OUTSTANDING SYMPOSIUM PAPER

Scaffolding carbon nanotubes into single-molecule circuitry

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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 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.

I. INTRODUCTION

Chemical, biological, and even mechanical sensor prototypes are all currently being 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 toward 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 non-covalent 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.[2–6]

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 particular the one-dimensional (1D) nature of single-walled carbon nanotubes (SWCNTs). The response of a 1D conductor like a SWCNT may be dominated by a single scattering site,[7–11] making such conductors extremely sensitive to chemical changes at those controlling sites. Figure 1 depicts the two architectures and the type of electronic signals that might be obtained from them. The ensemble device [Fig. 1(a)] may be advantageous as a commercial sensor demanding calibrated concentration dependence. The single-site sensor [Fig. 1(c)], on the other hand, may be a more useful tool for understanding transduction mechanisms and for studying single-molecule chemistry. For example, such circuits might directly transduce single-molecule interactions
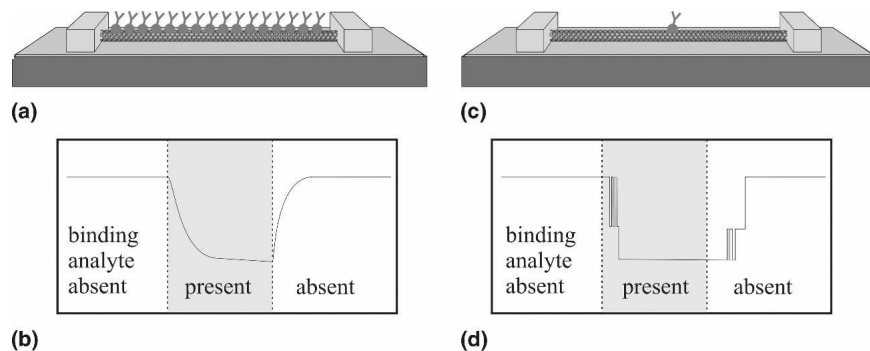
FIG. 1. Example of a common sensor architecture in which one or more CNTs are continuously coated with receptor groups (a) to produce a chemoresistive response (b). Because the CNT is a 1D conductor, a monofunctionalized device (c) can in principle provide the same level of signal and sensitivity while also identifying discrete, stochastic events associated with the chemical interactions, and the characteristics of their timing (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. Curves (b) and (d) are schematic representations of typical data in the literature.

such as recognition and docking with useful dynamic information, and they could be further parallelized to provide the same reliability and calibration as the ensemble device in Fig. 1(a). This premise has motivated our previous research into the fabrication of SWCNT circuits with point defects.[12] Here we describe the fabrication and testing of the single-site SWCNT architecture and provide a proof of principle of its transduction capabilities.

II. EXPERIMENTAL

To maximize the consequences of 1D conductivity, small-diameter SWCNTs have been used exclusively. SWCNTs with 1.1 ± 0.1 nm diameters were grown using chemical vapor deposition on a thermally oxidized silicon substrate[13,14] and then electrically contacted using Ti or Pd contacts defined by optical lithography. Devices were electrically characterized in air and those that 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.[12] Devices were placed in a custom electrochemical cell with the SWCNT constituting the working electrode. Platinum wires were used as pseudo-reference and counter electrodes, and the potentials were controlled with a potentiostat system.[15] The electrodes contacting the SWNCT, as well as all other exposed metal on the sample, 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 technique are described previously.[12,15,16]

To limit the SWCNT functionalization to a single site,

the two terminal conductance G of pristine SWCNT devices is monitored continuously during the electrochemical processing. Chemical alterations of the SWCNT sidewall can be individually distinguished as discrete jumps in the electronic signal $G(t)$.[12] 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. By monitoring the steps in real time, the chemical changes to the SWCNT sidewall are easily recognized and controlled.

After their initial oxidation, devices are 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 (Lakeshore Cryogenics VFTTP4, Westerville, OH) and imaged using vacuum atomic force microscopy (AFM; JEOL JSPM 5200; Tokyo, Japan). While AFM topography is not sufficiently sensitive to image the point functionalizations, modified AFM modes such as scanning gate microscopy (SGM) and Kelvin probe force microscopies (KPFM) do resolve the electronic changes.

In concert with electrical characterization, further chemical treatments can be done to tailor 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 this paper, we use a two-step protocol[17] optimized for the creation of defects with carboxyl functionalities. The first protocol step involves introduction of an epoxide or ether group, accomplished by oxidation and reduction of the SWCNT in H_2SO_4,[12] a step analogous to oxidation of graphite in H_2SO_4.[18] Oxidation of the epoxide in acids does not produce carboxylates but does prepare the site for successful attack by $KMnO_4$. In approximately 50% of the devices tested, oxidation followed immediately by exposure to $KMnO_4$ results in a defect site having a carboxylate[17];
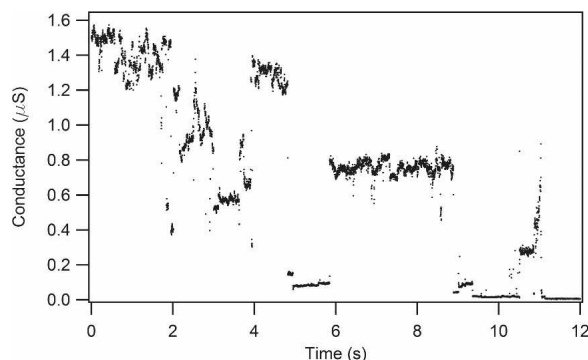
FIG. 2. Real-time electrochemical oxidation of a SWCNT sidewall in H_2SO_4. $KMnO_4$ is added to the acid at time = 11.2 s, immediately following the first drop in G below 0.01 μS.

the remaining devices can be successfully converted by repeating the protocol, with each cycle having a 50% yield. The desired chemical termination has been confirmed by conjugation assays, but it is most easily identified by a near-zero G that resists any electrochemical reduction.[12,17]

III. RESULTS AND DISCUSSION

Figure 2 shows a typical oxidation measurement performed in 1 M H_2SO_4 at a potential of +0.6 V versus Pt. As adducts attach and migrate along the SWCNT, sharp drops and multilevel 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.[16] 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 initiation of oxidation and to limit it appropriately. For example, once G has dropped to less than 1% of its initial value, continued oxidation usually ensures the creation of multiple functional sites. Alternatively, zeroing the oxidation potential as soon as this state is reached affords a high yield of mono-functional sites. The application of $KMnO_4$ converts existing defects into carboxylates but does not appear to create new damage on pristine SWCNT sections.[12]
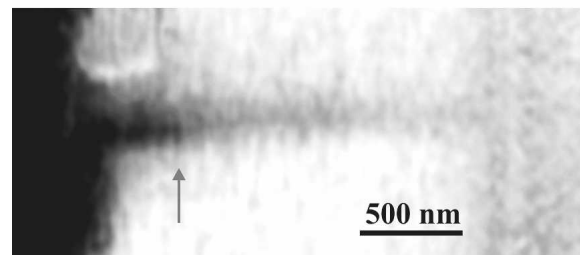
Figure 3(a) depicts the current-voltage (I-V) characteristics of a SWCNT before and after the introduction of
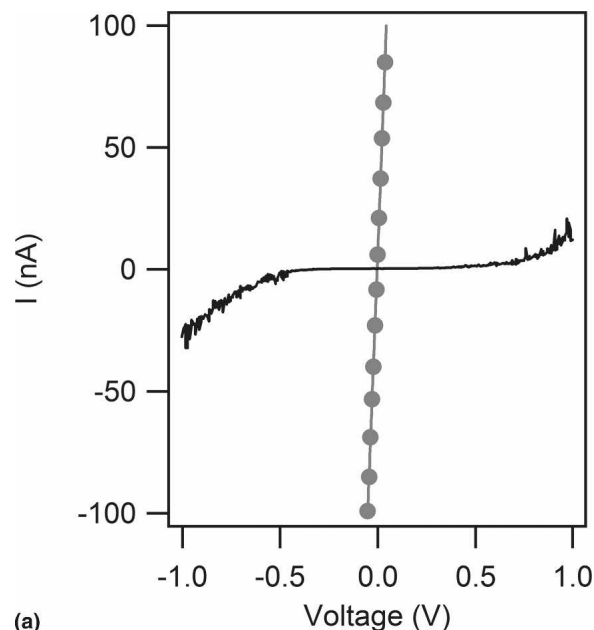
(a)
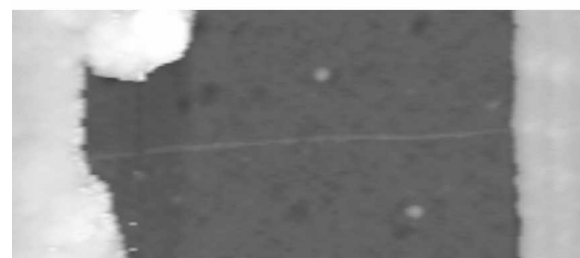
(b)

(c)

FIG. 3. (a) $I(V)$ of a SWCNT before any treatment (circles) and after electrochemical point functionalization. (b) AFM topography cannot readily resolve the chemical modification. (c) KPFM image of the SWCNT's electrostatic potential identifies an abrupt change in potential over a very short distance, corresponding to the high-resistance region (arrow) of the point functionalization.

a point oxidation and its conversion to a carboxylate. At low biases, the oxidation severely limits conduction and results in a nearly open circuit. High bias characterization proves the conduction barrier to be limited in extent, unlike the case of a completely oxidized SWCNT. Further temperature characterization has proven that the high bias conduction is thermally activated, as in Frenkel–Poole mechanisms.[16]

Scanning probe techniques prove the electrical effects

to be localized to small segments of the SWCNT. SGM and KPFM measurements directly image the local transconductance and potential gradients, respectively, of these oxidized sites.[19] An example KPFM measurement is shown in Fig. 3(c). Before oxidation, KPFM shows no substantial potential drop along the SWCNT; 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 observed change in I-V. Instead, the point functionalization appears to dominate the device conductance, an electronic effect that is ideal for transducing chemical dynamics at the site. The device can be considered a 1D metal-insulator-metal heterostructure in which only the insulating region displays the desired surface chemistry. Furthermore, this oxidized region provides mechanical stability to the device, which is not typically present in molecular electronics architectures relying on gaps or other spacers.

Once constructed, these circuits can exhibit interesting dynamic noise and fluctuations, a portion of which are presumably due to their molecular attachments. To test this hypothesis, point-functionalized devices have been characterized in the presence and absence of reagents chemoselective (a carbodiimide) and reactive (a carbodiimide and an anhydride) toward carboxylate groups.

Figure 4 depicts $I(t)$ at constant bias (100 mV) for two different SWCNT devices, each containing a defect site with at least one carboxylate-terminated group. For both devices, the nominal current fluctuations have a 1/f spectrum typical of pristine SWCNT conductors [Figs. 4(a) and 4(c)].[12,20] However, more complex fluctuations appear and are sustained when a chemoselective reagent is added to the measuring environment [Figs. 4(b) and 4(d)].

In the first case, the device is measured in aqueous 0.02 M phosphate buffer (pH 4.5) with and without the addition of 10 μM N-ethyl-N'-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC). [The phosphate buffer was prepared using dibasic sodium phosphate (Fisher Scientific) and phosphoric acid (pH 4.5), diluted with de-ionized water to 0.02 M.] EDC is a highly selective reagent uniquely suited for coupling reactions to carboxylates.[21] Before addition of EDC, the device exhibits a stable current with a mean value of 4 nA in buffer [Fig. 4(a)]. In the presence of EDC, $I(t)$ jumps between two stable current levels of approximately 4 nA and 1 nA [Fig. 4(b)]. The additional fluctuation is presumably due to chemical interactions or bonding between EDC and the carboxylate site. Although theoretical modeling has not yet addressed this specific system, a 75% drop in current is not at odds with the existing literature.[10,11]
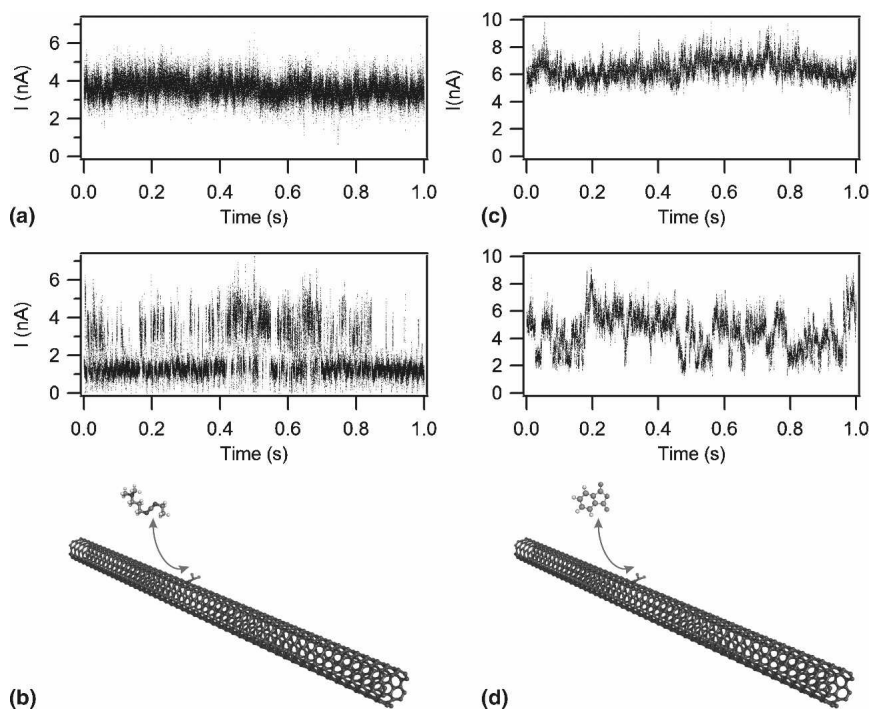

FIG. 4. Current versus time for two point-oxidized SWCNT devices, treated with KMnO$_4$ to produce carboxylate functionalities. Measurements in phosphate buffer (a) differ from measurements in the presence of buffer with 10-μM EDC added (b) by the presence of a two-level fluctuator. The second device is tested with 10-μM phthalic anhydride in ethanol, and similar changes are observed between when the anhydride is (c) absent or (d) present. The added fluctuations in (b) and (d) are presumably due to the presence of the carboxylate and its reactions with the reagents. A schematic illustration of each chemical system is depicted below the data.

The second device was measured in an ethanol environment and probed with 10-μM phthalic anhydride. This anhydride reacts with both carboxylates and ethanol but not the pristine SWCNT sidewall. In this sense, reactions are still selective to a single molecular site on the device. A stable current of 6–8 nA is recorded in pure ethanol [Fig. 4(c)], but more complex fluctuations occur in the presence of phthalic anhydride [Fig. 4(d)]. In addition to its original fluctuations, $I(t)$ now intermittently drops by 50% to about 2.5 nA. We believe that chemical events at the carboxylate generate this two-state fluctuation. Possible reactions with the carboxylate include either anhydride exchange with phthalic anhydride or transesterification from the ethyl ester of phthalate, arising from phthalic anhydride reaction with ethanol.

Discrete, two-level fluctuations are a hallmark of single molecule optical techniques,[22] and the presence of such signals from the modified SWCNTs is encouraging. A reagent-dependent sensitivity is clearly observed, and the new transduction appears to be limited to discrete, two-state events. A comparison of the EDC and anhydride results further suggests differences in the timing and duration of the events, as well as their relative effect on the SWCNT current. Further study is necessary to determine whether these attributes reproducibly vary for different reagents.

IV. 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 resolve the chemoresistive effects of the modified sites. When limited to a single site, single-molecule fluctuations can be directly observed in the device current that would not normally be possible in an ensemble measurement.

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