWNT can be oxidized into an insulating state and reduced back to a conducting state. This reversible conductance switching does not depend on field-effect doping and is more similar to the electronic effects of mechanically disrupted chemical bonds. Unlike mechanical bending, however, this redox switching requires no mechanical manipulation and is entirely controlled by electronic voltages. The relevant chemical processes can be slowed by approaching the reaction's threshold potential, at which point the twoterminal SWNT conductance reveals stepwise electronic changes consistent with individual bonding events.

Devices used in this study were fabricated using standard techniques [12] and then modified in a custom electrochemical cell. First, small diameter SWNTs were grown by chemical vapor deposition of methane at 950 °C using alumina-supported iron nitrates [12] or iron keggin molecules [13] as catalysts. Ti electrodes were fabricated on top of the SWNTs using optical lithography and allowed to form a passivating surface oxide. Some of the devices were further coated with an insulating layer of polymethylmethacrylate (PMMA), an effective electrolyte barrier [14-16] into which small windows were opened directly over the SWNT using electron beam lithography. The PMMA windows, which had typical dimensions of $1 \,\mu m \times$ 10 μ m, restricted the exposed area to a thin strip in which a single SWNT lay on bare SiO_2 surface [Fig. 1(a)]. The PMMA windows were determined to be immaterial to the



FIG. 1 (color online). (a) Atomic force microscopy image in which PMMA protects the entire device except for a short segment of exposed SWNT sidewall. Scale bar is 1 μ m. (b) Characterization and chemical modification proceeds with 5 independent electrodes: Pt counter and reference electrodes (CE, RE) to control the electrolyte, a backgate voltage V_g to affect the SWNT carrier concentration, and two working electrodes (WE) connected at either end of the SWNT device. (c) G(V) for a semiconducting SWNT FET, showing electrostatic modulation as a function of backgate voltage V_g in air and $V_{\rm WE}$ in deionized H₂O. Note that conventional definitions of V_g and $V_{\rm WE}$ require the top axis to be reversed.

experiments, having no discernible effect on any of the results described below. Nevertheless, the windows helped confirm that the primary chemistry was occurring on the SWNT sidewall and rule out the possibility of reactions at the Ti-SWNT interface [17].

The measurement configuration, an adaptation of previous work [4,5], is schematically depicted in Fig. 1(b). Completed devices were submerged in electrolyte with the exposed SWNT section acting as an electrochemical working electrode. Bare platinum wires in contact with the electrolyte were used as counter and reference electrodes. The setup constitutes a 4-wire extension of the typical 3-electrode electrochemical cell, since two independent electrodes contact opposite ends of the SWNT. The extra contact allows continuous monitoring of the SWNT conductance during electrochemical currentvoltage and chronoamperometry scans. A small bias (10-100 mV) applied to the SWNT limits the accuracy with which we can determine the SWNT half-cell potential, but the primary source of error is from the use of Pt as a pseudoreference.

Semiconducting SWNTs are very effectively gated on and off by electrolyte solutions [4,5], which capacitively couple to the SWNT carriers. Figure 1(c) depicts a typical SWNT conductance *G* as a function of the potential V_{WE} applied between the SWNT and the electrolyte, which in this instance is deionized H₂O. At moderate positive V_{WE} , the SWNT achieves a high-conductance state as it is electrostatically populated with positive (hole) carriers. This *p*-type behavior reproduces the FET characteristic measured in air using a backgate and is consistent with SWNT FET behaviors generally reported [1].



FIG. 2 (color online). (a) $G(V_{WE})$ for voltage ramps staying within and exceeding past the SWNT oxidation threshold $(V_{WE} > 0.9 \text{ V})$. An oxidation event results in a flat, zero conductance state stable until V_{WE} again exceeds the reduction threshold ($V_{WE} < 0.0 \text{ V}$). Reduction returns $G(V_{WE})$ to its original shape and magnitude (dashed curve). Measurements of G(t)at constant V_{WE} reveal sharp steps under oxidizing (b) and reducing (c) electrochemical conditions; two complete redox cycles from the same SWNT device are depicted here.

Beyond mere electrostatic doping, however, a positive $V_{\rm WE}$ is also an oxidative potential and the intimate contact between a SWNT and its surrounding electrolyte can promote chemical reactions [15]. Electrolysis of H_2O , for example, occurs above +1.3 V. While the SWNT happens to be more chemically stable than H_2O , this Letter specifically focuses on electrochemical oxidation in sulfuric acid (1 M H_2SO_4 in deionized water, Fisher Scientific). H_2SO_4 is effective for SWNT purification and separation because it does not normally oxidize the sidewall of a SWNT unless assisted by cavitation, defects, or other, more aggressive reactions [18-20]. Using an electrochemical potential, on the other hand, H₂SO₄ readily etches pits into crystalline graphite [21] and bulk SWNTs [20,22]. While such etching only slightly changes the conductivity of a graphite electrode [23,24], a SWNT is a one-dimensional conductor for which the oxidation of a single bond is sufficient to change G considerably, and the apparatus described above is ideal for measuring such effects. Theoretical modeling predicts that a single vacancy or substitutional dopant could affect *G* by 50% [25–29].

Figure 2(a) shows three $G(V_{\rm WE})$ curves acquired in H_2SO_4 . V_{WE} is uniformly cycled at a rate of 4 V/s up to and beyond the SWNT oxidation threshold, which is experimentally found to be at +0.8 V (vs Pt). Exceeding the threshold enables oxidative etching, which is observed indirectly as abrupt drops of the conductance to zero. Unlike the case of electrostatic doping, in which positive V_{WE} leads to carrier accumulation, this oxidation event produces a persistent open circuit behavior in which $G(V_{WF})$ is insensitive to carrier concentration over a wide range of bias. At negative bias, $V_{\rm WE}$ becomes a reducing potential and the SWNT can return to its original, conducting state. The dashed curve in Fig. 2(a) is acquired after a complete redox cycle and demonstrates that $G(V_{WE})$ curves before and after SWNT redox can be indistinguishable. The use of high-speed $V_{\rm WE}$ ramps and small excursions past the oxidation threshold allow such curves to be routinely acquired.

To clarify the process further, Figs. 2(b) and 2(c) show time traces of G(t) for a similar device biased at fixed V_{WE} under oxidating and reducing conditions. During oxidation, a small number of discrete jumps in G(t) lead to a stable open circuit. During reduction, the circuit remains open for a period of time but ultimately returns to a conducting state, again by discrete jumps. The initial G(+0.9 V) and the final G(0.0 V) values differ, but comparison with $G(V_{WE})$ indicates this effect to be primarily due to electrostatic gating. As proof, a second redox cycle is shown on the same axes. All four curves are obtained sequentially from the same SWNT, which can be cycled ten or more times in the absence of other contaminant reactants. Irreversibility most commonly occurs in the form of a slightly elevated oxidation threshold during the very first redox cycle (e.g. +0.9 V), and a failure to recover after many cycles or long oxidizing stresses. Thus, there is evidence that the chemical disruption of the SWNT is not fully reversible. Nevertheless, the degree of reversibility is much higher than has been observed in other chemical modifications of SWNT circuits [30], and future work may determine whether a particular contaminant species is responsible.

The lengthy latencies observed in Fig. 2 are a direct result of the biasing conditions. Near the threshold for oxidation or reduction, the mean time before a reaction event occurs can be extended to tens of seconds. Alternately, exceeding these thresholds by 0.3 V or more results in more immediate switching events with latencies ≤ 1 ms. While speedy switching is of practical interest, the threshold conditions shown here help to distinguish between SWNT conductance changes and Faradaic currents in the cell (i.e. transients between CE and WE).

Allowing for this possibility of reversible redox chemistry, the conductance $G(V_{\rm WE})$ of a SWNT may no longer be considered a single-valued function for $0 < V_{\rm WE} <$ 0.9 V. In this range, the SWNT can be in either of two electronic states—its pristine, high-conductance state or an oxidized, open-circuited one—with a large hysteretic memory. Some bistability is observed at intermediate $V_{\rm WE}$, but the SWNT tends to rapidly stabilize into one of its two end states. We note that this bistability makes the present mechanism distinctly different from the oxide-induced hysteresis described in the literature [7,8,14]. The thresholding behavior, by which the device is stable at $V_{\rm WE} =$ 0.7 V but unstable at 0.8 V, is a second distinct difference.

Even though the SWNT is "broken" from an electronic point of view, the reversibility indicates that chemical oxidation is relatively mild. The SWNT is not, for example, being macroscopically etched, since the loss of carbon atoms from the lattice into solution would almost certainly be irreversible. No structural gaps in the oxidized SWNT can be found within the resolution limits of atomic force microscopy. Apparently, the conduction channel is disrupted even though the SWNT structure is primarily intact, a combination of features predicted by theoretical modeling [25-29]. In fact, models predict that single-bond events should be sufficient to change G to the degree observed in Fig. 2. Our observations of stepped changes in G(t) and stochastic, voltage-activated timing are both suggestive of individual reaction events and single-bond kinetics. We therefore propose that the switching is due to local oxidation, perhaps confined to a single carbon bond for each jump in conductance. In this model, the electrochemical potential uniformly concentrates bisulfate $HSO_4^$ ions at the SWNT surface; conductance jumps result when one or more ions covalently bind to the sidewall, changing the conjugation from sp^2 to sp^3 . Identical electrochemical processes, with thresholds similar to those observed here, have been extensively studied for high quality graphite crystals [31] and bulk SWNTs [20,22] in H₂SO₄.

To further investigate the nature of the oxidized state, oxidized SWNT devices were removed from solution and placed in a vacuum cryostat for additional characterization. The vacuum environment allows more accurate measurements and higher source-drain potentials than can be achieved in the presence of conductive electrolyte.

Figure 3 shows the current-voltage (I-V) characteristics, acquired at $V_g = -10$ V, from one oxidized SWNT. The wide, zero-current plateau and the nearly exponential increase at high bias are characteristic of a nanometer-scale tunnel junction. Furthermore, measurements at T = 250, 150, and 77 K are nearly indistinguishable. Park et al. [29] predict that a single sidewall reactant will produce an electronically localized state with a 1.5 nm extent, which is in reasonable agreement with our junction behavior. Nevertheless, the I-V's do not have the correct functional form for a simple tunnel gap: the low bias conductance exhibits a cusp and the temperature dependence is small but reproducible and more marked at elevated temperatures [Fig. 3(b)]. These deviations from simple tunneling characteristics cannot be attributed to the SWNT itself, even accounting for Schottky emission [1] at the metal electrode interfaces.

Both the *T* and *V* dependence of the current empirically fit the expression $I(V,T) = aV \exp[(bV^{1/2} - c)/kT]$ where *a*, *b*, and *c* are all positive constants. As shown in Fig. 3(c), plotting $\ln(I/V)$ vs $V^{1/2}/T$ produces a family of straight lines with a common slope b = 900. In semiconductor junctions, this behavior corresponds to Frenkel-Poole emission [32], a process depicted in Fig. 3(d). In Frenkel-Poole emission, direct tunneling is assisted by localized states contained within a nonideal barrier. Thermal emission from the localized states, combined



FIG. 3 (color online). Electrical characterization of an oxidized SWNT. (a) *I-V* characteristics are highly nonlinear, approximately exponential in voltage, and nearly temperature independent at or below room temperature. (b) Differential conductance exhibits a broad, deep conductance suppression at small bias, corresponding to the low conductance state shown in Fig. 2. (c) The temperature and bias dependence are well fit by a Frenkel-Poole mechanism in which the current is primarily regulated by thermal emission from localized states within the barrier (d).

with their repopulation via direct tunneling, gives rise to a nonequilibrium steady state occupation and a temperaturedependent current. We interpret the agreement between the data and the Frenkel-Poole model to mean that the SWNT conductance is primarily regulated by one or more localized states in the oxidized region of the SWNT. These states should include those predicted by Park *et al.* [29], but we suspect additional involvement by charge traps in the SiO₂ directly underneath the SWNT.

In principle, I(V, T) measurements on a Frenkel-Poole junction uniquely determine the geometric width of the tunnel barrier and the mean depth in energy of the charge traps. While the SWNT data exhibit straight-line fits, the curve offsets do not coincide as they would for a planar junction and reasonable values for the tunnel barrier properties cannot be determined. The SWNT case is further complicated by series Schottky barriers at the Ti interfaces and poor thermal equilibration between the SWNT and the measured substrate temperature T. These two mechanisms cause deviations in the low bias and high current regions of Fig. 3(c). Furthermore, data acquired at the lowest sample temperature T = 77 K exhibit a different slope b unless an effective temperature T' = 120 K is used, suggesting that moderate self-heating is observed in this case.

Finally, the current literature on SWNT chemistry focuses almost exclusively on bulk reactions, in which it is difficult to discriminate between the reactivity of endcaps, defects, pristine sidewalls, and contaminants. The technique demonstrated here uses the SWNT as an electronic transducer, and can be designed to unambiguously address only the reactivity of the SWNT sidewall. In this sense, the technique complements and adds to characterization methods like Raman spectroscopy [20,22]. While the reversibility of the H₂SO₄ redox cycle had not been previously appreciated for SWNTs, the technique can surely be generalized to other conducting electrolytes. Effective use of the backgate should further extend the technique to a wider range of chemistries, including gas-phase reactions and reactions with organic or other insulating liquids. Furthermore, the chemical control illustrated here may complement efforts to build robust molecular circuits using SWNTs [33].

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