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SCANNING TUNNELING MICROSCOPY AND SPECTROSCOPY OF SHORT MULTIWALL CARBON NANOTUBES

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ABSTRACT

We report on the structural analysis of multiwall carbon nanotubes (MWNTs), produced by DC arc discharge in hydrogen gas, using a scanning tunneling microscope operated at ambient conditions. On a microscopic scale the images show tubes condensed in ropes as well as individual tubes which are separated from each other. Individual nanotubes exhibit various diameters (2.5-6 nm) and chiralities (0-30°). For MWNTs rope, the outer portion is composed of highly oriented nanotubes with nearly uniform diameter (4-5 nm) and chirality. Strong correlation is found between the structural parameters and the electronic properties in which the MWNTs span the metallic-semiconductor regime. True atomic-resolution topographic STM images of the outer shell show hexagonal arrangements of carbon atoms that are unequally visible by STM tip. This suggests that the stacking nature of MWNTs, may effect the electronic band structure of the tube shells. Unlike other MWNTs produced by arc discharge in helium gas, the length of the tubes are rather short (80-500 nm), which make it feasible to use them as a components for molecular electronic devices.

INTRODUCTION

Among the fascinating properties of Multiwalled Carbon Nanotubes (MWCNTs) are their electronic properties which make them reliable for applications as molecular electronic devices (field emitters[1], field effect transistors[2], ...etc). Combined with chemical stability MWCNTs show robust structures, which can survive severe strain and high currents. Moreover, since the single shell electronic properties are very much dependent on its structural parameters[3-7] (tube diameter and chiralities), MWCNTs should offer a possibility of switching between semiconducing and metallic states within the same tube. This switching between high and low conduction could be of significant technological importance (for example, constructing nano-integrated devices). Furthermore, as carbon nanotubes conduct electric current without heating, this would make them reliable for use as connectors in nano-electronic circuits. A vital step in developing technology based on carbon nanotubes is to customize their structural parameters (including their lengths). Liu *et. al* [8] developed a method to reduce the length of SWCNTs, however structural defects cannot be ruled out as a result of vigorous sonication in CH_2Cl_2. Here we present our STM investigations of pristine MWCNTs produced by arc discharge in H_2 gas. Topographic STM images show MWCNTs mainly condensed in ropes with relatively short

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lengths (80-500nm) and homogeneous diameters (4-5 nm). Because no chemical processing was used to reduce the lengths of the tubes we expect this method to be very reliable in producing defect-free short MWCNTs.

Experimental

The MWCNTs samples used for this study were prepared by the usual arc discharge method with H_2 as exchange gas. The preparation method is described elsewhere[9]. A mat of the Pristine samples were collected and sonicated in ethanol for a few minutes prior to being cast on a highly oriented pyrolytic graphite (HOPG) substrate for STM measurements. We have carried out STM measurements using a Digital Instruments NanoScope IIIa operated at room temperature in ambient conditions. High quality images of the nanostructure of MWCNTs were obtained by recording the tip (Pt–Ir) height at constant current. Typical bias parameters are 400 pA tunnel current and 50 mV bias voltage. The images presented here have not been processed in any way. Scanning tunnelling spectroscopy (STS) measurements were performed by interrupting the lateral scanning as well as the feed back loop and measuring the current (I) as a function of tip-sample voltage at a fixed tip-sample distance. A combination of STM and STS measurements on individual nanotubes allows us to investigate the structure and electronic properties, respectively.

High-resolution STM scans of MWCNTs, with a previously unachievable atomic resolution at room temperature, reveal visibility differences between carbon atoms of the outer wall of the tubes. These observations find a remarkable counterpart in Scanning Tunneling Spectroscopy (STS) measurements indicating that the current versus bias voltage characteristics depends strongly on the atomic locations[9]. Neither effect has been observed in single wall carbon nanotubes (SWCNTs). As the measurements on SWCNTs and MWCNTs are performed under same conditions for all samples, we suggest that these visibility asymmetries have an electronic origin in the weak inter-wall interaction in MWCNTs, in analogy to a similar effect observed in pristine graphite[10].

Results and Discussion

We first summarize our results for STM/STS of MWCNTs, then we shall focus on the results relevant to the atomic structure of the outer shell and inter-wall interactions.

In Fig.1 we show a raw STM topographic image of MWCNTs which are condensed in ropes. The background is the (001) surface of HOPG substrate. Although the diameter is fairly uniform (4-5 nm), the ropes have a length between 80-500 nm. Most of the ropes are highly oriented with respect to each other and the HOPG (001) surface. This indicates that there is a preferential orientation between the nanotubes and HOPG surface.

We have carried out CITS measurements on top of the nanotubes ropes. The results are shown in Fig. 2. The STM topographic image, Fig. 2(a), shows that some of the ropes are entangled with each other. We have found that this disorder introduces some effect like charge density modulation which decays out with 6-10 nm away from the entangled area. Similar behavior has been observed near carbon nanotube tips[11]. Fig. 2(b) shows the differential tunneling conductance, dI/dV, versus the bias voltage at three different locations on the nanotube ropes. A semiconducting behavior with band gap between 0.4 to 0.9 eV is clearly visible. The peaks correspond to Van Hove singularities at the onsets of one-dimensional energy bands of the carbon nanotube. The peaks are broad due to thermal fluctuations that tend to limit the energy resolution to 0.1 eV at room temperature.

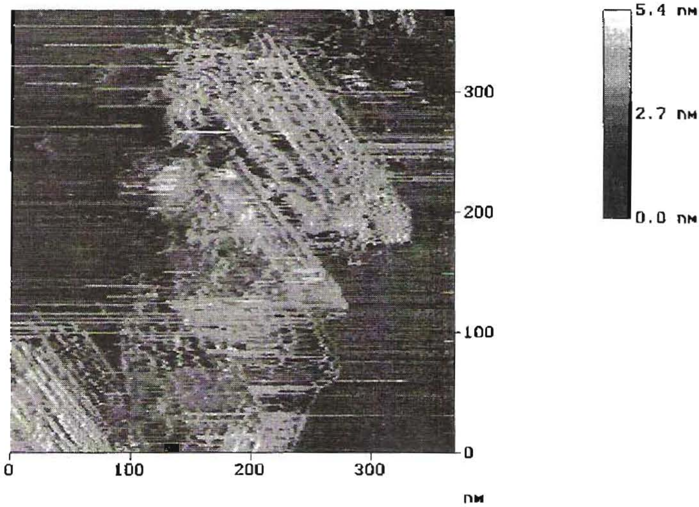

Figure 1. STM topographic image of MWCNT ropes. The length of the tubes are 80-500 nm.

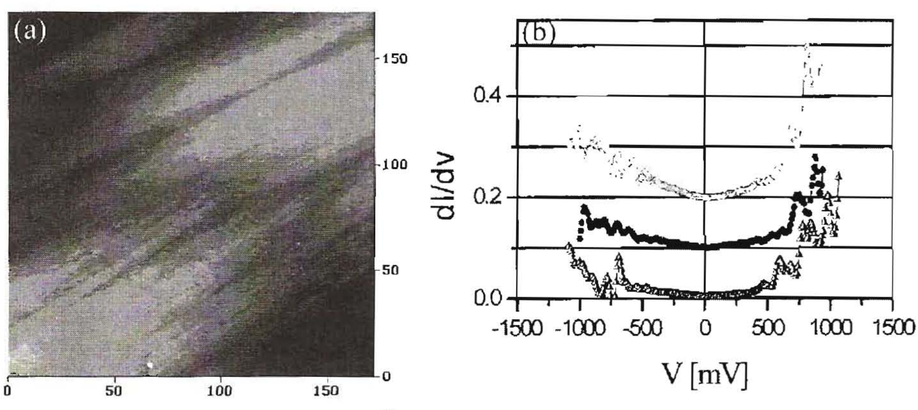

Figure 2. (a) STM topographic image of entangled MWCNT ropes. (b) The STS plot displays a semicoducting behavior with a band gap of 0.4-0.9 eV. For clarity, the curves are offset vertically by multiples of 0.1 nA/mV. The peaks correspond to Van Hove singularities at the onsets of one dimensional energy bands of carbon nanotube.

Figure 3 shows an atomic resolution image of a zigzag MWCNT with diameter 2.5 nm. The dark dots, which represent the centres of the carbon hexagons, show a lattice on a cylindrical surface, the nanotube wall. The nearest neighbour distance of the dark spots is 0.25 nm which compares nicely with the graphite lattice constant.

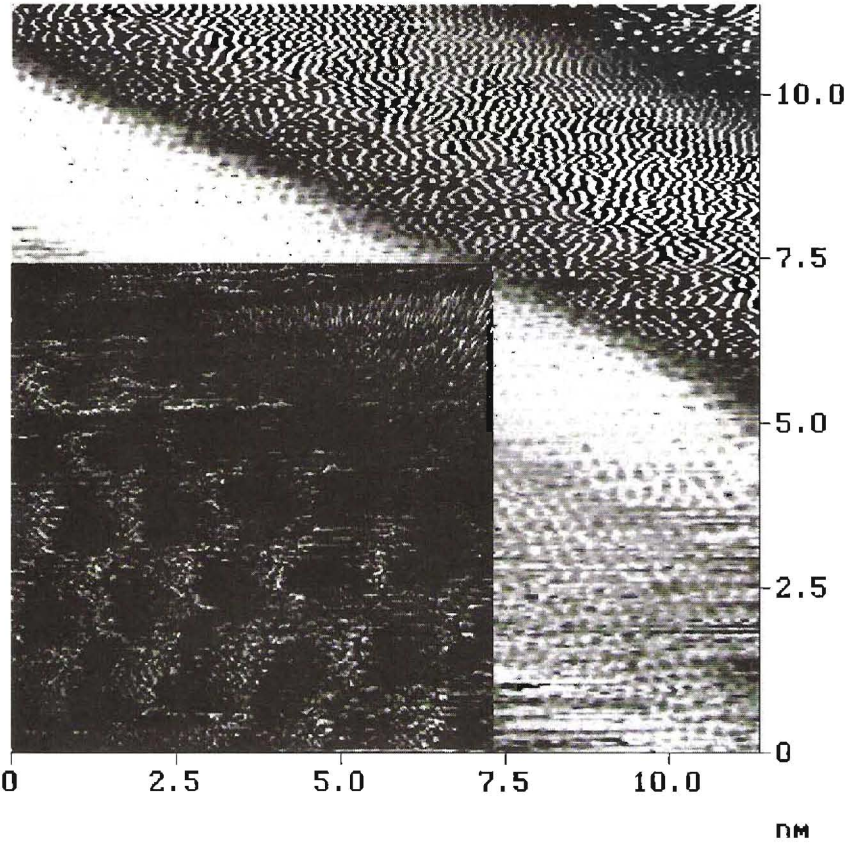

Figure 3. Atomically resolved STM topographic image of a zigzag MWCNT (the chiral angle is 30°). The dark dots are the centers of carbon hexagons. The inset shows a very high resolution of the same tube in the main image. Site asymmetry is clearly visible. The brightest spots (open circles) indicate atoms with no neighbor in the adjacent layer below, whereas atoms with such neighbors (solid circles) appear darker. This asymmetry is caused by spatial variations in the local electronic density of states.

The hexagon centers appear elongated along the tube circumference due to the geometrical distortion arising from the locally changing tip-sample arrangement due to the tube morphology.

On a higher resolution image(see Fig. 3 inset), we have examined the signal intensity at different atomic sites of MWNTs in Fig. 3 and found that some atoms are clearly more visible than others. This effect is not seen in the case of single wall nanotubes[7], but is reminiscent of the site asymmetry as in the case of HOPG[12].

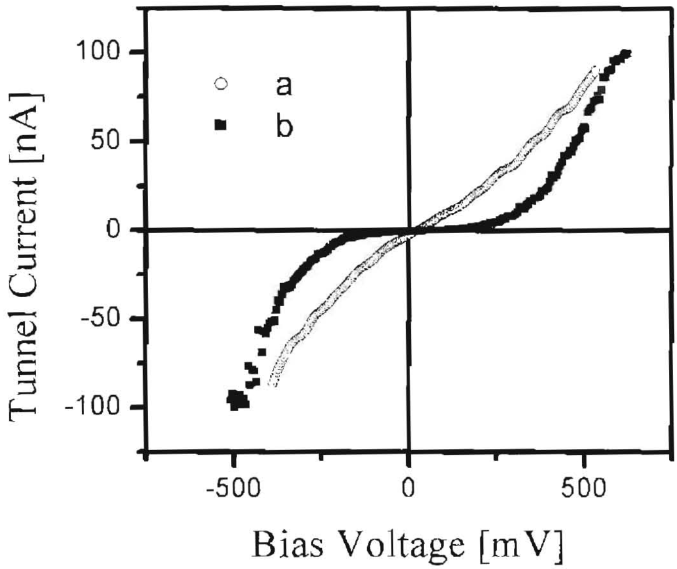

Figure 4. I-V scanning tunnelling spectroscopy of two MWCNTs; a) shows metallic behaviour for an armchair tube with a diameter of 3.5 nm; curve b) indicates the semiconducting behavior for a zigzag tube with a diameter of 2.6 nm.

As in our previous study of MWCNTs produced by arc discharge in He gas[13], we have observed strong correlations between tube geometrical parameters and their electronic properties. Results are shown in Figure 4. Curve a shows metallic behaviour for 3.5 nm armchair MWCNT as tunnelling current versus bias voltage exhibits linear dependence. Curve b suggests a semiconducting behaviour for 2.6 nm zigzag MWCNT as kinks at ±0.34 V are clearly visible.

CONCLUSIONS

In summary, we have presented structural analysis of MWCNTs produced by the arc discharge method in H_2 gas. Mesoscopic STM investigations show short nanotubes (80-500 nm) which are condensed mainly in ropes with almost uniform diameters (4-5 nm). A strong correlation is found between the structural parameters and the electronic properties, namely, MWCNTs can be metallic or semiconducting depending on the diameters and chiralities of the outer shell. STM images of the outer shell show hexagonal arrangements of carbon atoms that are unequally visible by STM tip. This suggests that the stacking nature of MWNTs, may effect the electronic band structure of the tube shells.

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