

# Functional single-molecule devices based on SWNTs as point contacts

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We present a universal lithographic methodology for creating single molecule devices based on single-walled carbon nanotubes as point contacts. These contacts are formed by electron beam lithography and precise oxygen plasma etching. Through robust amide linkages, functional molecular bridges with diamines are covalently wired into carboxylic acid-functionalized nanogaps to afford single molecule devices with desired functionalities.

In the scenario of device miniaturization motivated by the limits of the inherent quantum effects of conventional silicon-based devices, creating efficient optoelectronic devices using individual functional molecules, often termed “molecular electronics”, is one of the ultimate goals in nanotechnology.<sup>1,2</sup> Since the development of reliable techniques to produce conventional silicon-based devices with dimensions smaller than 10 nm is a formidable technological challenge, molecular electronics has been likened to a promising alternative to silicon in post-CMOS devices through a bottom-up

approach. Work in this area is still focused on the construction, measurement, and understanding of the electronic and photonic responses of nanoscale circuits in which molecular systems play an important role as pivotal elements. Over the past decade extensive experimental and theoretical efforts have been made toward fabricating metal–molecule junctions and building functional optoelectronic devices using individual organic molecules.<sup>3–6</sup> Quite a few different pathways have been developed including the mechanically controllable break junction,<sup>7,8</sup> electromigration break junction,<sup>9</sup> nanoparticle–molecule metal junction,<sup>10</sup> STM break junction,<sup>11–14</sup> self-aligned template method,<sup>15</sup> and so on. One of these techniques, which might have potential broad applications, is the so-called self-aligned lithographic approach for production of nanoscale electrodes.<sup>15</sup> The major advantage of this technique is that it is a self-aligned lithographic process able to produce large numbers of molecular-scale gaps with

remarkably high yield and precision. Through two-step reaction sequences, the “lock” molecules having been attached on the surface of metal electrodes hold the second functional groups, which have the strong affinity with the “key” molecules to finish the circuits. This “lock-and-key” approach is useful because it not only avoids the assembly and reactivity problems associated with dithiols, but it also offers a clear path to multifunctional molecular electronic devices. Although all these methods have many advantages, their limitations lead to large disagreement between experimental and theoretical results.<sup>11,13,16</sup> Current research in single-molecule electronics still suffers from several great challenges. One of the greatest challenges is the ill-defined bonding at the molecule–metal contact interface, even for the most commonly-used thiol–gold contacts.<sup>7–11,16,17</sup> Moreover, even if more conductive contact structures are built (such as alkylidenes on transition metals and on metal carbides),<sup>18,19</sup> molecular-scale metal

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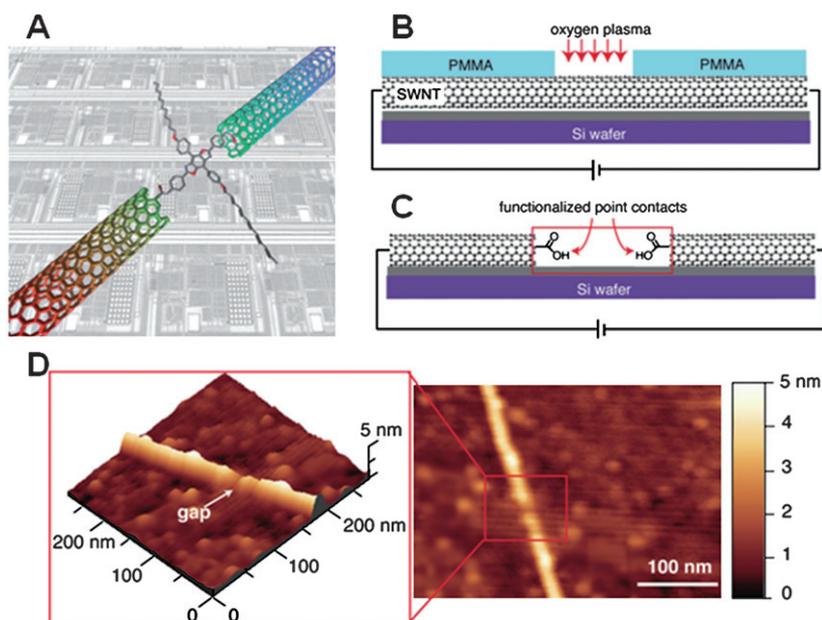


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electrodes are extremely difficult to fabricate and lack the specific chemistry for molecular attachment at their interfacial ends. To achieve reliable results, one should try as best as possible to consider the device fabrication process as a holistic one. The electrode materials, contact chemistry, and the molecular number to be tested are so closely inter-related that they cannot be optimized independently. An improved strategy would create a well-defined contact between the electrode and the molecule of interest, would have a limited number of binding sites, and would be intrinsically molecular in scale.

Single-walled carbon nanotubes (SWNTs), the paradigm materials in carbon families, have been regarded as one of the best nanostructural materials derived from bottom-up chemical synthesis approaches.<sup>1,2</sup> Carbon nanotubes have the simplest chemical composition and atomic bonding configuration but exhibit perhaps the most extreme diversity and richness among nano-materials in structures and structure–property relations.<sup>20–23</sup> SWNTs are one-dimensional (1D) ballistically-conducting nanowires that are intrinsically the same size as the molecules and easily processable for nanofabrication. SWNTs are formed by rolling up a graphene sheet into a cylinder along a certain lattice vector. This hints at useful conduction *via* the  $\pi$ -bonding network. Moreover, depending on the chirality and diameter, SWNTs can be either metallic or semi-conducting. This suggests different energy band alignment scenarios between SWNTs and molecules. These can be expected to yield a useful variety of device properties. Ultimately, SWNTs are molecular chemicals, and therefore we can, to an extent, tailor their chemical reactivity. As a result of all of these features, SWNTs should be ideal point contacts for single-molecule devices.

Recently we developed such a general approach to making SWNT electrodes for building single molecule devices as shown (Fig. 1A).<sup>24</sup> To fabricate the SWNT electrodes we start by preparing an array of SWNT transistors and spin-coating this array with a blanket layer of PMMA. Then we open a window (<10 nm) on top of individual SWNT transistors using ultra high-resolution electron-beam lithography (Fig. 1B). We then cut the



**Fig. 1** A) Schematic demonstration of holistic construction of a single molecule circuit. B) Very fine cutting of SWNT with oxygen plasma introduced through an opening in a window of PMMA defined with e-beam lithography. C) The results of oxidative opening of the tubes are point-contacts that are functionalized on their ends and separated by as little as  $\sim 2$  nm. D) AFM image of the gap cut into the SWNT. Inset: height profile of the isolated tubes.

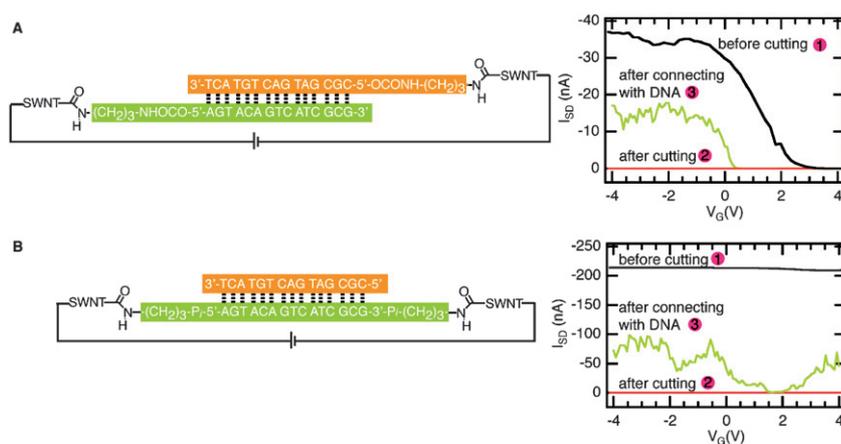
nanotubes through the window *via* oxygen plasma ion etching. Given the strongly oxidizing conditions of this method, we expect the cut ends of these half-tubes to be capped predominately with carboxylic acids (Fig. 1C). Fig. 1D shows an AFM image of one nanogap. By taking the imaging convolution of the AFM tip size into account, we can estimate that an upper boundary on the size of a typical gap in these micrographs is  $\sim 10$  nm. Under optimized conditions,  $\sim 20$ – $25\%$  of the tubes were completely cut. This method differs from the formation of SWNT electrodes by electrical breakdown, which has been used recently to realize pentacene nanotransistors.<sup>25,26</sup> Amide linkages are then used to covalently connect cut single-walled carbon nanotubes, which act as nanoscale electrodes to molecules that conduct electrical current (Fig. 1A). All of the elements in the resulting molecular circuits are naturally at small dimensions because the SWNTs are one-dimensional (1D) ballistic conductors or semiconductors that are the same size as the molecules being probed.

The chemical contacts provided by amide-linked molecular bridges are robust and can endure chemical treatments and environmental stimuli. This provides us with many opportunities to install capa-

bilities into the electrical devices that are inherent to the synthetic molecular backbones. Functionality can be installed in the molecular backbone that allows the creation of pH- and photo-gated switches.<sup>27–29</sup> Furthermore, this method allows for the assembly of multicomponent structures, which offer devices that are sensitive to protein/substrate binding and DNA hybridization.<sup>30,31</sup>

Most recently, we have developed a novel method of creating molecular electronic devices through two steps to measure the conductivity of a single DNA duplex, which is an area of substantial interest.<sup>31</sup> This method allows us to integrate individual DNA strands into SWNT electrodes, thus accomplishing the first measurements of the electrical properties of a single DNA duplex in its native conformation.

To make these measurements, DNA sequences having amines on their termini are coupled to the SWNT electrodes through the now-familiar amide linkages in a two-step strategy: acid activation and amide formation. Two different device connectivities are explored. In one case, both of the 5' ends of a DNA duplex are modified with amines, which are used to bridge each end of the half-tubes (Fig. 2A). In another case, both the 3' and



**Fig. 2** Source-drain current versus  $V_G$  at a constant source-drain voltage ( $-50$  mV) for: A) semiconducting SWNT device before cutting, after cutting and after connection with the DNA sequence shown; B) metallic SWNT device before cutting, after cutting and after connection with the DNA sequence shown.

5' ends of a single strand are amine-functionalized and linked to the SWNT gap. In either case the reconnected devices recovered their original electrical characteristics (p-type semiconducting or metallic) as shown in Fig. 2B. These measurements place the resistance of well-matched DNA duplexes with  $\sim 6$  nm length in the range of  $0.1$ – $5$  M $\Omega$ .

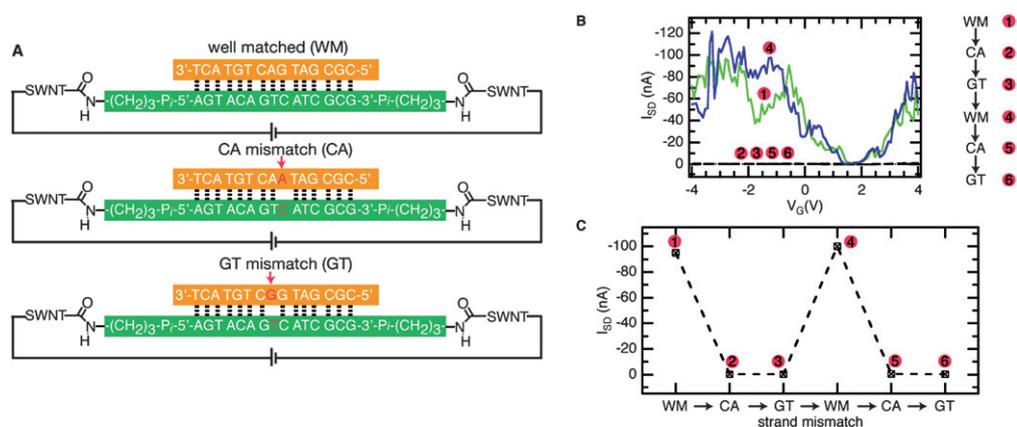
In a separate experiment, devices were also reconnected with mismatched DNA since DNA-promoted charge transport is found to be exquisitely sensitive to the integrity of the base pair stack.<sup>32</sup> As shown in Fig. 3, a device reconnected with a well-matched (WM) DNA duplex is dehybridized and subsequently rehybridized with two different strands with a mismatched DNA strand to generate CA and GT mismatches (Fig. 3A). Rehybridization

with a strand generating a CA mismatch reduces the current significantly and yields an increase in the ON-state resistance of nearly 300-fold from  $0.5$  M $\Omega$  to  $155$  M $\Omega$  (Fig. 3C). Replacing the CA mismatch with a GT mismatch does not change the device characteristics. The original ON-state resistance and current levels can be recovered by replacing the GT mismatch with the original WM sequence. It's important to note that the integrity of the DNA duplex is necessary for its conductivity. This is confirmed by another experiment where a blunt end restriction enzyme *Alu I* is used to cut the DNA, thus eliminating the conductive path. Since the enzyme only acts on DNA in its native conformation, this shows that the DNA duplex is intact when bridging the ends of the SWNTs.

In summary, we developed a reliable lithographic strategy for creating single molecule devices based on single-walled carbon nanotubes electrodes. Precisely cut single-walled carbon nanotube electrodes with gaps in the range of  $1$ – $10$  nm can be covalently wired by different single conjugated molecules through robust amide linkages. This strategy is reliable and allows a wide variety of single molecules, or small collections of molecules, to be tested electrically. Installation of functionalities in electrical devices can be achieved by employing a diversity of molecules with functional groups, for example, well-matched and mismatched DNAs. Although the research in this area is spreading swiftly, molecular electronics is still in its infancy and many of the remaining challenges are large. The development of new systems, where the electrode can function as a chemical reagent and serve as a platform for chemistry, is needed. Another formidable issue in molecular electronics is a great shortage of efficient integration strategies. Predictably, the next generation of devices would be a network of interfaces where the molecules function as pivotal elements to control the interfaces. More research is necessary to bridge hard electronics with the vast store of the soft molecular world.

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**Fig. 3** A) Replacing well-matched (WM) duplexes with CA and GT mismatches; B) Source-drain current versus  $V_G$  at a constant source-drain voltage ( $-50$  mV) for a SWNT device taken through the sequence 1 through 6. The current levels for curves 2, 3, 5, and 6 are  $\sim 300$  times lower. C) Source drain current at  $V_G = -3$  V at a constant source-drain voltage ( $-50$  mV) for the sequence 1 through 6.

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