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2005 Nanotechnology 16 2493

(http://iopscience.iop.org/0957-4484/16/11/004)

Nanotechnology **16** (2005) 2493–2496 doi:10.1088/0957-4484/16/11/004

Length control and sharpening of atomic force microscope carbon nanotube tips assisted by an electron beam

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Received 15 July 2005, in final form 19 July 2005
Published 13 September 2005
Online at stacks.iop.org/Nano/16/2493

Abstract
We report on the precise positioning of a carbon nanotube on an atomic force microscope (AFM) tip. By using a nanomanipulator inside a scanning electron microscope, an individual nanotube was retrieved from a metal foil by the AFM tip. The electron beam allows us to control the nanotube length and to sharpen its end. The performance of these tips for AFM imaging is demonstrated by improved lateral resolution of DNA molecules.

1. Introduction

Since their discovery [1], carbon nanotubes (CNTs) have been used for their remarkable electrical and mechanical properties in a wide variety of applications such as transistor elements [2], field emission tips [3], biosensors [4] and linear and rotational nanoelectromechanical systems [5, 6]. Despite the progress in the fabrication of CNTs, the precise placement of the CNTs as well as their directionality and the length control are still unsatisfactory. Even the selection of a single nanotube, as opposed to bundles of nanotubes, remains a challenge.

The high aspect ratio and the stiffness of CNTs make them ideal for use as scanning probe microscope tips, especially in AFM. Several methods have been used to fix the nanotubes to the end of an AFM tip, ranging from gluing [7], to growing via chemical vapour deposition [8] and recently by dielectrophoresis [9]. However, the method that has achieved a stronger attachment of the nanotubes to the AFM tip is electron beam deposition [10, 11]. Nevertheless, to improve the spatial resolution for AFM imaging requires us not only to affix the CNT in the axis of the tip but also to control precisely the nanotube's length [12–14]. Long CNT tips are suitable for imaging deep holes but are more likely to bend, while short CNTs are, in general, more useful for imaging flat samples. The ideal length of the CNT for high resolution AFM imaging is expected to be one that minimizes nanotube bending and thermal vibration.

Here we report on the successful positioning of an individual multiwalled CNT onto the end of an AFM tip. By using a nanomanipulator inside a scanning electron microscope (SEM), we retrieved a single CNT from a metal foil covered with CNTs, using an AFM tip [15]. The length of the nanotube is controlled by cutting the CNT with the SEM electron beam. Finally, the performance of these tips is demonstrated by imaging DNA molecules in air with amplitude modulation mode AFM.

2. Experimental section

The experiments were performed with a piezo-driven (Attocube, GMBH) nanomanipulator system mounted inside a FEI Sirion XL30 Schottky field-emission SEM. This system allows direct observation of the AFM tip movement and its interaction with the CNTs via SEM imaging. Nanometre resolution translation is achieved via piezoelectric controls. This system is integrated with an advanced user interface for manipulation processes that allows manual control of the AFM tip position. The SEM experiments were performed at room temperature in vacuum above 3×10^{-6} mbar.

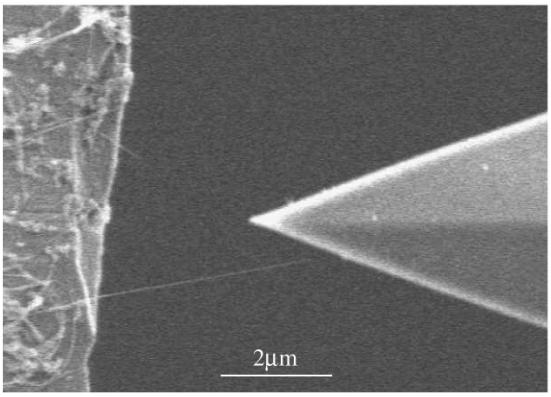

Figure 1. SEM image of an AFM silicon tip positioned closed to an isolated CNT aligned almost perpendicular to the metallic foil.

The multiwalled CNTs used here were prepared by the standard arc-discharge technique [16]. After purification, a 10 μl ethanol suspension of CNTs was deposited between two metallic electrodes placed on a clean glass microscope slide, separated by a 400 μm gap. CNTs were aligned on the edge of the electrodes when a 70 V–1 kHz AC signal was applied across the gap [17]. The metallic electrode with the CNTs was then mounted inside the SEM on the nanomanipulator with the CNTs positioned perpendicular to the plane of the AFM cantilever. SEM imaging allows us to control the motion of the AFM tip to bring it in contact with one CNT protruding from the edge of the electrode, as seen in figure 1. This method allows us to select the diameter (10–30 nm) of the CNTs. The AFM tip was then raised so that the free end of the CNT made contact with the surface of the AFM tip.

CNT–tip contact was indicated by the abrupt change of the CNT shape as the latter adhered to the tip through van der Waals forces. To improve this weak attachment, the CNT was then welded to the tip surface by directing the SEM electron beam at the junction between the CNT and the surface [18]. This produces the deposition of an amorphous carbon layer on the junction, through the dissociation of organic species present in the SEM chamber [19, 20], thereby mechanically pinning the CNT to the AFM tip surface. After holding the beam in this position for 5 min, the AFM nanotube tip was slowly displaced laterally to verify its attachment. Slight movements of the piezos allowed us to align the CNT, now fixed at both ends, and to straighten it with respect to the AFM silicon tip axis.

The electron beam is used to cut the CNT tip to the desired length. The software capabilities of the SEM are used to position the electron beam at any distance from the AFM silicon tip apex and in this way the final length of the nanotube tip is selected. At the selected length (distance) the nanotube is cut by scanning a single line perpendicular to the nanotube with the electron beam [21]. After 2 min, the electron beam starts to break the carbon bonds and cuts the CNT tip, as shown in figure 2. This method provides reliable and reproducible AFM nanotube tips with a precision in the length of about 2 nm. More than 40 nanotube tips of lengths varying from 50 nm to 4 μm have been fabricated. Several of them can be seen in figure 3. Multiwalled tubes instead of single wall have been used because for the same length they provide less bending and thermal vibration. Transmission electron microscopy (TEM) images showed that the cut is abrupt, but the application of a 2 V dc voltage across the carbon nanotube during the cutting process allows us to sharpen the end of the nanotube to the size of a single-wall tube, ~1.8 nm, as seen in figure 4. This sharpening process is critical for AFM operation because it provides tips that are simultaneously rigid (the shank of the tip has a multiwalled character) and very sharp at the end to improve image resolution [22].

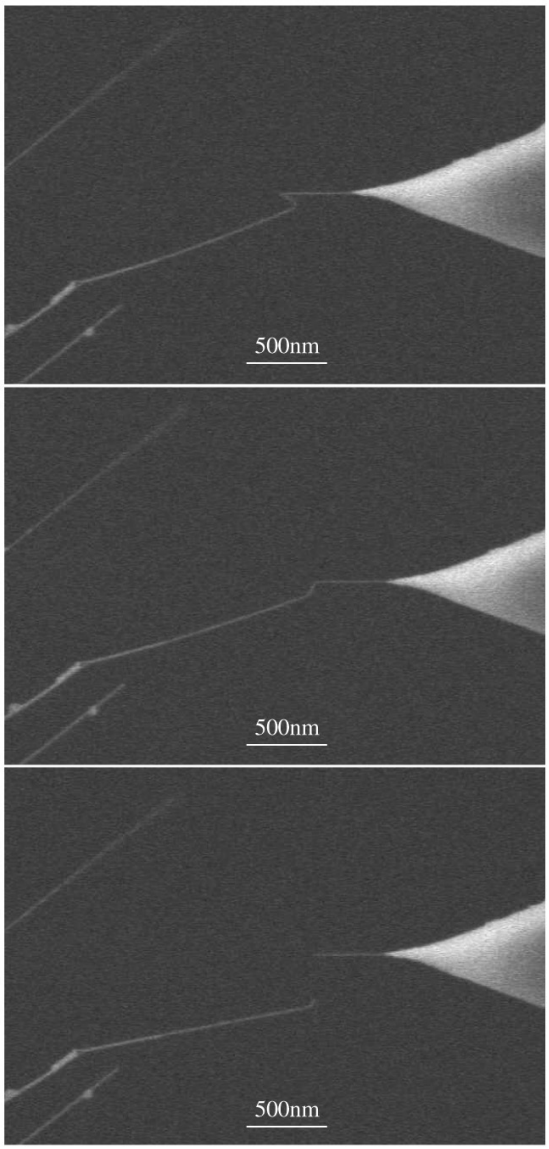

Figure 2. Top to bottom images show a sequence of the fabrication process of AFM carbon nanotube tips by the electron beam. The exposure of the multiwalled CNT to the electron beam produces the successive decapping of the CNT layers until it breaks in two. The final CNT tip is 300 nm.

3. Results and discussion

To characterize the AFM imaging properties of the produced CNT tips, they were mounted on a Nanoscope III AFM to

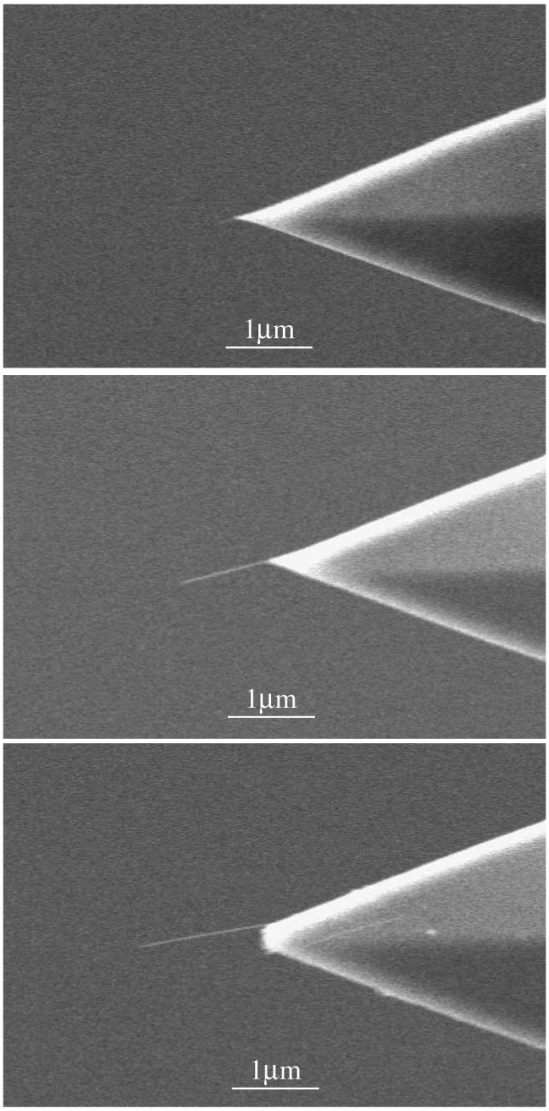

Figure 3. SEM images of several AFM carbon nanotube tips of different lengths (top to bottom) of 100, 1000 and 1500 nm.

image double-stranded DNA on mica [23, 24]. The AFM was operated in amplitude modulation mode (tapping) because the lateral and shear forces are minimized with respect to contact mode, making it suitable for imaging soft biological samples [25, 26]. We used a set point amplitude oscillation of 7 nm and a free amplitude of 12 nm. The engaging process was stopped when the force analysis started to show an interaction between the tip and the sample.

CNT tips produce sharper images of DNA molecules ($\sim 6 \pm 0.8$ nm in width) than regular silicon tips ($\sim 10 \pm 1$ nm in width). However, the quality of the image depends on the CNT length while the DNA height remains similar in any case (1 ± 0.2 nm). Long CNT tips ($\geqslant 100$ nm) produce sharp images (apparent width of $\sim 8 \pm 1$ nm) of the DNA but with a ghost image (see figure 5(a)) probably due to the bending and oscillation of the nanotube tip during the tapping process. Shorter CNT tips generate sharper DNA images (apparent widths of ~ 6 nm $\pm$ 0.8 nm). Significantly, these images reveal periodic features along the double-strand DNA chain.

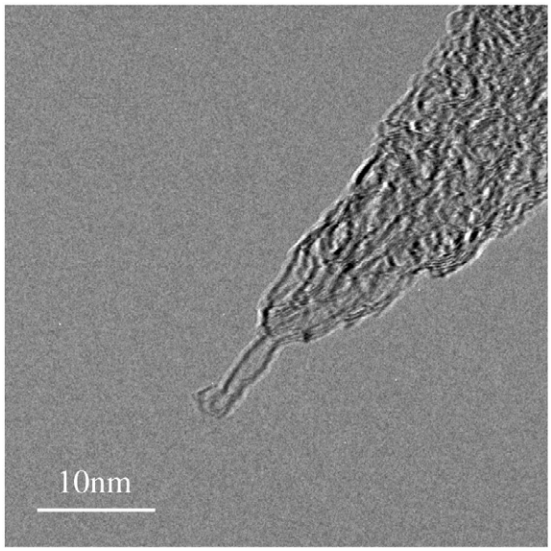

Figure 4. TEM image of the end of an AFM carbon nanotube tip after the sharpening process. The final diameter of the nanotube is 1.8 nm.

The measured periodicity is about 6–7 nm, i.e., approximately twice the helical turn length (3.4 nm). Those features could correspond to the visualization of the major grooves of the DNA that are facing the tapping CNT. According to this interpretation, the major grooves closer to the mica surface would not be resolved due to tip–surface convolution effects. We also note that the contrast and the periodicity along the DNA chain depend on the orientation of the DNA molecule with respect to the direction of the tip movement (figure 5(b)). This reflects a tip–molecule convolution effect that depends on the alignment of the molecule with respect to the scanning direction. This could be a factor in the observed periodicity. On the other hand, analysis of different DNA images generated by different nanotube tips allows us to establish that short CNT tips improve contrast and resolution. Due to proximity in the interaction of the electron beam with the end of the silicon tip, the smallest CNT tip that we can fabricate in a reproducible way is one of 50 nm. We have observed that this length is the one that provides the highest resolution for imaging biomolecules such as DNA.

4. Conclusions

We have developed a method to fabricate carbon nanotube tips for atomic force microscopy imaging with a precise control of the length and diameter of the tips. By using a nanomanipulator inside a scanning electron microscope, we retrieved, from a metal foil covered with CNTs, a single CNT with the AFM tip. The length of the nanotube is controlled by cutting the carbon nanotube with the electron beam. Finally, the performance of these tips is demonstrated by imaging DNA molecules in air with AFM operated in the amplitude modulation mode. The images reveal several periodic features along the molecule that could be associated with the major grooves of the DNA molecule. Results obtained with tips of different lengths suggest that carbon nanotubes of about 50 nm

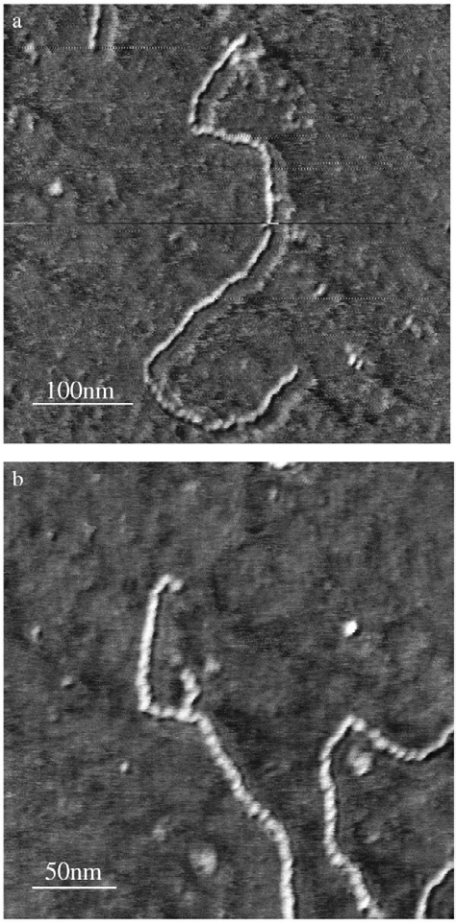

Figure 5. AFM images of double-stranded DNA deposited on mica. The images were acquired with CNT tips of lengths of (a) 300 nm and (b) 50 nm. Longer CNT tips produce ghost images while smaller CNT tips allow us to resolve periodic structures along the DNA molecule.

in length represent a compromise between length mechanical stability and ease of fabrication.

Acknowledgments

The authors thank Drs Shaul Aloni and Liang Fang for helpful discussions and Andrei Afanasiev for assisting in the CNT preparation. This work was supported in part by a grant from the NIH GM-32543 (CB), and a DOE grant DE-AC03-76DF00098 (CB). RG acknowledges financial support from the MCyT (Spain), contract number MAT2003-02655.

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