Scaffolding Carbon Nanotubes into Single-Molecule Circuitry

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ABSTRACT

While nanowires and nanotubes have been shown to be electrically sensitive to various chemicals, not enough is known about the underlying mechanisms to control or tailor this sensitivity. By limiting the chemically sensitive region of a nanostructure to a single binding site, single molecule precision can be obtained in order to study the chemoresistive response. We have developed techniques using single-walled-carbon-nanotube (SWCNT) circuits that enable single-site experimentation and illuminate the dynamics of chemical interactions. Discrete changes in the circuit conductance reveal chemical processes happening in real-time and allow SWCNT sidewalls to be deterministically broken, reformed, and conjugated to target species.

INTRODUCTION

Chemical, biological, and even mechanical sensor prototypes are all currently explored as possible applications for carbon nanotube (CNT) devices (*1*). In each case, researchers attempt to exploit the exquisite sensitivity of carbon nanotubes while directing this sensitivity towards a particular target. Because pristine CNTs and as-fabricated devices have cross sensitivities to a wide range of adsorbates including air and water, control over selectivity is a critical research problem. CNT functionalization techniques, in which sensitizing groups are added to a CNT, provide promising solutions to both enhancing sensitivity and directing selectivity. Both noncovalent coatings and covalent sidewall modifications have been used to engineer the electronic properties and environmental sensitivities of CNTs, at least in bulk or on films of networked CNTs (*2*).

While additions of chemical groups along a CNT certainly do lead to sensitivity enhancements, they also result in an ensemble measurement of the environment and do not take advantage of a CNT's dimensionality. In principle, the response of a 1-D system may be dominated by a single scattering site (*3*). In this limit, a CNT circuit can be used to directly transduce single-molecule interactions such as recognition and docking with useful dynamic information. Fig. 1 depicts the two architectures and the type of electronic signals which might be obtained from them. The ensemble device (Fig. 1A) may be advantageous as a commercial sensor demanding calibrated concentration dependence. The single-site sensor (Fig. 1B) is a more useful tool for understanding the transduction mechanism and for studying single-molecule chemistry, and it can be further parallelized to provide the same reliability and calibration as the ensemble device.

Here we describe the fabrication and testing of the single-site CNT architecture and provide a proof of principle of its transduction capabilities.
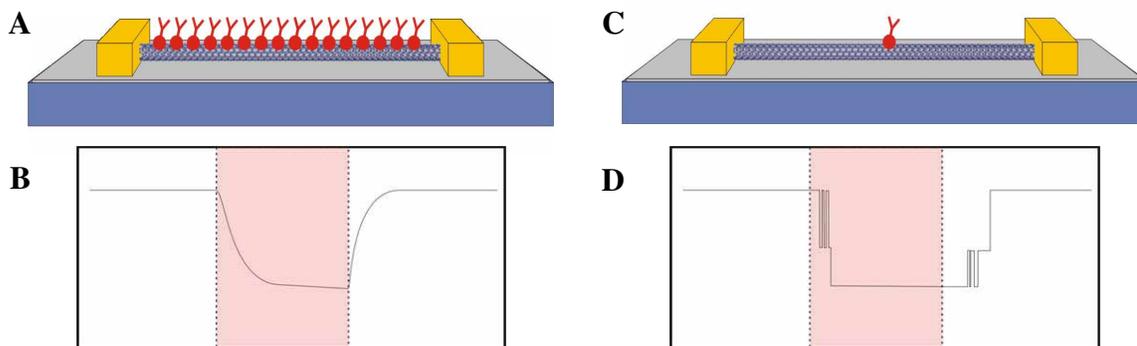
Figure 1*: An example of a common sensor architecture in which one or more CNTs are continuously coated with receptor groups (**A**) in order to produce a chemoresistive response (**B**). Because the CNT is a one-dimensional conductor, a singly-functionalized device (**C**) can in principle provide the same level of signal and sensitivity while also identifying discrete, stochastic events associated with the chemical interactions (**D**). While the former architecture is better suited for monitoring analyte concentrations, the latter enables real-time monitoring of single-molecule recognition and docking events.*

EXPERIMENT

To maximize the consequences of 1-D conductivity, single-walled carbon nanotubes (SWCNTs) have been exclusively used. The SWCNTs were grown using chemical vapor deposition on a thermally oxidized silicon substrate, and then electrically contacted using Ti or Pd contacts defined by optical lithography. Devices were electrically characterized in air and those which showed unusually high contact resistance or anomalous current-voltage features were discarded. Often, multiple devices were constructed from the same, long SWCNT, each having a channel length of 2 μm.

To produce devices with single-site functionalities, an electrochemical point-oxidation technique was used (*4*). Devices were placed in a custom electrochemical cell with the SWCNT constituting the working electrode. Platinum wires were calibrated versus SCE for use as pseudo-reference and counter electrodes, and the potentials were controlled with a customized potentiostat system (*5*). Electrodes contacting the SWNCT, as well as any other exposed metal, were protected by layers of polymethyl methacrylate (PMMA) so that only a small portion of the SWNCT sidewall was exposed to the electrolyte during oxidative treatments. Further details on the sample fabrication and electrochemical processing are described previously (*4-6*).

In order to limit the electrochemical functionalization to a single site, the two terminal conductance *G* of pristine SWCNT devices is monitored continuously throughout the electrochemical processing. Chemical alterations of the SWCNT sidewall can be individually distinguished in the electronic signal *G(t)*, as each covalent addition produces a discrete jump. The dynamics of *G(t)* during oxidation show a series of stepwise drops in G, and electrochemical reduction results in steps back up through the original values (*4*). By monitoring the steps in real time, the chemical changes to the SWCNT sidewall are easily recognized and controlled.

After initial oxidation, devices can be removed from the electrochemical cell and placed into a vacuum chamber to minimize further chemical changes. Point-oxidized SWCNTs were electrically characterized in a Desert Cryogenics vacuum probe station and imaged using vacuum

atomic force microscopy (AFM; JEOL JSPM 5200). Modified AFM modes such as scanning gate microscopy (SGM) and Kelvin probe force microscopies (KPFM) are also performed.

In concert with electrical characterization, further chemical treatments can be done to vary the functional group attached to each SWCNT. The electrochemically oxidized point defect is a versatile attachment site for different moieties, allowing a wide range of chemical tests to be accomplished. For example, a brief treatment with $KMnO_4$ results in the conversion of the defect to a carboxyl group (7). This functionality allows conjugation to be measured using standard carboxyl reactions with N-ethyl-N'-(3-dimethylaminopropyl) carbodiimide (EDC) or phthalic anhydride.

RESULTS and DISCUSSION

Fig. 2 shows a typical oxidation measurement performed in 1 M H_2SO_4, at a potential of +0.6 V vs. Pt. As adducts attach and migrate along the SWCNT, sharp drops and multi-level fluctuations are visible in *G(t)*. Individual steps are readily resolved when the electrochemical potential is maintained near the threshold of oxidation, since this slows the rate of stochastic oxidation events. Exceeding the threshold by more than 0.2 V often results in a rapid drop in *G* with little resolvable structure. Furthermore, any chemical dynamics within a single oxidation step are faster than our experimental resolution of 10 µs.

The combination of voltage control over the reaction rate and temporal control over the reaction extent allows devices to be deterministically modified. While reaction rates can, in principle, be determined from the stochastic events, a simpler experimental protocol involves a feedback mechanism from the measured *G*. We rely on the changes in *G* to determine the extent of oxidation and to stop the oxidation at an appropriate point. Two states are indefinitely stable: one corresponding to the initial SWCNT conductance G_i and one at which the low bias conductance has dropped to less than 0.01 G_i (8). Once *G* has reached the low state, continued oxidation usually ensures the creation of additional functional sites. Alternately, zeroing the oxidation potential as soon as this state is reached affords a high yield of singly-functional sites.
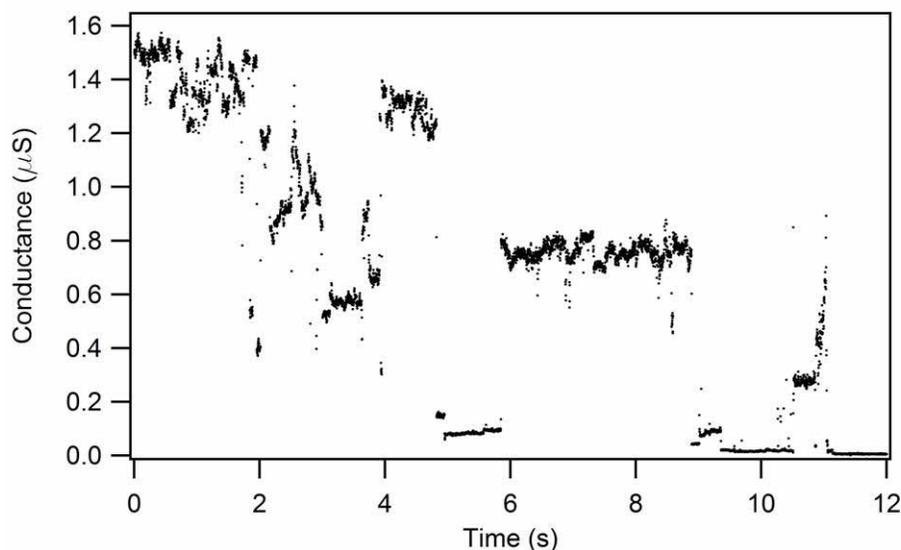

Figure 2*: Real-time electrochemical oxidation of a SWCNT sidewall*

Figure 3A depicts the current-voltage (I-V) characteristics of a SWCNT before and after the introduction of a point oxidation. At low biases, the oxidized site severely limits conduction and results in a nearly-open circuit. High bias characterization proves the barrier to be limited in extent, unlike the case of a completely oxidized SWCNT. Further temperature characterization (not shown) suggests the barrier to be thermally activated (6).

Scanning probe techniques prove the electrical effects to be highly localized to small segments of the SWCNT. SGM and KPFM measurements directly image the local transconductance and potential gradients of these oxidized states (9). An example KPFM measurement is shown in Fig. 3C. Before oxidation, KPFM shows no substantial potential drop along the SWCNT; but after oxidation, the same SWCNT exhibits a substantial voltage drop at a random site along its length. No voltage drop is observed at the contacts, indicating that contact resistance at the electrodes is not the cause of the change in I-V. In fact, the point functionalization appears to dominate the device conductance, an electronic effect which is ideal for transducing chemical attachments.

A complementary type of mapping employs chemical labeling to identify reactive sites. Regions of large local resistance in SWCNTs have been proven to have a one-to-one correspondence with regions of enhanced chemical reactivity (4, 5). Thus, the device can be considered a 1-D, metal-insulator-metal heterostructure in which only the insulating region displays the correct surface chemistry for further chemical functionalization. Furthermore, this oxidized region provides a mechanical stability to the device which is not typically present in molecular electronics architectures which rely on gaps or other spacers. Oxidized devices have been thermally cycled from 4 – 600 K with no sign of mechanical degradation.
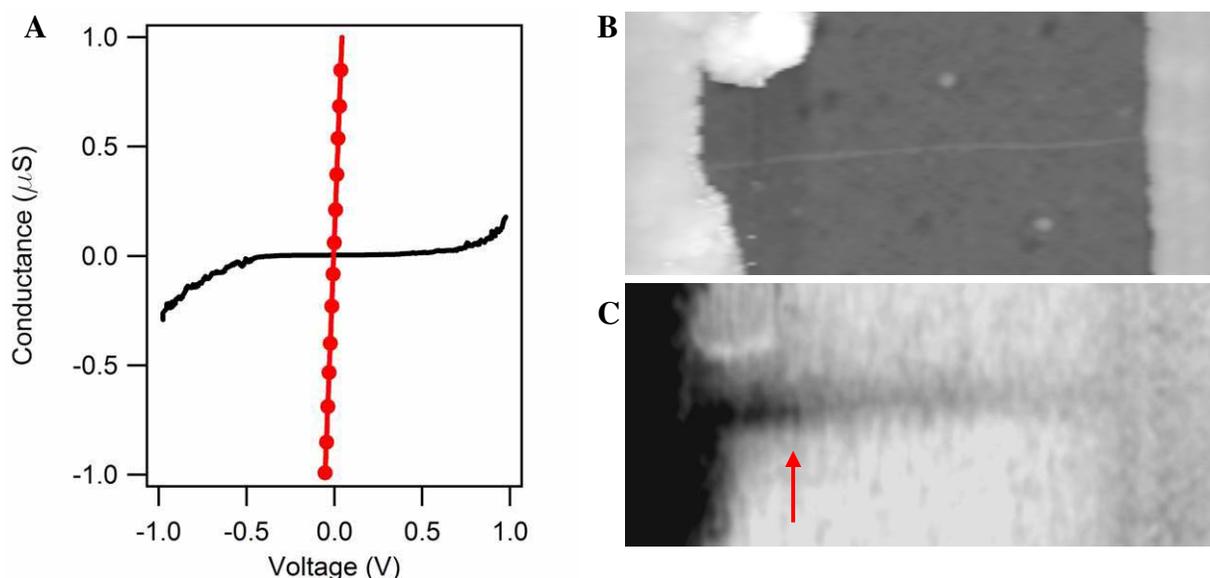

Figure 3: *(A) I(V) of a SWCNT before any treatment (red) and after electrochemical point functionalization (black). (B) AFM topography cannot readily resolve the chemical modification. (C) KPFM image of the SWCNT's electrostatic potential identifies a localized, high-resistance region (red arrow) corresponding to the point functionalization.*

Once constructed, these circuits exhibit interesting dynamic noise and fluctuations, which are presumably due to their molecular attachments. To test this hypothesis, various point-functionalized devices have been characterized as they interact with different reactive environments. For example, we have focused on chemoselective reactions with carboxylates produced by the point oxidation method.

Fig. 4 depicts $G(t)$ for a KMnO$_4$-treated SWCNT containing one or more carboxyl-terminated groups. Current fluctuations in air or solvent have a 1/f spectrum typical for SWCNT conductors (Fig. 4A) (*10*). More complex, two-level fluctuations are sustained when a chemoselective reagent is added to the solvent (Fig. 4B). The data shown here are for measurements in ethanol, with and without 10 µM phthalic anhydride. Similar results have been observed in water using 10 µM EDC. In both cases, the high selectivity of the reagent towards carboxylates, combined with the known importance of carboxylates on G, suggest that the switching in Fig. 4B can be attributed to a chemical process. Further analysis of the dynamics may provide direct insights into the kinetics of the carboxylate activation, potentially with single molecule resolution.
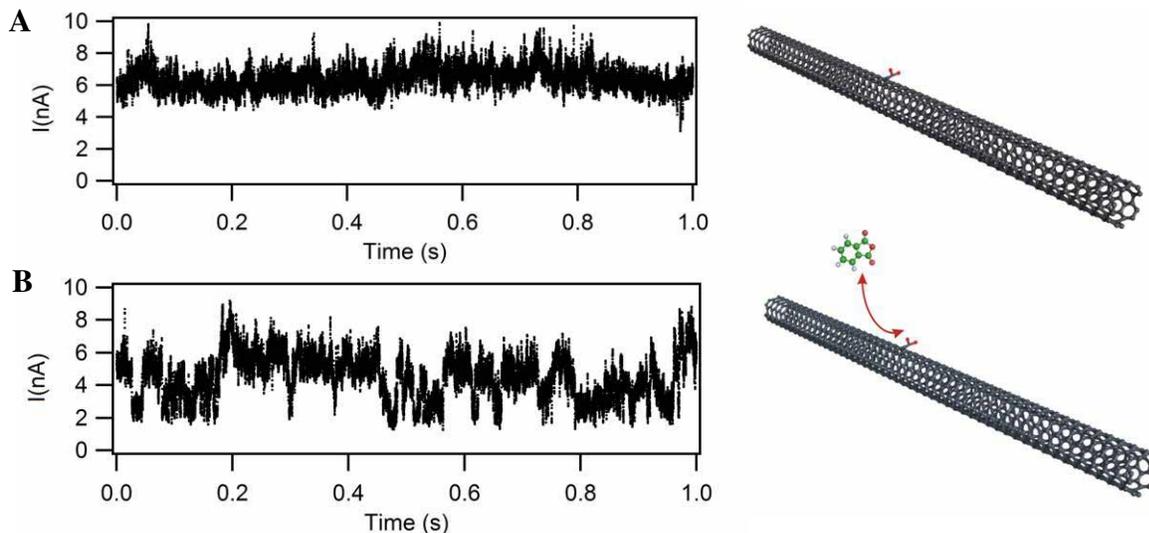

Figure 4: *Current vs. time for a point-oxidized SWCNT device having a carboxylate termination. Measurements in ethanol (**A**) differ from measurements in ethanol with 10 µM phthalic anhydride (**B**) by the presence of a two-level fluctuator. The added fluctuation is presumably due to the chemoselective interaction between the phthalic anhydride and the carboxylate.*

CONCLUSIONS

Tracking the conductance of a SWCNT device during electrochemical modification can help monitor and control the extent of SWCNT sidewall functionalization. Changes visible in $G(t)$ during this process give us insights into the details of the oxidation and can even help to tailor the functional attachments. Chemoselective chemical assays, combined with other characterization techniques such as KPFM, clearly resolve the chemoresistive effects of the modified sites. When limited to a single site, single-molecule fluctionations can be directly observed which would not normally be possible in an ensemble measurement.

ACKNOWLEDGMENTS

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