Electronic effects in scanning tunnelling microscopy of metal-filled multiwalled carbon nanotubes

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Abstract. We have used ultrahigh-vacuum scanning tunnelling microscopy to investigate the effects of Fe filling on the electronic structure of multiwalled carbon nanotubes (MWNTs). When imaged using constant current feedback, Fe-filled MWNTs exhibit striking contrast corrugations that strongly correlate to expected positions (from transmission electron microscopy) of the Fe fillings along the nanotubes. Furthermore, the corrugation in contrast corresponds to significant variations in local electronic structure as determined by tunnelling spectroscopy. These results suggest that inner cores of Fe-filled carbon nanotubes can exhibit considerable influence on the electronics of the outer shells of even large MWNTs.

Contents

1. Introduction 1
2. Experimental 2
3. Results 2
Acknowledgments 7
References 8

1. Introduction

Perhaps one of the more unusual properties of carbon nanotubes is their ability to be filled with a variety of metallic and non-metallic materials. Reports of the filling properties of tubes have been given by a number of researchers. The majority of these studies have centred on the structure of the filling material itself, using surface tension, wetting arguments, arc-discharge
and anode activation to justify the properties found [1]. Although there are a few studies that examine some intrinsic properties of the filling material [2], little is known about the nature of the interaction between the filling material and its carbon nanotube encasement. Given that the Fermi levels of the filling and encasing materials can be quite different, some interaction must be expected. Regardless of whether the filling forms a carbide with the innermost tubes or not, there can be many tens of layers of graphene material between the core filling and the outer shell of a multiwalled carbon nanotube (MWNT). Since the layers (as in graphite) are only weakly coupled, this suggests that irrespective of the effect the core has on the outer shells, it will be relatively small. Unfortunately, this does not seem to be the case. Recent studies using tunnelling microscopy on Cr-filled nanotubes have shown drastic modifications of the electronics of the outer tube, although no quantitative model yet exists for why this is so [3].

In this work, we present a scanning tunnelling microscopy (STM) and tunnelling spectroscopy (STS) study of Fe-filled multiwalled nanotube materials. In imaging, we find morphologies which closely correspond to those seen in transmission electron microscopy (TEM) for Fe-filled tubes. Contrast variations in these images, however, appear to correlate with the opening of a band gap in the MWNTs. This suggests the unexpected result, for MWNTs, that the filling of the tube introduces non-trivial modifications in the electronic structure that are extremely local.

2. Experimental

Fe-filled carbon nanotubes (figure 1(a)) were produced by chemical vapour deposition in which the decomposition of ferrocene and xylene mixtures was carried out in a two-stage reactor. As described elsewhere [4], an Ar : H₂ gas mixture was flowed through a preheater at 175 °C, whereas the xylene/ferrocene mixture was injected into the preheater via a syringe pump and capillary tube. The growth reactor was held constant at 700 °C. This process results in multiwalled carbon nanotubes, containing segmented Fe wires of approximately 50 nm up to several hundred nanometres in length, as seen in figure 1(b).

Figure 2 is a typical high-resolution TEM phase-contrast image of a tube sidewall taken by a Hitachi HF2000. The sidewalls of the tubes exhibit a high degree of structural order with a thin layer of amorphous carbon coating the outside of the material.

After growth, the sample was ultrasonically dispersed in ethyl alcohol using a high power ultrasonic probe for several minutes. It was then drop cast and dried onto a freshly cleaved highly orientated pyrolytic graphite (HOPG) substrate. Figure 3 is an SEM micrograph of the supported Fe-filled nanotubes used for the STM experiments, and a wide field view is shown as an inset. The SEM imaging voltage was 10 kV at 10 µA. The sample was transferred into ultrahigh vacuum (UHV) through a load-lock, where the residual solvent was pumped away. STM and STS measurements were performed at room temperature at a base pressure of <10⁻⁹ Torr. Tunnelling tips were mechanically formed Pt-Ir tips, and all imaging was done in a constant-current mode. The STM was calibrated in X-Y using HOPG atomic structure and in Z using Au (111) step heights.

3. Results

As shown in figure 4(a), some of the nanotubes appear corrugated in STM images. Furthermore, examination of the cross-sectional profiles (figure 4(b)) shows surprisingly small topographic
Figure 1. (a) Scanning electron micrographs (SEMs) and (b) TEM show the material to be pure with little amorphous carbon. Fe plugs are found at most tube tips, and the encapsulation of the Fe appears complete (inset in (b)). Fe plugs are also seen throughout the tube length. The overall morphology seen in these materials is similar to TEM studies of such materials already published [1].

heights. The structures imaged are dispersed across the substrate, and it is clear that they are tubes. However, they appear to be 2–5 nm in height, whereas the TEM images suggest a size distribution of 5–50 nm, generally not less than 10 nm.

These images show a relatively smooth surface of the tube and not the parallel lines expected from a multiple STM tip structure with a width of about 20 nm. This implies that tip convolution is nearly a minimum in the image; only a single micro-tip is imaging the tube [5] and the anomalous heights are not due to tip artifacts. At the very least, the maximum diameter that these tubes may have is not more than the width shown plus the width of the micro-tip used to image.
We note that when arc-grown or low Fe containing chemical vapour deposition MWNTs are imaged, the expected heights are observed with widths that show a significant tip convolution. Most importantly, we note that these structures are not the commonly seen defects for which HOPG is famous [6], because they are clearly continuous across steps and other surface features as shown in the figures.

To gain further insight, we used spatially resolved STS collected along the tube length. We use fixed-gap tunnelling spectroscopy where numerical differentiation and normalization,
Figure 4. (a) An STM image of a Fe-filled MWCNT imaged at 0.7 V and 0.5 nA. The support substrate is HOPG. (b) A line scan taken along the tube axis for 1400 nm shows strong variations in the image contrast.

\[(dI/dV)/(I/V)\] is used to convert the current–voltage curve into a differential conductance, which is corrected for the variations in tip height of the microscope at different locations. This is proportional to a local density of electronic states (LDOS) [7]. A converted tunnelling spectrum (LDOS) is shown in figure 5(b) taken from a 10 nm Fe-filled MWNT (figure 5(a)). The spectrum was taken from a region, 720 nm from where the tube appears to taper (marked by a ‘+’), in which no corrugation or anomalous contrast was observed. The tube appears smooth and featureless at this point. Notice that the LDOS exhibits the now familiar van Hove singular points associated with the band structure of the outer shell of these MWNTs [8] and a finite density of states at the Fermi energy indicating metallic behaviour as expected.

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Figure 5. (a) An STM image of a Fe-MWNT and (b) the LDOS or electronic density of states taken from the region marked with an ‘+’. Notice that the tube is smooth in this region with well-defined contrast. The van Hove singular points are observed in the outer-shell electronics of MWNTs and indicate a nearly one-dimensional character to the band structure. Typically, such well-defined singular points are also an indication of weak coupling between the graphene layers.

As spectra are acquired closer to the contrast variations (same tube as figure 5), we begin to observe changes in the overall electronic structure. A comparison between two positions near a large ‘dip’ in contrast is shown in figure 6. The positions that the spectra were acquired from are marked ‘A’ and ‘B’ and are labelled as to how close to the contrast ‘dip’ they occur. It is interesting to note that whereas the LDOS recorded at >700 nm away from a dip (as seen in figure 4) indicated a metallic tube with well-defined van Hove points as expected in these systems, the LDOS taken near the dips is significantly modified.

In fact, at ~400 nm from the contrast dips, the LDOS shows a well-defined gap beginning to open near the Fermi level. Spectra closer to the dip show an even more pronounced and well-formed band gap, and in the example of figure 6, the gap is nearly 0.5 V. Although these spectra were all taken on the same tube, the results hold generally for all samples studied. This is highly unusual for MWNT systems.
Figure 6. LDOS as determined from tunnelling spectra exhibit an opening band gap as one approaches the contrast dips observed in imaging.

The observed behaviour is quite similar to that seen in previous studies of Cr-filled nanotubes [3]. In that study, the contrast variations and dips were also interpreted as arising from changes in the electronic structure of the tubes. Thus, the property seems to be a general one for metal-filled nanotubes. Moreover, we associate the contrast variations with the positions of the metal plugs since generally such variations are observed to occur at the tube tips just as in the case of the Fe plugs.

In summary, we have presented an STM and STS study of Fe-filled multiwalled nanotubes. This study provides evidence that metal filling of MWNTs results in a strong tube-filling electronic interaction. The interaction can be extremely local as seen in the variations in tunnelling spectra along the length of the tubes. Surprisingly, the effects of filling seen on the outer layers appear far stronger than expected, particularly for large MWNTs.

Acknowledgments

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