Functionalizing Nanotubes for Novel Properties and Devices – an Integrated Theoretical and Experimental Approach

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Introduction: the objective of this project is to design the material properties of functionalized carbon nanotubes with a combination of realistic quantum-mechanical modeling and experimental synthesis and characterization. Functionalized carbon nanotubes display tunable structural and electronic properties, and promise to become for nanoelectronics a match for what DNA is for the life sciences. The recent development of synthetic methods to attach ligand molecules has been a major breakthrough, and opens the possibility to use molecular self-assembly and nanolithography techniques to arrange nanotubes in a device. An accurate control of the physical properties can also be made possible by target molecular functionalizations that tune the electronic response or the structural conformations. We have an integrated team to design such novel elements for nanoelectronic devices that combines 1) fundamental quantum-mechanical aspects of nanodevice design (Levitov), 2) realistic microscopic electronic-structure simulations (Marzari and Richardson), and 3) experimental nanoscale and spectroscopic probing, chemical synthesis, and device fabrication (Stellacci and Rao). These activities are complemented by on-going collaborations with European colleagues.

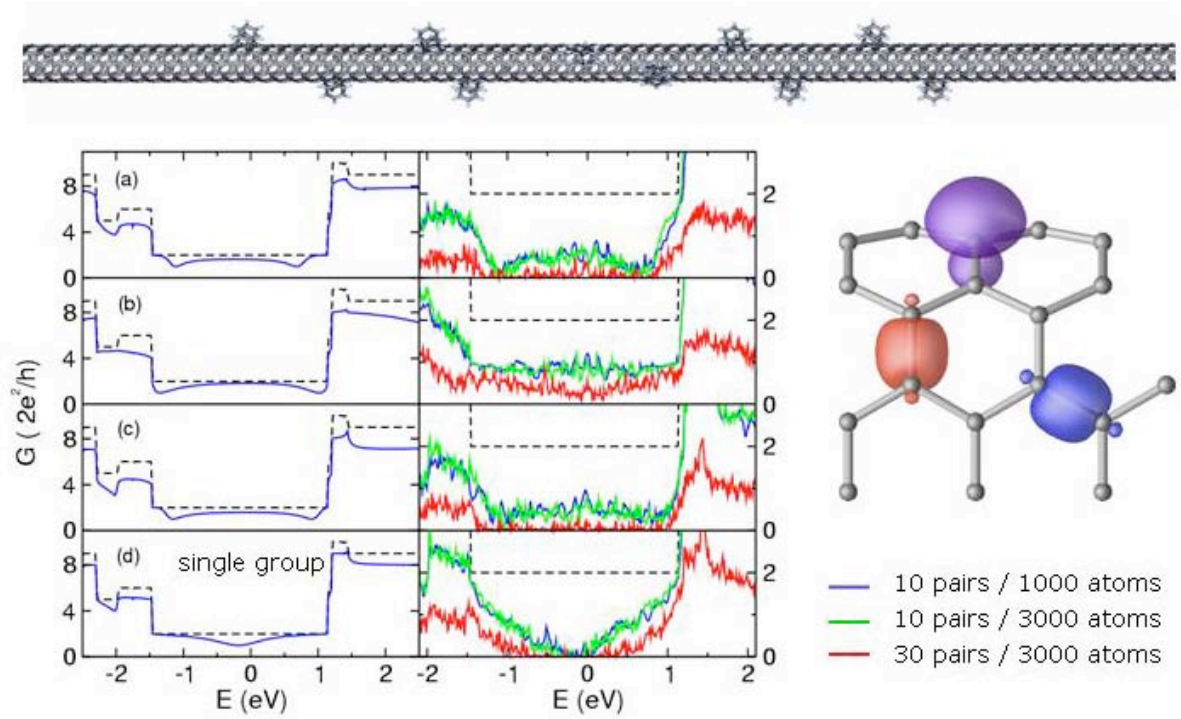

Figure 2: Top: A metallic (5,5) SWCNT has been functionalized in its central segment with phenyl moieties. Bottom left, left column: Scattering effects of a single impurity attached in different configurations and (right column) ensemble-average for the Landauer conductance of the nanotube depicted above, as a function of the density and length of the functionalized segment. Bottom right: Maximally-localized Wannier functions for the pristine (5,5) tube.

Thermodynamical and electronic properties of pristine and functionalized carbon nanotubes: We are using electronic-structure and linear-response techniques to characterize the structural and thermodynamical properties of carbon nanostructures [2], and have developed an original "exact" tight-binding approach, based on maximally-localized Wannier functions, to study with full first-principle accuracy the band structure and quantum conductance of nanostructures containing thousands of atoms [3]. With these tools we are investigating the thermal expansion and contraction of single-wall and multi-walled nanotubes, to evaluate their role as interconnects for nanoelectronics applications, and the effects of functionalization on the long-wavelength phonons populated at ambient temperature. Functionalization of the external wall of a single-wall carbon nanotube (SWCNT) with selected organic molecules such as carbenes, nitrenes, halogens, and aryl moieties alters the hybridization of the carbon atoms involved, and directly affects the transport properties of the tube (see Fig. 1 for the case of phenyl moieties acting as strong scattering centers).

Manipulation of nanotubes in optical traps: We propose that nanotubes, similar to atoms, can be trapped in the focus of a light source and manipulated by coupling to light using optical tweezers. This should allow to perform the basic steps of control, including lifting tubes from surfaces, orienting them in space, and transporting and depositing them on a surface at a prescribed location. While conventional optical tweezers can manipulate macroscopic objects in solution, the nanotubes, due to their small size and weight, can be controlled by light in free space (air or vacuum). Our analysis of an optically trapped nanotube indicates that the tube can be held against gravity using a reasonably small laser power which does not excessively heat the tube. The analysis we carried out includes effects such as the electric polarizability of nanotubes, and in particular the high-anisotropy of the electric susceptibility - this allows to split the confinement problem into two, one for the center-of-mass motion and one for its rotational motion. In both cases we find reasonably favorable confinement parameters.

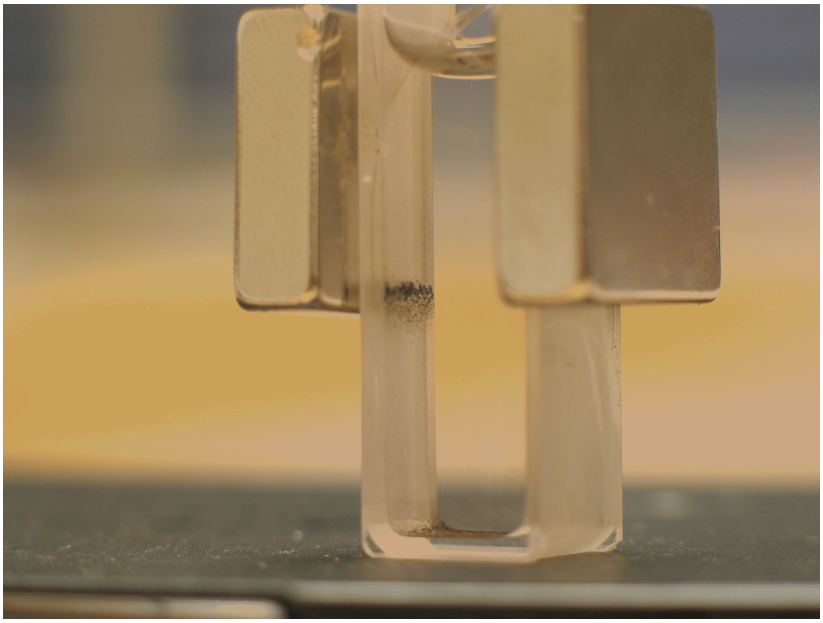

Figure 2: *Photograph of a cuvette filled with hexane on which two magnets (0.5 Tesla surface magnetism) are attached. The black powder that is viewable at the edge of the magnets is constituted on carbon nanotubes rings. The black powder at the bottom is constituted of amorphous carbon and broken rings.*

Nanotube rings: In collaboration with Prof. M. Prato, Universita' di Trieste, Italy, we have developed a novel chemical approach to synthesize rings of SWCNTs that have been extensively imaged with atomic force microscopy (AFM), to investigate their size and shape dispersity and their mechanical

properties. The main property that these nanotube rings have shown is a clear magnetic response to variable electric and magnetic fields [4], that we believe is due to the formation of eddy currents leading to a magnetic dipole. We have proven that these nanorings are magnetic: First, we were able to image rings using magnetic force microscopy (MFM). Second, we used an alternating gradient force magnetometer (AFM) to qualitatively measure the magnetic response of the rings. The most convincing proof came from a simple experiment (Fig. 2). We suspended in a cuvette the tubes between two strong permanent magnets (NdFeB 0.5 Tesla surface field). After a few minutes most of the carbon material collected at the edges of the magnets (where the magnetic field is stronger) while a certain percentage precipitated. The material found at the bottom turned out to be composed of amorphous carbon and of broken rings, while the material collected near the magnets was primarily composed of fully formed rings.

Nanotube coils: we have successfully setup a fully operational thermal CVD system for the bulk synthesis of helical coiled carbon nanotubes (HCNTs) and helical coiled carbon nanowires (HCNWs). Synthesis conditions for preparing HCNTs or HCNWs have been identified. In our process, ferrocene and indium isopropoxide are dissolved in xylene and injected into the reactor. In addition, acetylene is used as source of carbon in our CVD system. Ferrocene and indium isopropoxide are dissolved in specific atomic concentrations in xylene and immediately injected into our two-stage CVD reactor. Typically, the mixed-catalyst solution is injected at a rate of 1 ml/h. After ~2 hour run time, the inner walls of the quartz tube inside the furnace are densely coated with soot containing either HCNWs or HCNTs. By controlling the atomic ratio of In/(Fe+In) (Table 1), the composition of soot can be predominantly HCNWs or HCNTs. Fig. 3a shows the SEM image of HCNWs which exhibit a wider distribution in diameter and lengths, and does not grow as oriented arrays. We have observed different morphologies of HCNWs. For example, Fig. 3b shows a single HCNW in which the pitch of the HCNW changes twice. A HCNW that's tightly wound over a coiled carbon ribbon is shown in Fig. 3c.

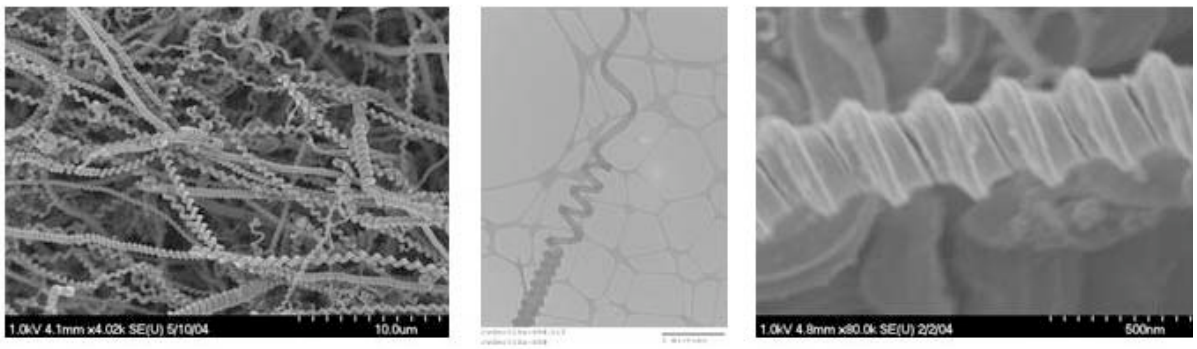

Figure 3: *SEM images of HCNWs prepared in our laboratory using the bimetal composition indicated in Table 1. (a) a dense mat of HCNWs, (b) a single HCNW exhibiting varying pitches, and (c) a single HCNW that is tightly wound over a helically coiled carbon ribbon.*

References

[1] For further information about this project email **marzari@mit.edu**
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