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Electronic structure at carbon nanotube tips

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Abstract. We discuss a number of recent observations on carbon nanotubes tips. Evidence from scanning tunneling microscopy (STM) and spectroscopy (STS) experiments [1] indicates that the topology of the carbon bond network at the tip, and in particular the relative location of pentagons in the curved regions of the caps, is ultimately responsible for the space-resolved electronic properties of the tubes. The theoretical analysis of the local density of (electronic) states (LDOS) is shown to be a powerful tool to rationalize the experimental data. Images of carbon nanotube tips acquired in field emission microscopy (FEM) experiments [2] can be related to the STM/STS observations.

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The properties of carbon nanotube tips are of extreme interest. The small radius of curvature of their tip makes carbon nanotubes attractive both as tips for scanning probe microscopes [1, 3] and as electron field emitters [4, 5]. Furthermore, the dynamical behaviour of the tip atoms, alone or in the presence of metal catalysts, is believed to be determinant for the tube growth mechanism, so that understanding the tip's role during growth may help to optimise the production yields in view of technological applications.

In spite of this, the tip structure remains one of the less well known aspects of carbon nanotubes. The extreme conditions at which nanotube synthesis takes place, in, for example, arc-discharge or laser ablation techniques, prevent any direct observation of the formation of nanotube tips during growth experiments. However, indirect experimental evidence and theoretical modelling have recently shed some light on the role of tube tips during nanotube synthesis [6, 7]. For instance, single-wall nanotubes (SWNTs) are experimentally known to grow only in the presence of catalysts [8, 9]. At the same time, first-principles simulations have revealed that closed tips quickly form at the edge of SWNTs in the experimental range of tube diameters and synthesis temperatures. Calculations indicate that these tips are chemically passive, and do not further incorporate carbon atoms from the gas phase (see [7]). From these considerations, it has been concluded that the role of clean tips at the end of SWNTs is that of preventing growth.

It is interesting to correlate the curvature of the tip with the chemical reactivity. Curvature builds up with the formation of pentagonal rings. According to Euler's theorem, twelve pentagons are sufficient to completely close a surface, while six suffice to form a closed cap at the end of a SW tube. Polygons with less than five edges also introduce a net curvature in a graphene sheet. However, their formation is energetically unfavourable, so that they probably anneal out as defects in well-ordered experimentally obtained structures. There are two reasons at least why the electronic structure (and the related local chemical reactivity) may be profoundly changed in the high-curvature tube regions with respect to that of the regular hexagonal bonding network. These are (1) the pure topological disturbance introduced in the graphitic bond topology by "wrong" fivefold rings and (2) the occurrence of hybridization between in-plane states and graphitic π-band electronic states [12]. The last mechanism has been shown to be responsible for the occurrence of high chemical reactivity at the tip of multi-wall carbon nanotubes (MWNTs) through a local increase in metallicity. These tips can close into a metastable "lip–lip interacting" structure characterized by $\sigma^* - \pi^*$ hybridization at the bridging bonds between two adjacent graphitic sheets. The antibonding character of the newly included states explains why these bonds can break and form at synthesis temperatures, and in turn why MWNTs can grow uncatalyzed [6].

When a carbon nanotube has stopped growing and is closed, the typical curvature at its tip is equal or inferior to that found, for example, in a C_{60} molecule. Hybridization effects with in-plane electronic states are, in this case, expected to be much less dramatic than at a growing MWNT tip. This opens the way to a study of the electronic properties of the curved network based exclusively on the correct topological representation of the network, which is sufficient to investigate mechanism 1 mentioned above. In other words, we as-

sume that the experimental LDOS at the tip of a closed nanotube depends mainly on the tip bond topology only. To check this assumption, the computed LDOS must be compared with the measured ones. STS is the ideal tool to probe experimentally the local LDOS in carbon nanostructures. A good approximation of the LDOS can be obtained from tunneling experiments as the differential conductivity $(\mathrm{d}I/\mathrm{d}V)/(I/V)$. Recent observations of this kind reveal that the tip LDOS of capped nanotubes of ≤ 2 nm diameter contains a sharp prominent peak located ~ 0.1 eV below the Fermi level, associated to "acceptor" electronic states localized at the tip apex [1].

To investigate the origin of these states we have performed computations with a simple $\pi - \pi^*$ model implemented in conjunction with a recursion technique [10]. Within such an implementation the problem of correctly reproducing the semi-infinite geometry of the capped tubes can be properly handled, while the computational time scales linearly with the system size. The hopping energy between nearest-neighbour atoms is the only free term in the model Hamiltonian, and does not vary with interatomic distances and local curvature. In particular, since the model would not connect different graphene sheets, such as the different coaxial walls in a MWNT, this analysis is by definition limited to the study of the LDOS in SWNT systems. To relate our results to observations on MWNTs, we notice that the outer capped layer of a MWNT is most likely to determine by itself the field emission properties of the entire tube, given that the field penetration below the first graphene sheet in a multilayer structure is very small.

We make computations on a variety of tip geometries, in an attempt to sample the sensitivity of the LDOS to a variety of tip features, such as open/closed termination, regular versus defective ring topology, tube chirality, tube size, and confinement (relative position) of pentagons. The LDOS of a few relevant structures, averaged on atoms located at different distances from the tip, are reported in Fig. 1. For the open tip of a (10,0) tube, a set of Fermi-energy-pinning localized "dangling" bond states are found in the middle of the electronic gap, as expected (Fig. 1a). States located at both edges of the electronic gap appear when a "messy" cap topology is added

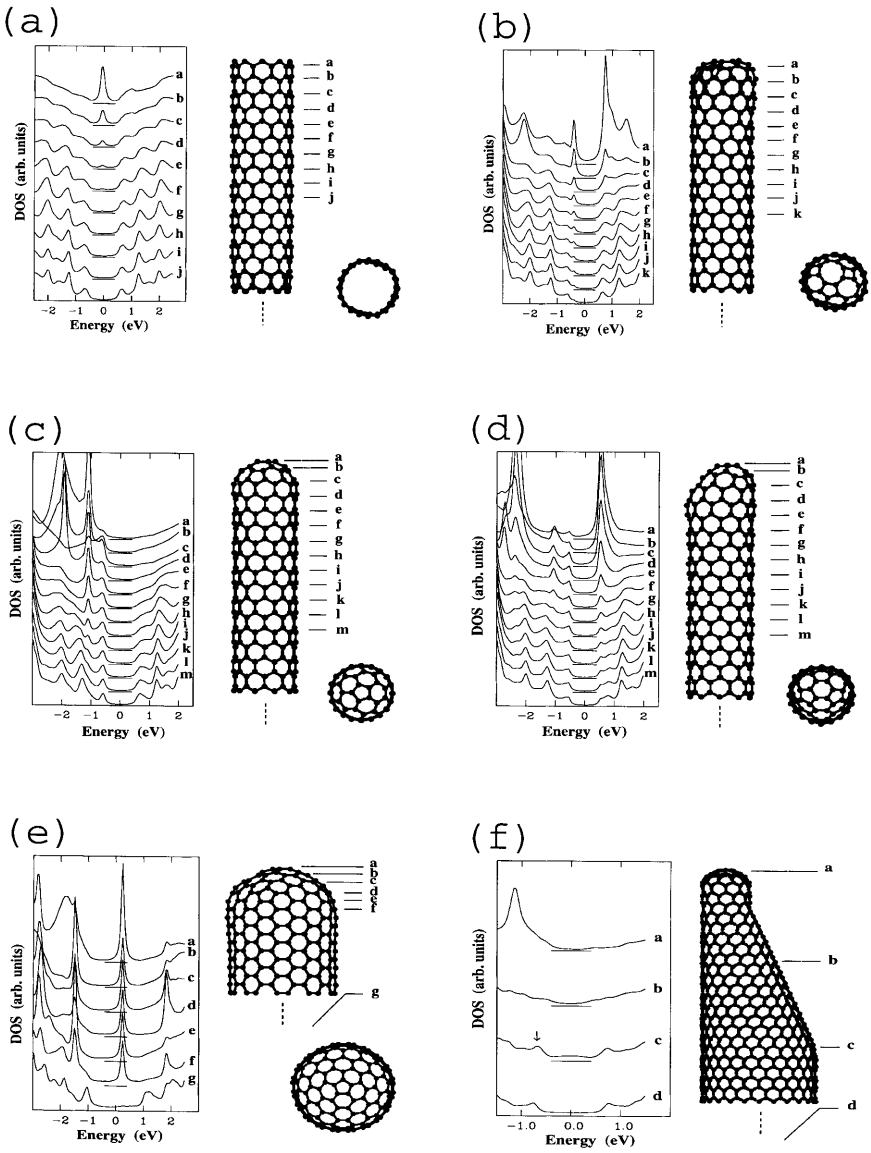

Fig. 1. Computed tight-binding LDOS for a number of SWNT tip terminations (see text)

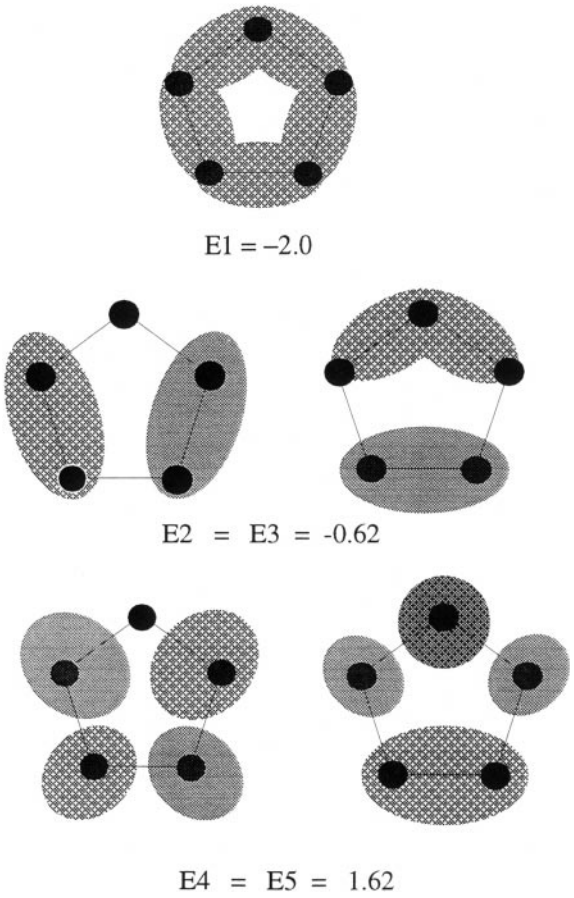

Fig. 2. Electronic states of a pentagonal ring using a simplified $\pi - \pi^*$ model with hopping term $\beta = -1$ and on-site energy $\epsilon = 0$ (see text). Occupied tip states close to the Fermi level observed by FEM show lobes consistent with the E2, E3 multiplet of the schematic

at the (10,0) tube end (Fig. 1b). (This topology was obtained in [6] by annealing for ~ 5 ps an open cap in a constant-temperature first-principles molecular dynamics simulation at ~ 3500 K). A prominent peak at ~ 1 eV below the Fermi energy is found if a "perfect" cap is substituted for the former one (Fig. 1c). If now a pentagon is "pushed away" from the other ones so as to obtain a sharper tip, localised tip states are found at about 0.5 eV above the Fermi level(Fig. 1d). By setting up a regular (10,10) tube tip with "armchair" chirality and a large tube diameter, the localised states peak appears sharper and closer to the Fermi level (Fig. 1e) [13]. In the experimental images, tube ends often display *conical* shapes. Figure 1f shows the computed LDOS for a (24,0) nanotube capped with a conical joint. The conical joint effectively reduces the tube diameter from 2 nm (in the bulk region labeled *d* in the figure) to 0.8 nm (at the tip labeled *n* in the figure). The convexity and concavity at the large and small ends of this conical section correspond to the presence of a pentagon and a heptagon in the bonding network, respectively. Besides the peak in the *n* region, similar to the one observed in Fig. 1c, we notice that the isolated pentagon in region *c* corresponds to the occurrence of an "acceptor" state peak in the LDOS.

These results are in good qualitative agreement with the experimental differential conductivity measures [1]. Taken as a whole, they indicate that the sharp resonant peaks experimentally found in the LDOS of the tip region mainly originate from the topological disorder introduced into the hexagonal bonding network by the presence of pentagons. As is clear from Fig. 1, the strength and energy position of the computed resonant states depend sensitively on the the tip bond topology. If we disregard the topologically defective tip in Fig. 1b (where, however, all carbon atoms still bind to three neighbours, and no unsaturated "dangling" bond is present), the structures investigated mainly differ in the relative position and degree of confinement of pentagonal rings at the nanotube end.

We now provide a simple argument which can help elucidate the interplay of pentagonal rings immersed in a hexagonal graphitic network and the LDOS of the structure. The energy multiplet structure of the π electron states of an isolated pentagonal ring includes the most stable total symmetric state and two occupied orthogonal bonding states having one nodal surface only. This is shown in Fig. 2, where the energies are computed by using a simple tight binding model, and where a formal hopping term $\beta = -1$ between nearest-neighbour atoms has been assumed and the on site energy term has been set to zero. This structure therefore has an "affinity" for a sixth electron in a bonding state, so that when the pentagonal ring is immersed in a metallic π-bonded hexagonal network, such state is occupied and screened by the other π electrons, becoming a resonant bonding state in the graphitic π band. This helps us interpret as an acceptor state the peak in the LDOS Fig. 1f, region *c*. The peak (indicated by an arrow in the figure) is more intense and is located at a higher energy (by $\simeq 0.1$ eV) than the π bounding peak in the bulk tube (Fig. 1f, region *d*). No such isolated peak is visible in the conical joint region *b* of the structure. Repeating the calculation on a different conical tip where the terminal region *a* contains only five pentagons instead of six (and, correspondingly, no heptagon, as follows from Euler's theorem), the acceptor peak is still found at the same energy position in the LDOS from the region *c* of the new structure [1].

It is clear from the results in Fig. 1 that whenever pentagons are located close to each other in a confined region of the structure, the measured LDOS is the result of some further interaction between individual pentagonal topological defects. This is consistent with the interpretation of the acceptor states as resonances in the π-bonded structure, and suggests that each of these states extends well outside the pentagonal rings which determine its main structure. The overall electronic structure in the systems of Fig. 1 is thus the result of interacting topological defects. The relation between the position of pentagons and the main structures in the LDOS seems to suggest that while localised states are always present, more disordered unsymmetric structure (like those in Fig. 1b,d) will produce peaks of higher energy, while "tidier" structures (like those in Fig. 1c,e,f) are more likely to produce states in the occupied regions of the energy spectrum. However, the recursion method used does not provide information on the localisation of individual states; to obtaindirect insight into the structure of localised electron states one can resort to FEM experiments and to ab initio theoretical computations.

If occupied "high-lying" states containing π bonding lobes are located on pentagonal rings in the LDOS of nanotube tips, these states should be revealed by field emission experiments, which are performed at negative sample bias. In these experiments, the patterns collected by the CCD or the video camera are, to first approximation [14], a direct image

of the emitting electronic states. To be a good candidate for emitting tunneling electrons in a FEM experiment, an electronic state should be localised in the high-field regions of the structure, it should be occupied and it should be close in energy to the Fermi level. From classical electrostatics, the high-field region of a conducting nanotube immersed in a static electric potential is that of highest curvature, i.e. the tip region, where most pentagons are located. If almost degenerate emitting states are present due to some underlying multiplet structure of the emitting site (e.g. remindful of the occupied degenerate states in the five-member ring shown in Fig. 2), field emission from individual nanotube tips should reveal it by showing, for example, correlated "switching" of the observed patterns in successive FEM images. Field emission experiments showing multiple-lobe patterns resembling the schematics of the E2 and E3 HOMO states in Fig. 2 have recently been performed, and will be reported in detail elsewhere [2]. In these experiments two-lobed images are often observed to "rotate" by $\sim 110°$ (i.e. close to 108°, which is the internal angle in a pentagon) between consecutive images. In the light of what has been said so far, these switches may be ascribed to changes in the probability ratio of tunnelling between almost degenerate emitting states which emit electron one at a time. We speculate that these switches may be due to changes with time of the local environment of the emitting tube. Indeed, it can be easily calculated that with realistic local fields an energy differnce of about 0.1 eV between two states in a multiplet is sufficient to rule out coherent emission from both states. Preliminary results from ab initio computations indicate that energy splittings of ~ 0.2 eV are typically associated to multiplets of occupied tip states which are located on pentagonal rings and whose main lobe structure is strongly resemblant of that of the E2 and E3 states in Fig. 2. Characteristic four-lobed images are also obtained in the FEM experiments, which can be interpreted as the superposition of two two-lobed structures whenever a switching event takes place during the acquisition time of an image (which is of the order of 1 s in the low-field regime).

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