Synthesis of Carbon Nanotubes into Large Scale Functional Devices

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We have been working in the following areas of carbon nanotube research under the NSF support.

- Chemistry, physics and applications of carbon nanotubes.
- Controlled synthesis of ordered nanotube architectures on surfaces; catalytic patterning of surfaces by microfabrication and soft lithography techniques.
- Development of new catalyst materials for nanotube synthesis.
- Controlled integration of chemically synthesized nanowires into addressable structures for physical measurements.
- Condensed matter physics at the nanometer scale; electron transport studies of carbon nanotubes; nanotube quantum dots; ohmic contacts and ballistic transport.
- Electromechanical properties of nanowires.
- Molecular electronics. Electronic devices based on individual nanotube molecular wires including single-electron transistors, field effect transistors, p-n junctions and Esaki diodes.
- Surface science in nanowires; metal-carbon nanotube interactions; molecule-nanotube interactions; chemical gating effects; alkaline metal doping effects; non-covalent functionalization of nanotubes.
- Research in miniature chemical sensors for detection of small molecules and biological systems.
- Development of large scale nanotube scanning probes by direct chemical synthesis combined with microfabrication and soft lithography; new nanolithography approaches at the 10 nm length scale.

Carbon nanotube is a material that offers exciting opportunities in basic science and technology. The electrical properties of nanotubes span from metallic, semimetallic to semiconducting depending on their atomic structures (i.e., charality). Mechanically, nanotubes have high Young's modulus and tensile strength (~ 100 times higher than steel). It is our belief that the future aspects of nanomaterials in general hinge upon controlled synthesis. We have been developing chemical vapor deposition methods to grow nanotubes on catalytically patterned substrates at desired sites with controlled orientation, diameter, length and potentially chirality. The chemistry involved includes rational design and synthesis of catalyst materials, elucidation of their chemical and physical characteristics, and investigation of various hydrocarbon feedstock and growth conditions. The success in chemical synthesis has enabled new approaches to address the physical (electrical, mechanical, electromechanical) properties of individual nanowires and explore new types of nano-devices (field effect and high temperature single-electron transistors; p-n junctions; chemical sensors; scanning probes). The following are specific achievements of our work.

(A) Synthesis of single-walled carbon nanotubes (SWNT) on patterned substrates

- ***Growth of isolated nanotubes on specific surface Sites***

(J. Kong et al., Nature, 395, 878, 1998)

A chemical vapor deposition (CVD) growth strategy has been developed collaboratively by our group and Quate to grow individual single-walled nanotubes at specific sites on flat silicon oxide substrates. The approach involves methane CVD on substrates containing catalyst islands patterned by electron beam lithography. 'Nanotube chips' with isolated SWNTs grown from the islands are obtained.

- ***Synthesis of self-oriented multi-walled carbon nanotubes***

(S. Fan, et al., ***Science,*** *283, 512, 1999)*

A growth method is developed to obtain ordered multi-walled nanotube (MWNT) architectures. Porous silicon with patterned iron squares is used as the substrate. Regularly positioned arrays of nanotube towers were grown on the substrate by CVD of ethylene. Electron microscopy imaging reveals that the MWNTs within each tower are well aligned along the direction perpendicular to the substrate surface (*see Figure F1*). The nanotube arrays have been explored as field emitter arrays. This is an example demonstrating that large-scale nanotube devices can be obtained by direct chemical synthesis.

- ***Suspended single-walled nanotube networks with directionality***

(A. Cassell et al., J. Am. Chem. Soc. 121, 7975-7976)

(N. Franklin et al., Adv. Mater., 12, 890, 2000)

We developed a method to grow ordered single-walled nanotube (SWNT) structures by methane CVD on catalytically patterned substrates. The growth starts with developing a liquid-phase catalyst precursor material. The catalyst precursor material is contact-printed onto the tops of pillars pre-fabricated on a silicon substrate. SWNTs grown from the pillar tops tend to direct from pillar to pillar (*Figure F2*). Well-directed SWNT bridges are obtained in an area of the substrate and the directions of the SWNTs are determined by the pattern of the elevated structures on the substrate.

(B) Integration and ohmic contacts to SWNTs

(H. Soh et al., Appl. Phys. Lett., 75 (1999) 627-629*)*

Our controlled growth approach readily leads to SWNTs originating from controlled surface sites, and have enabled us to develop methods to integrate nanotubes into addressable structures (*Figure F3*) for the purpose of elucidating their fundamental properties and building devices with interesting electrical, electromechanical and chemical functions. The SWNTs grown from specific sites on substrates are contacted by metal electrodes via lithographic patterning and electron beam evaporation. Ohmic contacts to individual nanotubes are achieved with Ti metal electrodes. Metallic nanotubes exhibit resistance as low as 10 kohms have been reliably obtained.

(C) Synthesis of single-walled nanotubes for scanning probe tips

(E. Cooper et al., Appl. Phys. Lett., 75, 3566, 1999)

We succeeded in directly synthesizing single-walled nanotubes on AFM silicon pyramids. Our approach is to place catalytic materials onto an AFM cantilever, and then carry out CVD growth. Since nanotubes tend to cling to the surface (side) of the silicon pyramid, properly oriented nanotube tips are obtained this way. We have used the SWNT tips to perform lithographic writing with AFM and achieved feature sizes < 10.

(D) Nanotube chemical sensors

(J. Kong et al., Science, 287, 622, 2000)

We have shown that chemical sensors based on individual or ensembles of SWNTs can be obtained to detect electron withdrawing (e.g., nitrous oxide, NO_2) and electron donating molecules (ammonia, NH_3). An individual semiconducting SWNT, upon exposure to 200 ppm NO_2, exhibits an electrical conductance increase by up to three orders of magnitude in a few seconds. On the other hand, exposure to 2% NH_3 causes the conductance to decrease by up to two orders of magnitude. As a general comparison, conventional solid state sensors for NO_2 and NH_3 typically operate at temperatures > 400 °C, whereas conducting polymers provide only limited sensitivity. Semiconducting SWNT sensors are advantageous in terms of the high sensitivity and fast response at room temperature. The chemical sensing mechanisms are related to the question of how molecular species interact with nanotubes and affect their electrical properties, a topic that is now actively explored by researchers.

(E) Nanotube electromechanical properties

(T. Tombler et al., Nature, 405, 769, 2000)

We have grown individual SWNTs from patterned catalyst sites across pre-fabricated trenches on SiO_2/Si substrates. This lead to an individual SWNTs partially suspended over the trenches. AFM tip is used to repeatedly push down the suspended nanotube and then retract. We observe that the nanotube conductance decreases each time the AFM tip pushes the nanotube down, but recovers as the tip retracts. The conductance is found to decrease by a factor of two at ~ 5 degree bending angle (strain ~ 0.3%), but decrease more dramatically by two orders of magnitude at a bending angle ~ 14 degree (strain ~ 3%, figure 13d). Simulation finds that at relatively small bending angles, the conductance of the SWNT exhibits appreciable decrease, but the decrease is relatively gradual. The conductance decrease is caused by the relatively large C-C bond distortions in the nanotube region near the tip. At large bending angles, the nanotube conductance decreases dramatically, as sp^3 bonding sets into the nanotube structure. These results suggest that SWNTs could serve as reversible electro-mechanical transducers that are potentially useful for nano-electro-mechanical devices.