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Chemically Tunable Nanotube Electronics

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Especially with rapidly developing methods to synthesize and to fabricate nanostructures of different chemical compositions and shapes of increasing complexity, nanoscale materials that exhibit unique properties will play an important role in emerging and next generation technologies. Advances in diverse areas from nanoelectromechanical systems, miniaturized sensors, photovoltaics, and biological tags to high performance large area electronics are currently being considered. A critical aspect in all of these applications is the influence of surfaces and interfaces which inevitably arises from the large surface-to-volume ratio inherent to all nanoscale materials. The main focus of this project lies in fundamental understanding of interfacial/surface chemical effects on the electronic, optical, and mechanical properties of nanoscale materials incorporated into electronic devices and circuits. Our interdisciplinary research program combines synthesis, modeling, chemistry, device fabrication, and characterization to explore chemically tunable properties of carbon nanotubes and to develop efficient routes to incorporate novel phenomena into functional devices and architectures.

Single-walled carbon nanotubes are considered here as the prototypical nanoscale material containing atoms all at the surface. Carbon nanotubes also possess extraordinary properties such as ballistic transport with mean free path on the order of micrometers[2] and the highest density normalized elastic modulus.[3] In order to preserve and to exploit these properties within potentially manufacturable devices, effects arising at the interfaces need to be well understood. Nanotube/electrolyte interface is considered here initially as it provides readily accessible means to vary the surrounding environment in a controlled manner (concentration, pH, composition of electrolyte etc.). Chemical functionalization and interfacial effects on the electronic and mechanical properties of nanotubes in model device configurations will be examined. Insights from these studies will in turn be exploited to develop systems with unparalleled capabilities including tunable transistors/diodes and chemically selective resonators which can be integrated into a novel systems architecture suitable for analog RF, digital as well as memory circuit implementations.

Once we can understand and control them, the highly sensitive properties of SWNTs to variations in the local chemical environment can be exploited to "tune" their electronic performance. As an example, we have shown that the adsorption of polymers with chemical groups of varying electron donating/accepting ability can allow controlled doping of SWNT transistors as shown in fig. 1.[4] Careful examination of electron injection from polymer chemical groups have led to new insights on band gap dependent doping processes in semiconducting SWNTs.[5] Complimentary studies on metallic SWNTs is questioning how we should consider electron-phonon coupling in low dimensional materials in general.[5] Addition of electrolytes in the polymer films has allowed facile and high efficiency

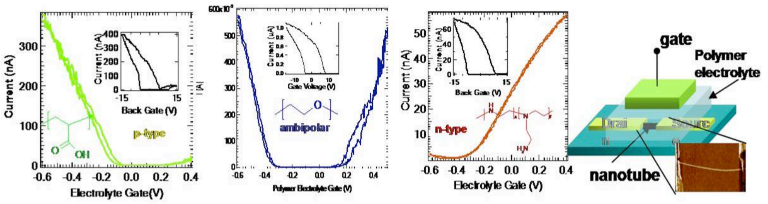

Fig. 1. Controlled doping of SWNT transistors by simple polymer adsorption. Varying the electron donating/accepting ability of chemical groups of the polymer can lead to "tuning" of the doping levels to allow p-, n-, and ambipolar devices.

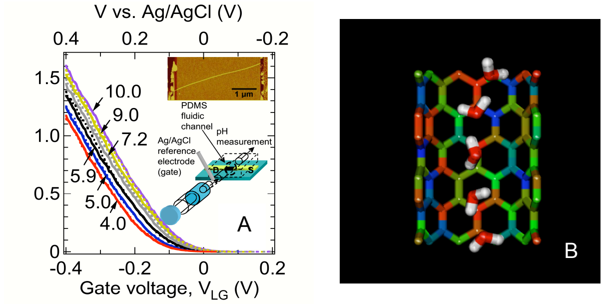

Fig. 2. (**A**) pH dependent electrical characteristics of a SWNT transistor integrated with a microfluidic channel. Upper inset is the AFM image of the device. The pH response may be associated with local chargeable groups. (**B**) Simulation of water molecules in a partially charged (10,0) SWNT.

electrostatic gating of SWNTs while providing short Debye lengths to screen out extraneous effects of the surrounding environment. This advantage of the electrolyte systems, is allowing new studies in optical and electrical properties of SWNTs in aqueous solution. The first key step is in the understanding of how "pristine" SWNTs behave in controlled chemical environment. To this end, we have examined how SWNTs' electronic properties are affected by the pH of the surrounding aqueous solution containing inert electrolyte KCl.[6] There is a systematic positive shift of the threshold voltage with increasing pH as shown in fig. 2A. This electrical response of SWNTs may be explained by local chargeable groups. Modeling and simulations are being carried out on SWNT/water systems help explain the experimental observations (fig. 2B).

Along with these studies on "pristine" systems, we have also examined functionalized SWNTs where we can fine-tune the response of SWNTs and introduce selectivity. One such example employing single strand DNA functionalized SWNT is shown in fig. 3.[7] DNA functionalization is carried out by dialyzing individually cholate suspended SWNTs in the presence of DNA resulting in cholate removal and DNA adsorption. Photoluminescence spectra of the initial cholate-SWNT and final DNA-SWNT solutions show a bathochromic shift which has been attributed to a change in the coverage of the SWNT surface in water. The small cholate molecules are able to pack the SWNT surface more densely than the oligonucleotide strands. Optical properties of these functionalized SWNTs that are sensitive to the local chemical environment have been exploited to examine DNA hybridization process and opens new directions in developing sensor materials for medical and life sciences, environmental science, and microbiology.[8, 9]

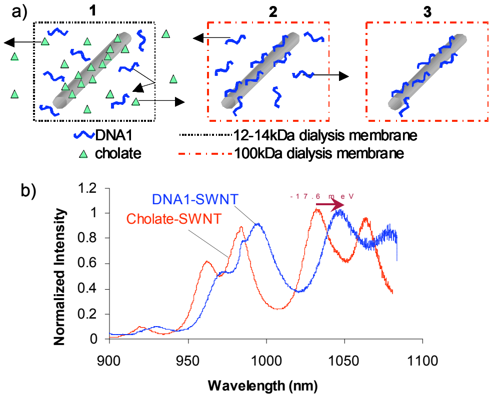

Fig. 3. (**A**) Assembly of DNA on SWNT is achieved by replacing initial surfactant cholate with single strand DNA. (**B**) Comparison of initial cholate-SWNT and final DNA-SWNT photoluminescence spectra.

In order to incorporate these chemically tunable properties of SWNTs into functional device architechtures, we have initiated parallel efforts in SWNT device fabrication. Two of the biggest challenges in any prospects of SWNT-based electronics are the electronic inhomogeneity issue and difficulties in patterning. The electronic inhomogeneity problem is where a random mixture of metallic and semiconducting SWNTs leads to degrade device performance. The second major hurdle is the ability to align and place SWNTs into useful patterns. To this end, we are incorporating aligned growth techniques[10] with electronically selective chemistry[11] to remove metallic SWNTs (or suppress their electrical conductivity). Figure 4 shows aligned an SEM image of SWNTs grown directly on miscut quartz substrate along with a schematic of electronically selective covalent functionalization with 4-Bromobenzene diazonium tetrafluoroborate to suppress metallic conductivity. These two processes are being incorporated into SWNT device fabrication steps to achieve large arrays of SWNT devices which will be used as the platform to incorporate the chemically tunable properties of SWNTs into electronics, optoelectronics, and electromechanical systems.

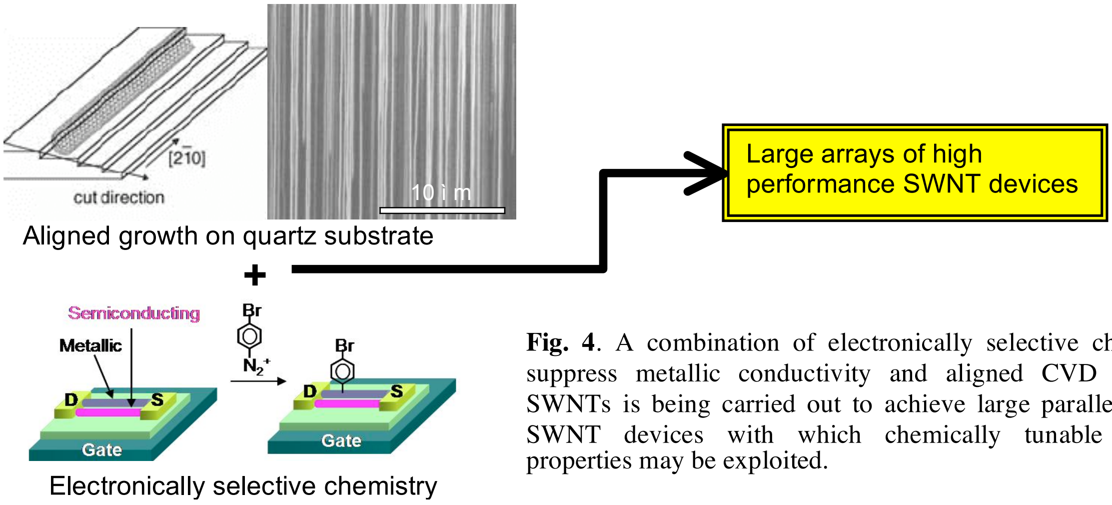

Fig. 4. A combination of electronically selective chemistry to suppress metallic conductivity and aligned CVD growth of SWNTs is being carried out to achieve large parallel arrays of SWNT devices with which chemically tunable electronic properties may be exploited.

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