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Imaging Wet Individual Single Walled Carbon Nanotube at Atomic Level

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Abstract: Wet individual Single walled carbon nanotube was observed at an atomic level with high resolution. This observation was achieved in a liquid cell containing water using a modified non-contact mode atomic force microscopy (NC-AFM) which, we believed, becomes the powerful tool for imaging nano-material in atomic scale. Consequently, the topography image showed many hexagons network of carbon atoms forming the outer surface of SWCNT. The analysis of the scanned SWCNT, by NC-AFM probe, revealed the presence of two sites of an armchair and zigzag structures.

INTRODUCTION

Researchers in the field of microscopy agree that the transmission electron microscopy (TEM) have certain limitations. The electron scattering by carbon is weak and the contrast in TEM image is low and difficult to see the outer surfaces structure. In case of the carbon nanotube (CNT), only the border can be imaged by TEM and the trunk of CNT appears invisible. However, the study of this nano-material required sophisticated and powered tools to accomplish better understanding and controlling surface morphologies. Recently, the whole morphology of the carbon nanotubes were largely studied by scanning electron microscopy (STM) in air [1-3] However, as well known, the chirality depends strongly on the current-voltage characteristics which creates a disadvantage [4,5].

In this matter, our research work on improved non-contact mode of the atomic force microscopy (NC-AFM) had been fruitful. It known that in NC-AFM, the system vibrates at few nanometers up to the sample surface as the tip comes cross of it. The oscillation amplitude of the cantilever is monitored and used for a feedback system. Any modification in the detection system of vibration or/and feedback device effect the sensitivity of measurement and thus the resolution in imaging. Among the advantage of using liquid cells for the NC-AFM is to allow operation with the tip and the CNTs fully immersed in liquid which reduces the total force that the tip exerts on the SWCNT. Manipulating the NC-AFM in liquid environments has proven to be an indispensable technique for the successful application of NC-AFM to biomaterials or bio-systems including studies of the interaction between solid-liquid interfaces. In this short report we presented a modified NC-AFM as microscope for high resolution imaging SWCNT in water environment using liquid cell where thermal fluctuation and air effects are absent. Beside considering water as source of life, research studies on the physical and chemical properties of water at the nanometer scale have grown [6-8]. Recently, Koga *et al.* [9] had reported simulations of the behaviour of water encapsulated in carbon nanotubes. He suggests the existence of a solid-liquid critical point and of a variety of new ice phases that not seen in bulk ice. G. Hammer *et al.* [10] and M.S.P. Sansom *et al.* [11] conducted investigations on the simulation of studies on the possibility that water molecules could flow inside SWCNT under certain consideration of approximate calculations. Our work constitutes, thus, the first experimentation to image the surface of SWCNTs in water environment using a liquid cell NC-AFM. Further experiment in parallel with theoretical studies of Hammer and colleagues are imminent for better understanding some predictions.

Experimental Setup

Single walled carbon nanotube SWCNT was produced by hydrogen arc discharge method using the following characteristics: a pressure of 450 Torr and a current of 60A. Then, it was immersed in pure Milli-Q water cell. A drop of the heterogeneous-solution was deposited onto a freshly cleaved mica surface without any treatment and constituted an easy and simple method. The advantage of using mica substrate is that it decreases the nanotubes adhesion and the atomic resolution imaging as a well-known test structure. A commercially available AFM instrument (JEOL: JSPM-4500) was used in this experiment with major modifications. The original frequency modulation (FM) demodulator was replaced with a newly developed FM detector [12]. The phase problem is solved by over sampling and iterative phase retrieval. High-resolution imaging was performed using Non-contact mode of the atomic force microscopy by modifying the detection system of the signal received by the photodiode, with a phase-shifted feedback device and adding amplitude feedback electronics. We used a cantilever with a lower spring constant as 0.06 N/m which is typically used for non-contact mode in air, to compensate for viscous coupling between the tip and surrounding water. The tip, in silicon nitride, has sharp edge as 10 nm of radius and resonant frequency of 10 kHz to minimize the convolution with SWCNT. The cantilever was baked at about 150 °C in UHV chamber for few hours before use for better resolution. Measurements were

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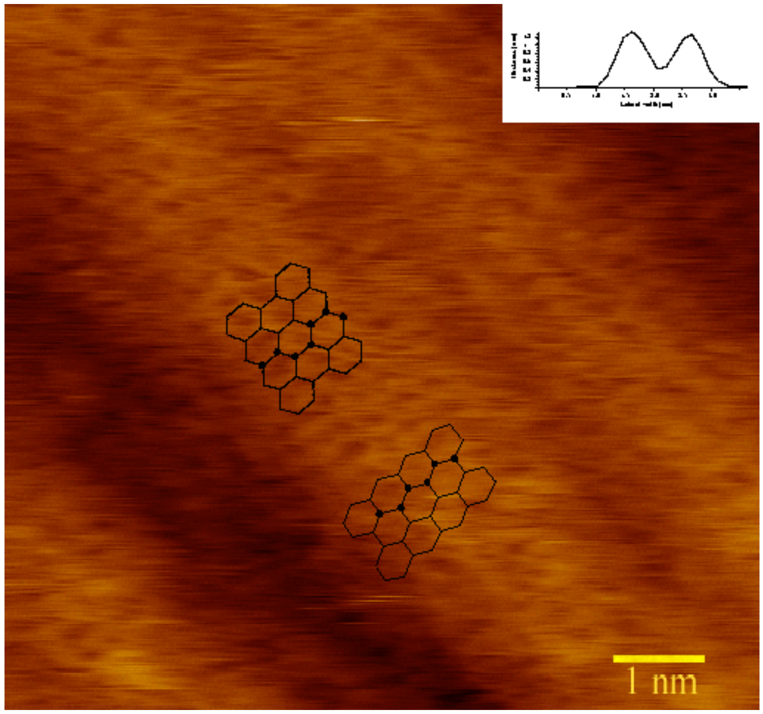

Fig. (1). Wet single wall carbon nanotube imaged at high resolution non-contact mode of the modified atomic force microscopy. Note that individual SWCNTs are spaced about 0.35 nm and the hexagon network showed an armchair and zigzag structures at the upper and lower portions, respectively. We reconstituted ideal armchair and zigzag configurations with schematic drawings as projected on the image. The NC-AFM line profile is also scanned showing the diameter and the space between two SWCNTs.

done repeatedly in a water environment at room temperature without observation of damaging the sample.

Results

Therefore the following figure showed the atomic resolution of SWCNT in water environment using the modified NC-AFM. The hexagonal structure network of the SWCNT can be seen with periodicity and a well-ordered feature. The analysis obtained for the image indicated that the SWCNT has a diameter of about 1.2 nm and the wall spacing of about 0.35 nm which coincides with those found by other researchers. The approximate distance between carbon-carbon atoms in hexagon is 0.14 nm. These geometrical characteristics, determined by the AFM line profile, characterize the SWCNT in bundle. Moreover, the concern SWCNT seems to have, at least, two different sites: armchair and zigzag structures. We notice that zigzag structure, which is nonhelical configuration, is rare in SWCNT and the chiral one is dominant [13]. We suggest that the accurate SWCNT had a twist or distortion. Our previous work showed the high flexibility of SWCNT [14]. Referring to the figure, the presence of the armchair and zigzag structures predicted that the concern SWCNT is metallic rather than a semiconductor nanotube. Evidently, further experimental and theoretical work is necessary to understand this feature structure of this amazing material.

As we know, SWCNT strongly adhered to the substrate after evaporation of solvents such ethanol, cyclohexan, chloroform, toluene…though it is flexible and free of movement in solution. The dry environment influenced the level of hardness, stiffness of SWCNT and the mechanical properties. The liquid cell may be well suited for comparative studies performed under similar air moisture conditions. Water could play a protective role from the air contamination over longer periods of time. We think that imaging SWCNT in liquid cell will be interesting to characterize it in solution. An important aspect concerning roughness is the morphology observed in air requested an uniform surface while in the liquid cell the uniformity of material surface does not effect the resolution.

On the other hand, the image was scanned 10 times with the same resolution and had no significant drift or energy lost of the cantilever-tip due to the absence of air and the water reduce the interaction of tip-SWCNTS. This technique has led to achieve better imaging stability.

This finding may open research areas to study the interaction and behavior of carbon nanotubes with different liquids: volatile or nonvolatile, viscous or fluid.

CONCLUSION

To date, single walled carbon nanotube surface has been imaged in air by scanning tunneling microscopy with atomic resolution. In the present work, we imaged in water wet SWCNT by non-contact mode atomic force microscopy with atomic resolution environment using a liquid cell. It is interesting that we found both zigzag and armchair structure on the same SWCNT. The techniques of operating in liquid environment using NC-AFM may open new horizons to study the interaction and the behavior of carbon nanotubes with various liquids including oils. It may raise the questions on using CNT based nano-electronic devices in wet environments in near future.

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