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Electronic Properties of Single-Walled Carbon Nanotubes

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This communication describes scanning tunnelling microscopy investigations of the electronic properties of single-walled carbon nanotubes (SWNTs). First, the unique relationship between the atomic structure and electronic properties of SWNTs is presented. Second, structural defects in nanotubes are addressed, and quantum size effects in SWNTs are discussed. Lastly, the effects of magnetic impurities on the low-energy properties of metallic SWNTs are discussed. Applications and prospects for future research directions are considered.

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Introduction

Carbon nanotubes are cylindrical, extended-fullerene structures that have attracted considerable attention from both scientific and technological communities. This interest is not surprising in light of their promise to exhibit exceptional physical properties that may be exploited in areas from advanced composites to nanoelectronics.[1–3] The unique electronic properties of carbon nanotubes offer great intellectual challenges and potential for new applications. For example, theoretical calculations predicted that single-walled carbon nanotubes (SWNTs) could exhibit either metallic or semiconducting behaviour depending only on diameter and helicity.[4–6] This ability to display fundamentally distinct electronic properties without changing the local bonding was experimentally confirmed by scanning tunnelling microscopy (STM),[7,8] which is able to resolve simultaneously, the atomic lattice and the electronic density of states of a material.

SWNTs can be viewed as a strip cut from a graphene sheet, which is then seamlessly rolled up into a tube. The diameter and helicity of a SWNT are defined by the roll-up vector $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n,m)$, which connects crystallographically equivalent sites on this sheet. $\mathbf{a}_1$ and $\mathbf{a}_2$ are the graphene lattice vectors, and n and m are integers. Electronic band structure calculations can predict the (n,m) indices, which determine whether a SWNT will be a metal or a semiconductor.[4–6] SWNTs are metallic if their (n,m) indices satisfy the condition where $(n-m)/3$ is an integer; otherwise, the SWNTs are semiconducting. As grown, their lengths are typically greater than 1 μm with diameters around 1 nm. This combination of a high aspect ratio (ca. 1000 : 1) and nm-sized diameters offers an opportunity to study how size and dimensionality determine their physical properties.

Seminal STM studies by Wildöer et al.[7] and Odom et al.[8] have experimentally verified how different structural geometries of SWNTs exhibit distinct electronic behaviour. High-resolution images of SWNTs reveal a graphite-like honeycomb lattice, which enables the determination of the (n,m) indices from the image. As an example, the measured chiral angle and diameter of the tube in Figure 1*a* constrain the (n,m) indices to either (11,2) or (12,2). On the other hand, the chiral angle and diameter of the SWNT in Figure 1*b* constrain the indices to (14,–3) and show that this tube has a chirality opposite to that of the SWNT in Figure 1*a*. Subsequent characterization of the electronic properties by tunnelling spectroscopy revealed whether the nanotubes were metallic or semiconducting. Specifically, current (I) versus voltage (V) data were measured and differentiated to yield the normalized conductance $(V/I)dI/dV \equiv$ LDOS, which provides a good measure of the local density of electronic states (LDOS).

I–V curves recorded on the two tubes exhibited very different characteristics, and the LDOSs were quite distinct. Noticeably, the DOS of the tube in Figure 1*a* is finite and constant, and hence the indices of the tube are (11,2). The DOS of the tube assigned (14,–3) in Figure 1*b* shows an absence of electronic states at low energies but sharp peak increases, which correspond to the conduction and valence bands of a semiconductor. In addition, the semiconducting energy gaps are found to be independent of helicity, and to depend inversely on the diameter of the nanotube.[7,8]

By extending the energy range over which measurements are recorded, spikes or peaks are observed in the DOSs of nanotubes that are characteristic of one–dimensional (1-D) materials.[7,9,10] When spectroscopic measurements are made on atomically resolved nanotubes, it is also possible to compare the experimentally determined DOS quantitatively

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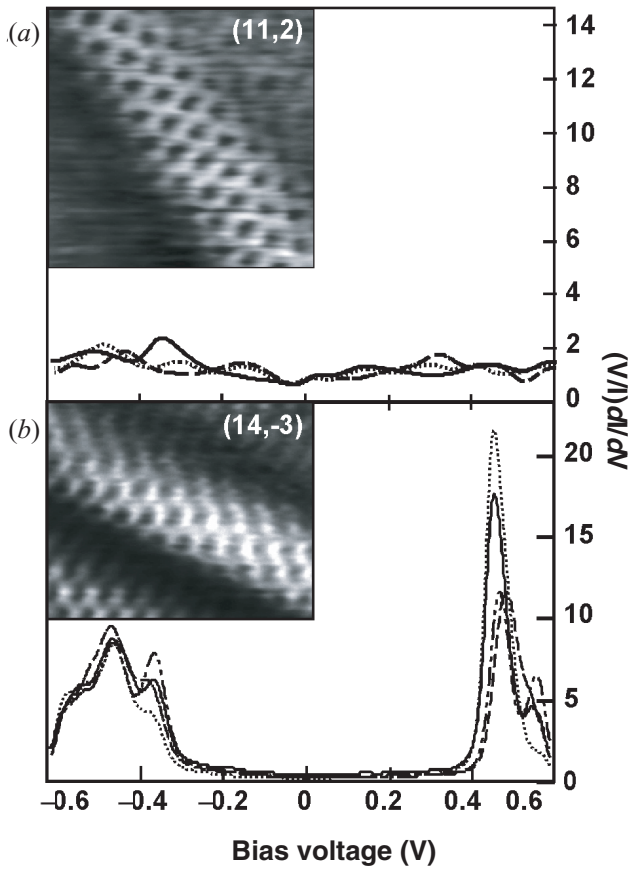

Fig. 1. STM imaging and spectroscopy of SWNTs. (*a*) Calculated normalized conductance (*V/I*)*dI/dV* calculated from *I–V* curves recorded at several positions on the tube in the inset. The inset shows a constant current image of the metallic nanotube. (*b*) Calculated normalized conductance (*V/I*)*dI/dV* calculated from *I–V* curves recorded at different sites on the tube in the inset. The inset shows a constant current image of the semiconducting nanotube. Adapted from ref. 8.

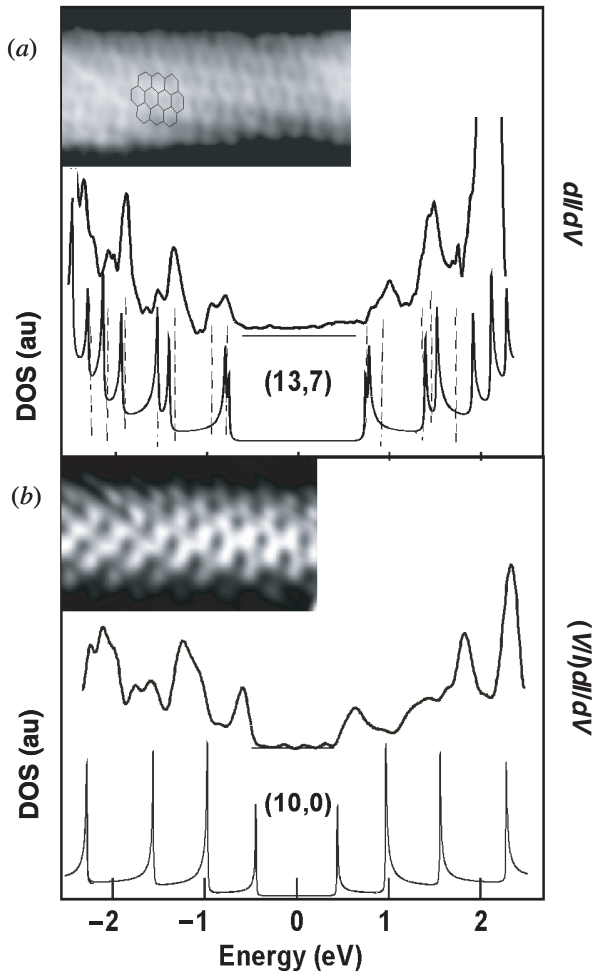

Fig. 2. STM imaging and spectroscopy of SWNTs. (*a*) A comparison of the DOS obtained from an experiment (upper curve) and a π-only tight-binding calculation for a (13,7) SWNT (lower curve). The broken vertical lines indicate the positions of van Hove singularity in the tunnelling spectra after consideration of thermal broadening convolution. The inset shows an atomic resolution image of the (13,7) tube. Adapted from ref. 10. (*b*) A comparison of the DOS obtained from an experiment (upper curve) and a calculation for a (10,0) SWNT (lower curve). The inset shows an atomically resolved image of the (10,0) SWNT. Adapted from ref. 11.

with that resulting from a simple π-only tight-binding calculation. Kim et al.[10] reported the first detailed comparison of experimentally and theorectically determined DOS on a metallic tube with indices (13,7), and Odom et al.[11] characterized a semiconducting tube with indices (10,0). The spectroscopic data show (up to ± 2 V) good agreement with the calculated DOS based on the (*n*,*m*) indices obtained from the resolved STM image (Fig. 2).

The characterization of semiconducting and metallic SWNTs, with subtle changes in their structure, confirms the remarkable electronic behaviour of the nanotubes, and represents a significant step forward in understanding these 1-D materials. In fact, these properties have already seen utility in applications. To mention a few, metallic nanotubes can function as interconnectors between device elements in nanoelectronics,[12] or as nanometer-sized electrodes in electrochemical reactions.[13] In addition, semiconducting nanotubes can function as active elements in field-effect transistors[14] or as chemical sensors to detect the presence of certain gases.[15]

Do carbon nanotubes exhibit other interesting properties besides semiconducting and metallic behaviour? A number of STM experiments have investigated and uncovered new phenomena that suggest the electronic properties of SWNTs are quite rich. This article will provide a brief overview of several of these STM studies, from structural defects in nanotubes to magnetic impurities in nanotubes.

Structural Defects

Carbon nanotubes can exhibit a variety of structural defects, from bends, twisting, and collapse[16–18] to pentagon–heptagon (5–7) pairs in the hexagonal network.[19, 20] SWNT intramolecular junctions can be formed by interposing one or more 5–7 pairs in-between two nanotube sections with different (*n*,*m*) indices. The resulting morphological change,

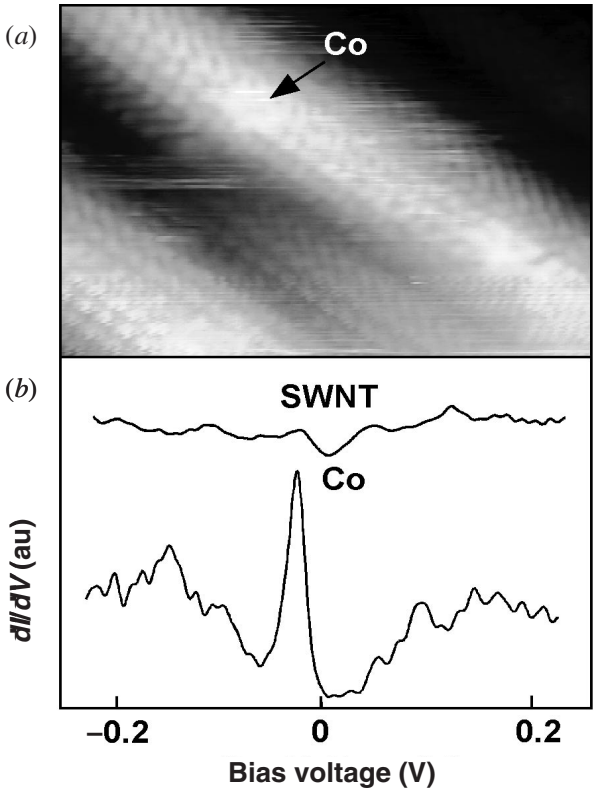

Fig. 3. (*a*) An STM image of 0.5 nm Co clusters situated on individual SWNTs. (*b*) Differential conductance, *dI/dV*, calculated from *I–V* curves taken over the bare nanotube ca. 7 nm away from the Co, and above the Co cluster in (*a*). The feature identified as a Kondo resonance appears over the Co. Adapted from ref. 28.

i.e. the angle at which the two nanotube segments join seamlessly, and the electronic nature of the junction, depend on two factors: (i) the number and topological arrangement of the 5–7 pairs, and (ii) the (*n*,*m*) indices of each nanotube segment. Theoretical models have predicted that metal–semiconductor (M–S), metal–metal (M–M), or semiconductor–semiconductor (S–S) junctions are possible in SWNTs.[21–22] Ouyang et al.[23] resolved the atomic structure and electronic properties of two types of junctions, M–S and M–M. Spatially resolved tunnelling spectroscopy indicated that there were no localized states at the M–S interface, which suggests that this intramolecular junction can behave as an ideal Schottky diode. Unlike M–S junctions, M–M junctions showed new, low-energy features at the junction interface. These studies provide insight to how intramolecular junctions might be used in carbon-nanotube-based nanoelectronics.

Quantum Size Effects

Investigations of finite-sized SWNTs offer an opportunity to probe the connection between, and evolution of electronic structure in, periodic molecular systems. STM can, in principle, probe the transition from 1-D delocalized states to molecular levels. Under normal operating conditions, STM can image and record tunnelling spectra on the 1-D nanotubes. After this characterization, it is then possible to exploit the STM tip to manipulate the nanotubes. Voltage pulses applied between the STM tip and nanotube sample can systematically cut nanotubes into short lengths.[11,24] Subsequently, these finite-sized nanotubes can be characterized spectroscopically. Venema et al.[25] first reported investigations of quantum size effects in a ca. 30 nm metallic (*n*,*m*) nanotube shortened by STM voltage pulses. Tunnelling spectra showed an irregular step-like behaviour that corresponded to quantized energy levels entering the bias window as the voltage was increased. They compiled over 100 consecutive spectra into a spectroscopic 'map', which reflects the electronic wavefunction of the nanotube, and were able to observe discrete electron standing waves. LeMay et al.[26] also imaged the electronic wavefunctions of shortened carbon nanotubes of similar length. Odom et al.[11,27] characterized finite-sized effects in both metallic and semiconducting SWNTs with lengths down to three nanometers. Shortened metallic tubes exhibited an energy level spacing that depended inversely on their length, while shortened semiconducting tubes showed nearly identical spectra at all lengths.[27] These experiments are informative for understanding how the electronic structure in molecular systems depends on length and are useful for future designs of potential nanotube devices.

Magnetic Perturbations

Another extension of STM studies of SWNTs is to introduce magnetic perturbations to the nanotube system. These studies are important for investigating new physical phenomena (magnetic impurity in a 1-D host) as well as for determining the robustness of the intrinsic properties of a nanotube. To this end, Odom et al.[28] decorated SWNTs with magnetic Co clusters (ca. 1 nm in diameter) and recorded spectroscopic data above the cluster (Fig. 3*a*). These measurements revealed a strong resonance peak at zero bias (the Fermi energy) above the clusters, which is absent above the bare nanotube (Fig. 3*b*). Moreover, spatially resolved spectroscopic data showed that the length scale over which the impurity influenced the electronic spectrum of the nanotube was ca. 2 nm, as the peak feature systematically decreased in amplitude at increasing distances from the Co center. The resonance lineshape observed in the tunnelling spectroscopy above the Co clusters was fitted to a modified Anderson single-impurity model,[29] and a 'Kondo temperature' (indicative of when the magnetic impurity will affect the properties of its nonmagnetic host) for the Co/SWNT system was found to be ca. 90 K.

In addition, Odom et al.[28] created magnetic nanostructures consisting of a Co cluster in a SWNT quantum box. These nanostructures were characterized spectroscopically, and similar to magnetic impurities on uncut SWNTs, a resonance peak was observed above the Co. Moreover, the spectra exhibited an energy-level spacing representative of the nanotube length. One notable difference was that the peak amplitude at the Fermi energy appeared significantly enhanced relative to the other energy level peaks. This enhanced conductance provides evidence of the sensitivity of the electronic properties of metallic nanotubes to magnetic impurities, even in finite-sized structures.

Summary

Many of the fascinating overall structural and electronic properties of SWNTs are now in hand, but these studies have really only scratched the surface. Future work addressing the role of defects and other structural perturbations, the connection between extended and finite-sized molecular clusters, coupling to metallic and magnetic systems, as well as other directions, will help to further define the fundamental physics of these systems and the emerging concepts in nanotechnology.

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