Carbon Nanotube Tips

for MAC Mode AFM Measurements in Liquids

Application Note

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Atomic force microscopy (AFM) is a powerful technique in revealing the microscopic structure of a variety of materials down to nanometers. While it has become an essential technique for surface characterizations, there are some long-standing problems in obtaining consistent high-resolution AFM images. For instance, the radius and shape of the very end of the AFM tip vary from one tip to another. During many measurements, Si_3N_4 or Si tips have been found to wear down quickly, resulting in a loss of tip sharpness. Thus, much effort has gone into the search for wear-resistant AFM tips.

Carbon nanotubes, which feature sharp geometry, intrinsic electrical conductivity, and mechanical resilience, are now being used for AFM and scanning tunneling microscopy (STM) tips. It has been demonstrated that carbon nanotubes attached to AFM tips exhibit advanced imaging capabilities (1). Carbon nanotubes are formed of perfectly graphitized, closed, seamless shells; dimensions are typically about 1 to tens of nanometers in diameter and several microns in length. Owing to their flexibility, carbon nanotube tips are resistant to damage from tip crashes. The slenderness of carbon nanotubes permits imaging high-aspect-ratio surface features. Carbon nanotube tips offer a solution to the common tip-wear problem and have been successfully demonstrated in lithographic oxidation of hydrogen-passivated silicon surfaces (2).

Since carbon nanotube tips present a well-defined atomic configuration at the very end of the tip, they provide a good model system to study tip-sample interactions. In addition, current studies of single-biomolecular forces between sample surfaces and modified AFM tips face the problem of unknown tip geometry and, therefore, unknown number of molecules involved. The single-molecule bond-rupture forces are typically derived with mathematical models assuming a roundtrip with certain radius. With carbon nanotube tips, particularly close-domed tips, it is possible to modify the very end of the tip with biomolecules in a well-controlled manner so that the single-molecular interaction can be measured directly from the force-distance curve. The development of carbon nanotube tips for measuring biological samples, especially in buffer solutions, is of great interest.

A carbon nanotube tip prepared by the previous method has been demonstrated to work well with tapping mode in air (1); however, the carbon nanotube was quickly lost after the tip was immersed in fluid. This is likely due to the disturbance to the tip and the surrounding liquid by the large acoustic vibration applied to the AFM cantilever holder during tapping mode operation. It is obvious that in order to use these carbon nanotube AFM tips in fluids, the disturbance to the liquid needs to be minimized. Magnetic AC Mode (MAC Mode) provides an immediate solution for this problem. By directly driving the AFM cantilever with an oscillating magnetic field, the background resonances from the cantilever holder and fluid body are minimized. As a result of the better signal-to-noise ratio achieved with this technique, much smaller amplitudes can be used and the interaction between the tip and the sample can be dramatically reduced. In this application note, we demonstrate the feasibility of using carbon nanotube tips for MAC Mode measurements in fluids.

The multiwalled carbon nanotubes were attached with an acrylic adhesive to the pyramidal tip of a silicon nitride cantilever with a spring constant k = 0.1 N/m. The back of the cantilever was coated with a proprietary magnetic material and magnetized along the flexible axis of the cantilever (3). AFM measurements were taken with an Agilent microscope controlled by a MAC Mode module interfaced with a controller unit. The cantilever was driven at a frequency of about 30 kHz by a solenoid under the sample plate during MAC Mode measurements within water solution.

Figures 1(a) and (b) show the AC oscillation amplitude and the DC deflection of the cantilever recorded simultaneously as functions of the tip-sample position (Z). The measurements were carried out with a nanotube bundle at the very end of the silicon nitrite pyramidal tip. The sample was a piece of freshly cleaved mica in water solution. Both Figures 1(a) and (b) were measured during tip approach to

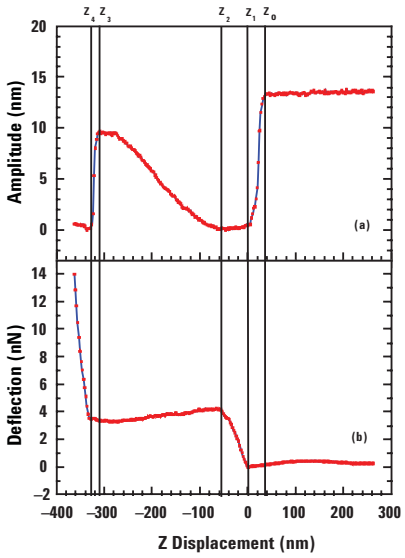


Figure 1. The change of the (a) AC oscillation amplitude and (b) DC deflection signal of the cantilever vs. the sample surface-tip distance. The cantilever was prepared with carbon nanotubes at the tip and magnetic films coated at the back. The measurements were carried out on a freshly cleaved mica surface under double deionized water. The cantilever oscillation was driven by a MAC Mode module at 30 kHz.

the sample. The points corresponding to changes in these two curves are marked at Z_0 = 34.4, Z_1 = 0, Z_2 = –56.5, Z_3 = –311.8, and Z_4 = –333.9 nm, respectively. In the region with $Z > Z_0$, the cantilever freely oscillates with amplitude of about 13 nm. When the tip of the nanotube touches the mica surface first at the near-normal incidence, the oscillation amplitude starts to decrease. The amplitude drops to zero at $Z = Z_1$ (0 nm) when the farthest point of the tip at free oscillation touches the surface. The cantilever is then snapped onto the surface and is pushed up as it is moved further toward the surface in the region between Z_1 and Z_2. The deflection of the cantilever rises, indicating the increase of the force applied at the nanotube. At $Z = Z_2$ (–56.5 nm), the force applied onto the nanotube rises to about 4.2 nN, resulting in the buckling of the nanotube.

It is known that nanotubes can be reversibly bent when a force exceeding the Euler buckling force is applied (4). Assuming the Young's modulus of the nanotube is similar to that of in-plane graphite (Y ≈ 1 Tpa), the Euler buckling force of a nanotube with a length L ≈ 277 nm and a diameter r ≈ 5 nm can be calculated as (1):

$$F_{EULER} = \pi^3 Y r^4 / 4L^2 \approx 4 \text{ nN}.$$

This number agrees very well with Figure 1. At $Z < Z_2$, the nanotube is bent so that the force applied at the nanotube maintains a constant value at about 4 nN over a rather large distance $Z_{tube} = Z_2 - Z_4$ = 277 nm, as indicated by the constant DC deflection signal in Figure 1(b). This value corresponds to the length of the single nanotube in the surface normal direction. Within the range between Z_2 and Z_3, the AC oscillation amplitude of the cantilever, however, increases as the tip is pushed against the surface.

When the cantilever is moved further toward the surface at $Z = Z_3$, the single nanotube is completely bent away so that the nanotube bundle touches the surface. The bundle acts as a rigid tip since it has a much higher buckling force (for example, 2.8 μN^2). The soft cantilever is deflected again after the oscillation amplitude decreases to zero at $Z = Z_4$. If the movement of the piezoelectronics tube is reversed right after the bundle touches the surface, the single carbon nanotube clearly recovers to the full length at the near-normal incidence and identical force-distance curves can be obtained in the successive cycles. The force-distance curves demonstrate the resilience and reversibility of the nanotube AFM tips under a reasonable force load.

Images of the surface morphology can be taken by setting the set point just slightly lower than Z_0. With this setting, the single carbon nanotube tip slightly touches the surface at the near-normal incidence angle so that the very end of the carbon nanotube is used as the probe during imaging. The nanotube is fully extended during imaging. Figure 2 shows the image of a vapor-deposited Au film on a mica surface in the distilled water. The Au film has been exposed in the air for several months without any treatment before the use. The image is the same as that acquired by contact mode AFM with a normal tip. The surface is quite rough, with a root-mean-square Z displacement of about 20 nm over a 2x2 μm^2 area. The image is stable over several hours, which demonstrates the ability of carbon nanotube tips for imaging a rough surface within water solution.

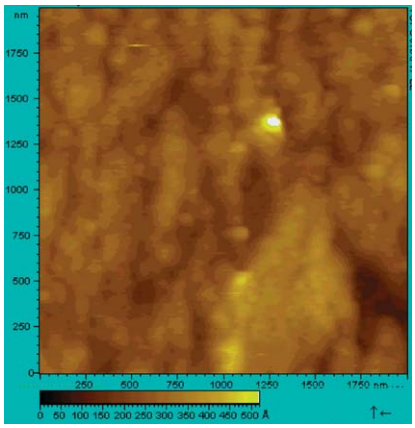


Figure 2. The image of a 2000-Å Au film on mica in water solution measured with a carbon nanotube tip using MAC Mode.

As we discussed earlier, our ultimate goal of using carbon nanotube tips in MAC Mode is to achieve consistent high-resolution images of soft biomolecules in solutions. Figures 3(a) and (b) show two images of plasmid DNA molecules deposited on freshly cleaved mica surfaces from a 1-µg/ml solution. About 10-mM $MgCl_2$ was introduced into the solution to enhance the bounding of DNA molecules to the mica surface. These images present a lateral resolution of 5 – 8 nm. The resolution is slightly worse than the best one (~3 nm) obtained by normal MAC Mode tips (5); however, the carbon nanotube tips did not show the multi-tip problem

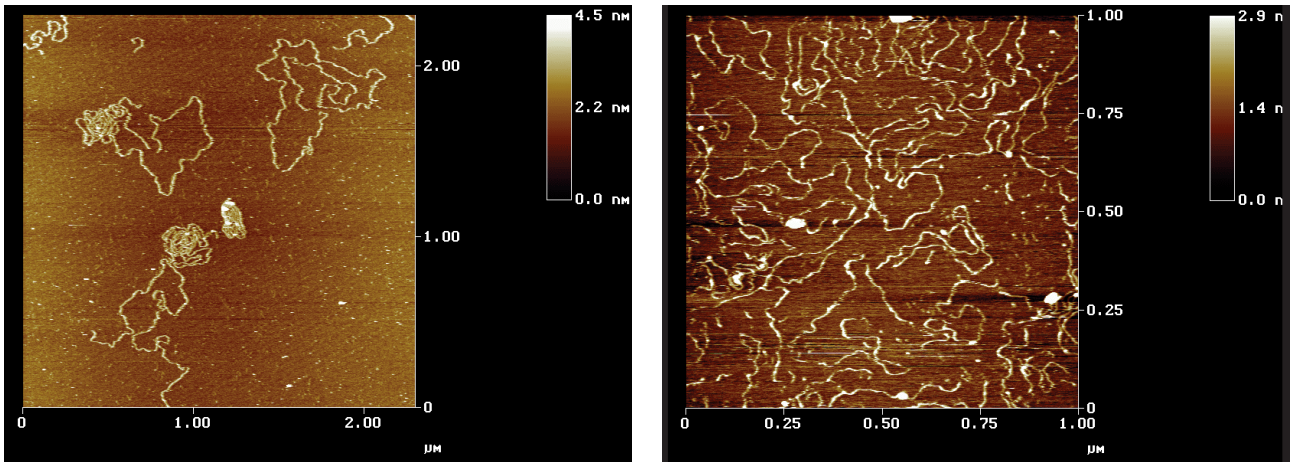
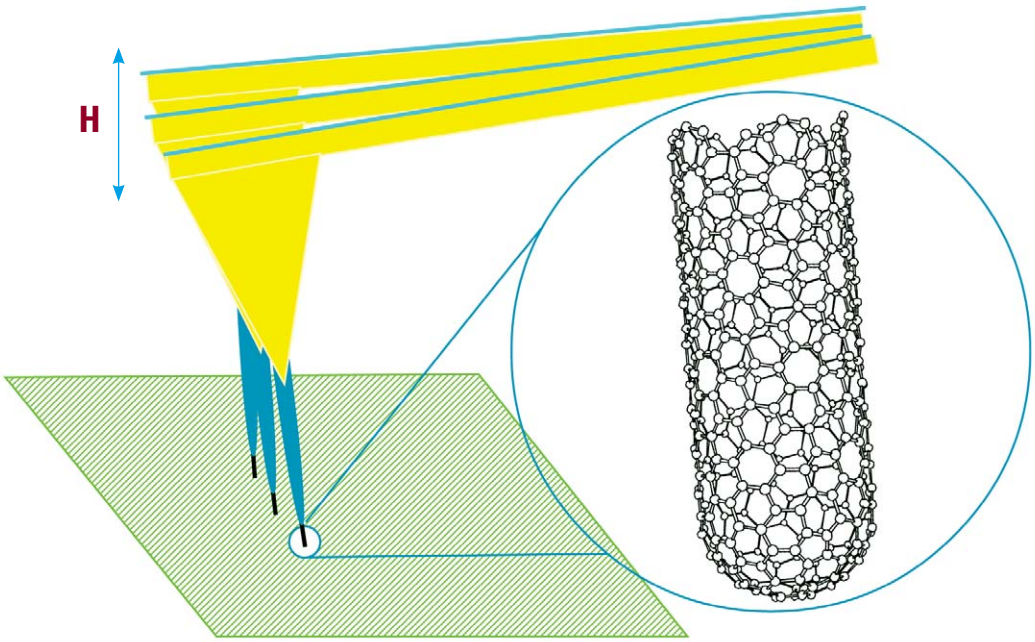


Figure 3. Two images of plasmid DNA molecules adsorbed o n freshly cleaved mica surfaces in 1-mM $MgCl_2$ solutions. The measurements were taken with single carbon nanotube AFM tips under MAC Mode control.

that is often encountered when using normal MAC Mode tips. Clearly this is because the images were taken with a well-defined single carbon nanotube tip. The resolution is limited by the diameter of the nanotube (that is, about 5 nm in this experiment). One can expect that a close-domed single-wall nanotube tip could provide a higher resolution. The operation of MAC Mode with smaller oscillation amplitude would also help improve resolution. Further studies on these issues are in progress.

In summary, we have successfully demonstrated that carbon nanotubes attached to MAC Mode AFM tips can be used in imaging both hard and soft surfaces in water solution. Consistent high-resolution plasmid DNA images were obtained with carbon nanotube tips. The resolution is defined by the diameter of the nanotube. Typically, a single nanotube is extended over the bundle; thus, the multi-tip problem is easily avoided. So far, the major difficulty is in the weakening of the attachment of nanotubes to the pyramidal tip by solvents. The method of gluing nanotubes onto AFM tips using acrylic adhesive is not satisfactory in solutions. We have tried to enforce the attachment by introducing cross-links in the polymer, coating another metal film, or depositing carbon film at the pyramidal tip with an electron beam. We have seen great improvements, but it is still not a trivial task. Ultimately, we hope that carbon nanotubes could grow directly from the AFM tips by chemical vapor deposition. The mechanical strength of these nanotube tips would be much better than those prepared by the adhesive method.



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Revised: 11/08/06

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Printed in USA, March 21, 2007
5989-6376EN

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