I. Introduction

Single-walled carbon nanotubes (SWNTs) represent a new class of materials for investigating fundamental one-dimensional (1D) physics and for exploring nanoelectronics and molecular electronics. Among the many interesting properties exhibited by nanotubes, it is the electronic properties of SWNTs that are arguably the most significant characteristic of this new material. A single SWNT can be either metallic or semiconducting depending only on diameter and chirality, while the local carbon–carbon bonding remains constant. The ability to yield both metallic and semiconducting SWNTs without doping is unique among solid-state materials and has led to speculation that SWNTs might thus serve as a key building block for carbon-based electronics.

II. Theoretical Background and Initial STM Studies

A SWNT can be viewed as a seamless cylinder obtained by rolling-up a section of a two-dimensional (2D) graphene sheet (Figure 1A). The structure of a SWNT is uniquely determined by the roll-up vector, \( \mathbf{C}_n = n \mathbf{a} + m \mathbf{b} \equiv (n,m) \), where \( \mathbf{a} \) and \( \mathbf{b} \) are the graphene primitive vectors and \( n,m \) are integers (Figure 1B). The translation vector, \( \mathbf{T} \), is directed along the SWNT axis and perpendicular to \( \mathbf{C}_n \); the magnitude of \( \mathbf{T} \) corresponds to the length of the \( (n,m) \) SWNT unit cell. Once \( (n,m) \) is specified, other structural properties, such as diameter \( (d) \) and chiral angle \( (\theta) \), can be determined: \( d = (3^{1/2}/\pi)a_c(n^2 + m^2)^{1/2} \) and \( \theta = \tan^{-1}[(3^{1/2}n)/(2n + m)] \), where \( a_c \) is the nearest-neighbor carbon atom distance of 0.142 nm. Among the large number of possible \( \mathbf{C}_n \) vectors, there are two inequivalent high-symmetry directions. These are termed “zigzag” and “armchair” and are designated by \( (n,0) \) and \( (n,n) \), respectively.

The basic electronic band structure of SWNTs can be derived from a graphene sheet while neglecting hybridization effects due to the finite curvature of the tube structure. Graphene is a semimetal with valence and conduction bands degenerate at only six corners (\( \mathbf{K}_0 \)) of the hexagonal first Brillouin zone. The Fermi surface of the graphene sheet is thus reduced to these six points (Figure 2A,B). In SWNTs, the wavevector \( \mathbf{k} \) is quantized along the circumferential direction due to periodic bound-

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Abstract

Recent scanning tunneling microscopy studies of the intrinsic electronic properties of single-walled carbon nanotubes (SWNTs) are overviewed in this Account. A brief theoretical treatment of the electronic properties of SWNTs is developed, and then the effects of finite curvature and broken symmetry on electronic properties, the unique one-dimensional energy dispersion in nanotubes, the interaction between local spins and carriers in metallic nanotube systems, and the atomic structure and electronic properties of intramolecular junctions are described. The implications of these studies for understanding fundamental one-dimensional physics and future nanotube device applications are also discussed.
and otherwise it should be semiconducting. From the criteria \( \mathbf{k} \cdot \mathbf{C}_h = 2\pi q \), we thus expect that SWNTs are metals when \( (n-m)/3 \) is an integer, and otherwise they are semiconductors.

The 1D band structure of SWNTs can be further constructed by zone-folding the 2D graphene band structure into the 1D Brillouin zone of an \((n,m)\) SWNT, and the electronic density of states (DOS) can be computed from the band structure by summing the number of states at every energy level. Several important characteristics of the electronic properties of SWNTs can be immediately obtained from this \( \pi \)-only tight binding model. First, SWNTs exhibit well-defined spike-like features in the DOS, that is, van Hove singularities (VHS). Second, the DOS at \( E_F \) is zero for semiconducting SWNTs \((n-m \neq 3q)\) but nonzero (albeit small) for metallic SWNTs \((n-m = 3q)\). Third, the VHS spacing has a characteristic \( “1–2–3” \) pattern relative to \( E_F \) (with spacing \( 2\pi – 2\pi – 4\pi \)) for semiconducting SWNTs, and \( “1–2–3” \) from \( E_F \) (with spacing \( 3\pi – 6\pi – 9\pi \)) for metallic SWNTs, where \( \xi = 2\pi/3|\mathbf{C}_h| \).

Fourth, the first VHS band gaps for semiconducting and metallic SWNTs are \( E_{\pi}^F = 2\xi\sqrt{3}\mathbf{d}_t \) and \( E_{\pi}^M = 6\xi\sqrt{3}\mathbf{d}_t \), respectively, and are independent of chiral angle \( \theta \) to first order.

The first experiments that addressed directly these basic theoretical predictions were carried out by Odom et al. and Wijido et al. using low-temperature STM. These initial STM studies characterized the atomic structures and electronic DOS of SWNTs, and thereby confirmed the existence of both semiconducting and metallic SWNTs for a wide range of structures. Subsequently, Kim et al. and Odom et al. reported the first detailed comparisons of experimentally determined SWNT VHS with tight binding calculations for metallic and semiconducting tubes. The good agreement between theory and these experiments showed that the essential physics of SWNT band structure is captured by the \( \pi \)-only model. However, other important issues, such as the effects of finite curvature and broken rotational symmetry, which are essential to a complete understanding of SWNTs’ electronic properties and potential device applications, were not addressed. We examine these and other fascinating questions below.

III. Finite Curvature Effect of SWNTs

For a SWNT with sufficiently small diameter, the hybridization of \( \sigma \), \( \sigma^* \), \( \pi \), and \( \pi^* \) orbitals can be quite large. Full-valence tight binding calculations and analytical calculations for a Hamiltonian on a curved surface have suggested that the finite curvature of SWNTs will strongly modify the electronic behavior of SWNTs and open up small energy gaps at \( E_F \). Recently, Ouyang et al. and Kleiner et al. have independently developed a Fermi-point shifting model to provide a direct understanding of finite curvature effects. Briefly, in this model, the finite curvature is found to induce shifts of the Fermi points of SWNTs from original \( K_0 \) (Figure 3). For example, the Fermi points of “metallic” zigzag SWNTs are found to shift away...
from the $K_B$ points along the circumference direction (Figure 3A), while the Fermi points of armchair SWNTs shift along the tube axis (Figure 3B). The shifts in zigzag tubes imply that wavevectors predicted to yield “metallic” zigzag SWNTs will no longer pass through the shifted Fermi points, and hence a small gap with $E_{gc}$ will form in the DOS. In contrast, an isolated armchair SWNT will remain truly metallic because the shift occurs along the allowed wavevector.

Ouyang et al. carried out the first direct studies of curvature-induced gaps in SWNTs using low-temperature STM. Figure 4A shows a typical atomically resolved image of a (15,0) SWNT. The VHS determined experimentally and calculated using a $\pi$-only tight binding model show excellent agreement (Figure 4B) and suggest that finite curvature does not perturb the larger energy features of the SWNT electronic structure. However, these data also showed a gaplike feature near $E_F$. High-resolution normalized tunneling spectra (inset in Figure 4B), which are proportional to the local DOS, clearly show that the local DOS at $E_F$ are reduced to zero (i.e., a true energy gap), with gap width well fitted with the above predicted $1/R^2$ dependence. The single fitting parameter used in this study, $\gamma_0 = 2.6$ eV, was also found to be in good agreement with the values determined in earlier STM studies. In summary, these experimental studies have shown conclusively that previously predicted “metallic” $(n,0)$ SWNTs are actually narrow gap semiconductors.

IV. Broken Symmetry Effect of Armchair SWNTs

As discussed in the previous section, finite curvature will not affect the metallic nature of isolated armchair SWNTs due to their high symmetry. This suggestion is consistent with experimental data shown in Figure 5A. For this isolated (8,8) SWNT, the measured DOS was nonzero and constant at $E_F$, as expected for a metallic system (Figure 5B). However, theories also predict that if the
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**Figure 6.** Summary of the observed pseudo gaps versus tube radius. Each experimental data point (△) represents an average gap value measured on a distinct \((n,n)\) tube. Theoretical results are also shown for comparison: the solid square and dashed line correspond, respectively, to the gap value of a (10,10) tube and radius dependence of the gap widths from ref 24; the open square is for a (10,10) tube from ref 23. The solid circle shows the value calculated for an (8,8) tube from ref 14.

n-fold rotational symmetry of an armchair SWNT is broken, for example by tube–tube interactions within a tightly packed bundle, a gap will open at \(E_F\) and strongly reduce the conductance of the armchair SWNT. Odom et al. and Ouyang et al. first reported the existence of energy gap features near \(E_F\) in armchair SWNT bundles. For example, the local DOS measured for an (8,8) SWNT packed in the bundle (Figure 5C,D) show a clear suppression around \(E_F\), in contrast to the data for the isolated (8,8) SWNT. Experiments also suggested that these inter-tube interactions do not perturb the electronic band structure on a large energy scale (> 0.1 eV) because both isolated and bundled tubes show similar VHS features.

The detailed gap structure observed in bundle armchair SWNTs (inset in Figure 5D) differs from the curvature-induced gaps in that the local DOS are largely suppressed but not reduced to zero; for this reason, these gaps are termed “pseudo gaps”. Similar gap features were observed in other armchair SWNT bundles, with gap values ranging from 80 to 100 meV in the (10,10) through (7,7) SWNTs, respectively (Figure 6). These experimental pseudo gap widths fall within the same range as theoretical predictions. Particularly, our experimental data exhibit a weak inverse dependence on the SWNT radius, which is qualitatively consistent with theoretical predictions. However, deviations between experiment and theory are also clear when making detailed comparisons. One possible origin for these differences is that STM experiments were carried out on SWNTs at the surfaces of bundles, while most theoretical calculations have been based on periodic lattices with higher local coordination. Future calculations carried out on structures accurately modeling STM experiments should help to address such differences.

Our experiments also have several important implications. First, the experimental observation of truly 1D metallic behavior in isolated armchair SWNTs on Au (111) substrate implies that the tube–Au substrate interaction does not strongly perturb the band structure. Second, the presence of sizable pseudo gaps in armchair tube bundles will modify electrical transport, and the very low DOS at \(E_F\) will make extended states in such tubes susceptible to localization. From a positive perspective, the existence of pseudo gaps in armchair SWNTs should make these samples sensitive to doping and could enable their applications as nanosensors.

**V. Energy Dispersion of Armchair SWNTs**

SWNTs are predicted to exhibit a unique linear energy dispersion at low energies \((E_F/\gamma_0 \ll 1)\), which contrasts the parabolic dependence expected from a conventional free-electron picture and will define the behavior of electrons near \(E_F\). However, experimental determination of this unique feature of the band structure has been lacking.

Ouyang et al. first applied the STM to elucidate the 1D energy dispersion of SWNTs by characterizing in detail energy-dependent quantum interference of electrons scattered by defects in metallic nanotubes. Defects in metallic tubes are frequently found to induce modulations in the DOS with a period larger than that of the normal nanotube lattice. In the specific example shown in Figure 7, tunneling spectra as well as atomically resolved images recorded away from the defect (~8 nm) clearly identify that this tube is an isolated (13,13) SWNT. In contrast, tunneling spectra recorded near the defect region show nine new low-energy peaks within the first VHS peaks and demonstrate that the amplitude of these peaks oscillates along the tube axis (Figure 7).

The oscillations in the DOS at specific energies can be understood in terms of resonant electron scattering from defect-related quasi-bound states, which has been reported in recent SWNT theoretical studies and transport measurements. From this picture, Ouyang et al. modeled the energy-dependent oscillations as the interference between an incident 1D plane wave, \(e^{ikx}\) (where \(x\) is position), of energy equal to that of a defect quasi-bound state and the resonantly backscattered electrons with reflectivity \(R^2 = |R|^2 e^{-4\phi}\), where \(\phi\) is the phase shift. This approach leads to an expression for the spatial oscillation in the DOS:

\[
\rho(k_x) = 1 + |R|^2 + 2|R|\cos(2\pi x + \phi)e^{-2\lambda l_x},
\]

where \(l_x\) is the phenomenological coherence length used to account for inelastic scattering processes.

This model provides excellent fits to the energy-dependent oscillatory data (Figure 7) and further yields the energy dispersion, \(E(k)\) vs \(k\) (Figure 8A). Significantly, these data show that the dispersion is, indeed, linear near \(E_F\) and agrees well with the relationship predicted for armchair SWNTs, \(E(k) = (3/2)a_{cc}\gamma_0 k - k_F\). These fits also yield a value of \(\gamma_0 = 2.51\) eV that is in good agreement with previous experimental values from STM studies, and a value of \(k_F = 8.48 \pm 0.05\) nm\(^{-1}\) that is also consistent with the predicted value, \(k_F = 2\pi/(3\gamma a_{cc}) = 8.52\) nm\(^{-1}\), for an armchair SWNT.

Lemay et al. also recently reported an STM study of 1D energy dispersions in metallic SWNTs by imaging the wave functions in finite size (~40 nm) nanotubes. The
physical principle behind this study is the same as that in our quantum interference method: the 40 nm long tubes can be taken as the system with two defects (both ends) that reflect two pairs of Bloch waves. However, this study focused on chiral tubes packed in a bundle and neglected the significant effects of finite curvature and tube–tube interactions reviewed above.

One interesting but important issue further raised by Ouyang et al. is the relationship between the defect parity and the symmetry of the energy bands in armchair SWNTs. Comparison of the experimental energy dispersion with the band structure calculated for a (13,13) armchair SWNT (Figure 8B) demonstrates that our experimental data are in excellent agreement with the calculated \( \pi \) band, although no data overlap with the \( \pi^* \) band.\(^{26}\) The absence of the \( \pi \) band can be understood in terms of parity matching.\(^{23}\) Briefly, the \( \pi \) and \( \pi^* \) bands of armchair SWNTs have opposite parity,\(^{15}\) and thus if the defect in Figure 7A has odd parity, then electrons in the \( \pi \) band (even parity) will not be scattered by the defect, whereas electrons in the \( \pi^* \) band (odd parity) can be scattered when their energies match a defect quasi-bound state. Although more experiments are needed to provide a deeper understanding of this important issue, we believe that this new work highlights the potential of resonant scattering as an approach for investigating fundamental issues of parity and symmetry breaking in 1D SWNTs and nanowires.

**VI. Kondo Phenomena in 1D SWNTs**

SWNTs provide exciting opportunities to study other fundamental issues in 1D electron hosts. For example, the availability of SWNTs enables one to probe how 1D electron systems interact with magnetic impurities, that is, the Kondo effect in 1D. The Kondo effect, which describes the interaction between a local magnetic moment of a magnetic impurity and conduction electrons of a nonmagnetic host, is a well-known phenomenon that leads to anomalous transport behavior in bulk systems of dilute magnetic alloys.\(^{22}\) Briefly, at low temperature the electrons of the host tend to screen the local spin of the magnetic impurity, resulting in a change of the local DOS at \( E_F \) around the site of the magnetic impurity, i.e., the emergence of a Kondo resonance.\(^{33}\) The Kondo resonance should disappear above the Kondo temperature, \( T_K \), which characterizes the interaction strength. In STM experi-
SWNTs, which suggested that the observed peak was due to magnetic Ag clusters or with Co clusters on semiconducting nanotubes. New resonance peaks were not observed with nonmagnetic clusters. The cluster exhibited a strong resonance peak near 0.8 eV, and spectroscopy data recorded directly above the cluster and 7 nm away from the cluster. Constant current image of a larger Co cluster (~1 nm) on a SWNT, and corresponding dI/dV measured at points indicated in the image. Adapted from refs 21 and 38.

Odom et al. first studied the interaction between the local spin of Co clusters and extended and finite size SWNTs. STM images showed that Co clusters could be readily observed on atomically resolved metallic SWNT (Figure 9), and spectroscopy data recorded directly above the cluster exhibited a strong resonance peak near $E_F$. Spatially resolved measurements further showed that these peak features systematically decrease in amplitude and ultimately disappear after several nanometers. The new resonance peaks were not observed with nonmagnetic Ag clusters or with Co clusters on semiconducting SWNTs, which suggested that the observed peak was due to the interaction of a magnetic spin with the SWNT conduction electrons. In addition, analyses of the resonance revealed new characteristics about the effect of dimensionality compared with 2D systems. In 2D systems, the Kondo resonance is usually evident as a dip or antiresonance in the tunneling conductance, while in 2D systems, the Kondo resonance is usually evident as a dip or antiresonance, depending upon the details of the interference. The Kondo resonance for 2D systems was recently observed in STM investigations of magnetic atoms on noble metal surfaces.35–37

Odom et al. also studied the Kondo effect in a very short metallic SWNT, where the energy level spacing of the conduction electrons was larger than $k_BT_K$ (vs normally $\ll k_BT_K$ in extended systems), by characterizing the DOS on and near Co clusters before and after cutting a SWNT host to ~1 nm. The spectra recorded after cutting not only resolved the expected discrete eigenstates separated by ~0.15 eV, due to the quantum finite size effect, but also showed that the peak amplitude at $E_F$ was markedly enhanced relative to those of the other level peaks. The enhanced conductance at $E_F$ provides evidence of how sensitive the electronic properties of metallic nanotubes are to magnetic impurities, even in finite size structures where the level spacing is much larger than $k_BT_K$.

These initial studies suggest that metallic SWNTs are ideal hosts for studying the basic physics of the Kondo effect in 1D systems, although the magnetic clusters (~1 nm) explored in this first report also complicate analysis compared to the ideal of a single atom spin center. In this regard, future studies of the 1D Kondo effect could benefit substantially by using single magnetic atoms or molecules that have well-defined (and controllable) spin and can be registered precisely with respect to the underlying SWNT atomic lattice.

VII. Intramolecular Junctions of SWNTs

SWNTs are also expected to play an important role in nanoscale device applications. An exciting idea in this regard is to create SWNT intramolecular junctions (IMJs). Theoretical work suggested early on that two different tubes could be connected seamlessly by interposing one or more pentagon–heptagon (5/7) topologic defects between two nanotube segments of different helicity. Although transport measurements provided indirect evidence for the existence of proposed IMJs, direct characterization of these potentially important structures was lacking until the recent work of Ouyang et al.45

Analysis of atomically resolved images has enabled the identification of IMJs. For example, the data in Figure 10A show that the upper and lower portions of the nanotube have similar diameters (1.57 ± 0.07 nm) but significantly different chiral angles, where $\theta$ is $-3.9^\circ$ ± 0.8° and $-10.5^\circ$ ± 0.8° for upper and lower portions, respectively. Therefore, the SWNT indices of the upper and lower regions can be assigned as (21,–2) and (22,–5), respectively, and moreover, the interface between SWNTs can be further modeled (Figure 10B). The spectroscopic evidence for the overall IMJ structure (Figure 10C) shows that the upper and lower portions correspond to a semiconductor and metal, respectively. Hence, these results demonstrate that the IMJ is a M–S junction—a basic building block for nanoelectronics.

Spatially resolved tunneling spectroscopy also enabled us to investigate the detailed interface properties of this and other IMJs. From the data shown in Figure 10C, this junction has a very sharp metal–semiconductor interface: the semiconducting VHS gap decays across the IMJ into the metallic segment within ~1 nm, whereas the distinct spectroscopic features of the metallic tube appear...
to decay more quickly across the junction interface. Ouyang et al. used atomic models of the interface to compare calculated and experimentally measured DOS of this IMJ. Two low-energy structural models (Figure 10B), containing three and four 5/7 pairs, respectively, were analyzed. Significantly, the local DOS (Figure 10C) obtained from tight binding calculations for model I agreed well with the measured local DOS across the IMJ interface, while model II exhibited low-energy states around −0.10 eV not observed in experiment. Hence, it was possible to assign the structure of model I as a reasonable representation for the observed (21,−2)−(22,−5) IMJ.

Similar direct and detailed characterization of metallic−metallic (M−M) IMJs has also been carried out, and recently, much more complicated junction structures have been observed and studied. For example, Figure 11A shows one single hybrid tube consisting of three different segments: armchair (11,11)−zigzag (19,0)−armchair (11,11). Spatially resolved spectroscopic measurements (Figure 11B) further support this structure, which is analogous to macroscopic metal−insulator−metal devices. The ability to characterize directly the atomic structure and electronic properties of IMJs by STM has important implications for applications, since it provides a clear means for assessing synthetic efforts designed to prepare specific IMJs. We believe that such work could open up significant opportunity both for fundamental investigations of resonant scattering and for the controlled growth of intramolecular SWNT nanoelectronic devices.

VIII. Concluding Remarks

Scanning tunneling microscopy has contributed significantly to our understanding of the fundamental structural and electronic properties of individual and bundled SWNTs. Studies of defect-free SWNTs have shown that the electronic properties of nanotubes depend not only on radius and chirality but also on their detailed curvature and local environment. Previously predicted “metallic” zigzag tubes are actually narrow gap semiconductors with gap magnitudes depending inversely on the square of the SWNT radius, whereas isolated armchair SWNTs do not have energy gaps and are truly metallic. In addition, armchair SWNTs in bundles exhibit large pseudo gaps at EF due to tube−tube interactions. STM was also used to determine directly the unique linear 1D energy dispersion of SWNTs through the analysis of resonant scattering and quantum interference. As 1D systems, SWNTs were also used to study fundamental interactions between magnetic clusters and 1D electron hosts. Last, direct atomically resolved characterization of intramolecular junctions in as-grown SWNT samples by STM demonstrated the existence of IMJs and could have important implications for
the controlled introduction of defects for nanoelectronic device applications. In short, we believe that the results discussed in this paper open a window into this fascinating 1D system. Future efforts promise to be rewarded with answers to very fundamental scientific questions, and importantly, these results should push from a firm intellectual footing the application of SWNTs in future nanotechnologies.

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