Single-walled carbon nanotube probes for high-resolution nanostructure imaging

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Single-walled carbon nanotube (SWNT) tips have been used to image nanostructures with high resolution. Studies of gold nanocrystal standards showed that SWNT tips provide a significant improvement in lateral resolution with respect to multi-walled nanotube tips and microfabricated Si tips. The nanotube tips were also used to resolve substructure within SWNTs deposited on surfaces. These results suggest that observed 1.5 nm high structures can correspond to several SWNTs aligned in parallel. In addition, SWNT tips exhibited superior resolution compared to conventional tips when imaging biological nanostructures, such as double-stranded DNA. The potential and future challenges of SWNT tips are discussed. © *1998 American Institute of Physics.* [S0003-6951(98)03149-0]

Nanostructures are currently the focus of intense fundamental and applied research.[1–3] This interest is not surprising in light of the novel size- and structure-dependent properties exhibited by nanostructures and the promise to impact broad areas of technology.[1–3] Critical to much of this work is an understanding of size-dependent properties, including the charging energy of nanocluster and nanotube devices, and the optical emission from semiconductor quantum dots.[1,2] Routine characterization of nanostructure size thus represents an important aspect of research, and one that is becoming increasingly difficult with the push to ever smaller structures. Herein, we describe an approach that exploits the unique size and mechanical properties of single-walled carbon nanotubes (SWNTs) as probe tips in atomic force microscopy (AFM) to meet this challenge.

AFM is widely used to characterize inorganic, organic, and biological nanostructures.[3–5] The feature resolution obtained by AFM is determined in large part by the size and shape of the imaging probe tip.[5,6] Commercially available probes consist of microfabricated pyramids of Si or Si_3N_4 that have end radii of curvature as small as 10 nm but are often much larger.[6,7] The end radii and shape of these tips thus place significant constraints on lateral resolution and the ability to image narrow and deep features. Partial compensation for these limitations of conventional pyramidal tips can be achieved by image reconstruction or restoration.[8] Alternatively, to circumvent the effects of tip-induced broadening, the height of a nanostructure (e.g., a nanotube) is often taken as a measure of the diameter; however, this approximation implicitly assumes that the true shape of the structure is known.

Carbon nanotube tips represent a potential breakthrough in probe technology in several regards.[9–12] First, the cylindrical geometry of these tips can be used to image deep structures, such as gratings, with excellent fidelity.[9] Second, nanotubes can elastically buckle above a critical force.[9,13] Buckling limits the maximum force applied to a sample, which can prevent damage to delicate organic and biological samples, and at the same time makes the tips very robust. Third, the small diameter of individual nanotubes, which is ~1 nm for SWNTs,[14] offers the potential for very significant improvements in lateral resolution. Our recent AFM studies of a biological nanostructure, $A\beta$ (1–40) protein-derived fibrils, showed that multiwalled carbon nanotube (MWNT) tips can provide a 10%–30% improvement in lateral resolution compared with the best microfabricated Si tips, and moreover, preliminary measurements using SWNT tips showed even higher lateral resolution.[10] Finally, we have recently demonstrated that the ends of carbon nanotubes can be functionalized to create chemically and biologically sensitive imaging probes.[11,12]

SWNTs were prepared and purified by reported methods.[14,15] SWNT ropes were mounted onto the pyramids of Au-coated Si cantilevers using an acrylic adhesive under the direct view of an optical microscope, operated in dark-field mode. The as-made nanotube tips were optimized for imaging by applying a bias voltage between the tip and a sputtered Nb surface; this process shortens and sharpens the tips.[10–12] Images were acquired with a Nanoscope III AFM (Digital Instruments, Santa Barbara, CA) under ambient conditions in tapping mode as described previously.[10–12,16]

The resolution of the SWNT tips was first analyzed by recording images of monodisperse 5 and 10 nm Au nanocrystals.[17] Because these nanocrystals are spherical and relatively incompressible, the tip radius can be calculated from the nanocrystal heights and widths measured from images.[18] A summary of our results is presented in Table I. On average, we find that SWNT tips yield a ~70% improvement in lateral resolution compared with conventional Si tips. The calculated SWNT tip radii determined from several independent tips, 3–6 nm, were as much as 3–5 and 2–3 times smaller than conventional Si and MWNT tips, respectively. This significant decrease in tip size does not, however, produce mechanically unstable probes. Indeed, we find

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TABLE I. Comparison of the resolution of Si, MWNT, and SWNT tips.

Tip	Au nanostructure standard (in nm)[a]	Apparent full width at half-maximum (in nm)	Estimated tip radius of curvature (in nm)[b]
Etched Si FESP	5	17.2±2.0	11.5
	10	25.6±2.9	17.3
MWNT FESP	5	13.0±2.1	6.0
	10	19.0±2.5	8.6
SWNT FESP	5	10.6±2.6	3.4

[a]The particles were assumed to be spherical with mean diameters, based on company specifications, of 5.72 and 8.44 nm for the 5 and 10 nm gold colloids, respectively.
[b]Estimates of the tip radius are generated by restoring images of known gold spheres using standard deconvolution techniques assuming a spherical tip imaging a spherical feature (Ref. 18).

that the SWNT tips are more robust than larger, sharp Si tips.

To explore further the applications of high-resolution nanotube tips, we have investigated the structure of SWNTs dispersed on highly ordered pyrolytic graphite (HOPG) and Au(111) substrates. Previous AFM images of such dispersed samples have been interpreted as individual SWNTs on the basis of the ~1.5 nm heights of the observed features.[15,19,20] However, it is known that during growth SWNTs form ropes consisting of strongly bound, parallel tubes in a hexagonal lattice.[14] It is thus possible that the observed features in AFM images actually correspond to several parallel tubes, like logs within a raft, lying on the surface. We have used AFM imaging with SWNT tips and scanning tunneling microscopy (STM) to explore this possibility.

Figure 1(a) shows a typical AFM image of a deposited SWNT sample. The height of the structure, 1.7 nm, is similar to that expected for a single nanotube, while the observed full width at half maximum (FWHM) of the structure, 11.5 nm, is larger than a single SWNT. Previous work with Si tips has simply attributed much larger widths (>20 nm) to tip-induced broadening.[15,19] However, sections taken across this image (and similar nanotube images) recorded with the SWNT tip exhibit broadening and a dip that are consistent with the presence of at least two nanotubes lying side by side [Fig. 1(b)]. We have quantitatively investigated this possibility by simulating the observed cross section.[21] The results of this simulation [Fig. 1(b)] are consistent with a structure in which two SWNTs are aligned parallel to one another; that is, like a log raft. Significantly, all of the SWNT structures of <2 nm height observed to date with our high-resolution probes exhibit a raft-like structure with two or more parallel tubes. This point is further substantiated by scanning tunneling microscopy measurements of dispersed SWNTs in ultrahigh vacuum (UHV) at 77 K.[22] A STM image of a SWNT rope [Fig. 1(c)] clearly illustrates repeating 1.5–2 nm features corresponding to at least four SWNTs lying parallel to each other. Atomic-resolution STM images of the individual SWNTs in raft-like structures, which are commonly observed in STM measurements, further show that these are distinct tubes and not a multiple tip artifact.[22] These observations confirm our AFM results, and thus suggest caution in attributing <2 nm high features in low-resolution AFM images to isolated SWNTs.[15,19,20]

To further explore the application of SWNT tips for high-resolution imaging, we have studied the important biological nanostructure, DNA. Lambda DNA (New England Biolabs, Inc., 330 pg/μL) in 1 mM $MgCl_2$ was adsorbed onto mica for 10 min, thoroughly rinsed in distilled, deionized water, and dried under a stream of nitrogen, immediately prior to imaging in air. A typical image is shown in Fig. 2(a). The heights of the DNA strands were calculated to be 0.36 ±0.07 nm, consistent with earlier work.[23] The FWHM measured using SWNT and Si tips, 5±1 nm and 15±3 nm, respectively, demonstrate a very significant threefold improvement for our SWNT tips. In addition, we occasionally observed DNA FWHM values as low as 3 nm. Hence, we believe that SWNT tips also offer significant potential for imaging biological nanostructures.

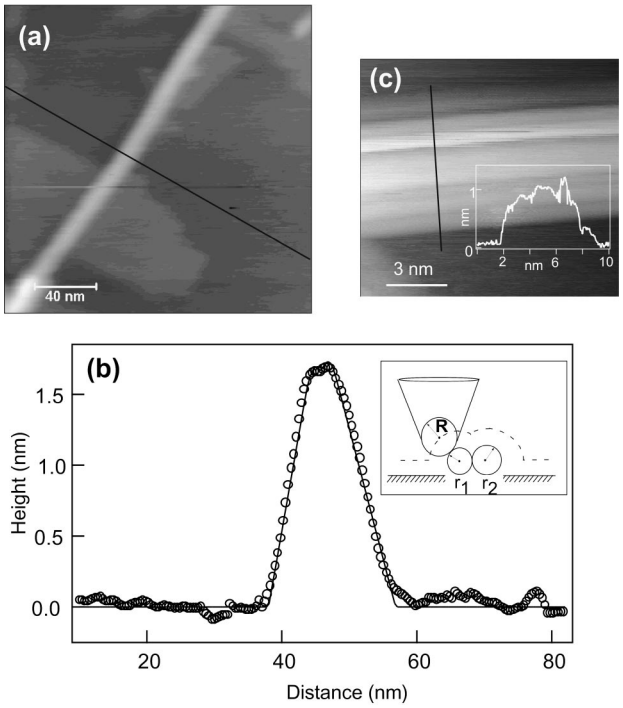

FIG. 1. (a) AFM height image recorded in air on a SWNT rope deposited on HOPG. (b) The height cross section (open circles) corresponding to the line in (a). The solid line corresponds to a simulation for a hard-sphere model (Ref. 21) (inset) in which a spherical tip of radius R scans over two circular cross-section nanotubes of radii, r_1 and r_2. The initial tip radius used in the simulation was fixed at the typical value (5 nm) determined from images of the 5 nm gold nanocrystals. The final parameters determined from the simulation were: nanotube-1 (left) and nanotube-2 (right) diameters=1.70±0.02 and 1.72±0.02 nm, respectively; tip radius=5.5±0.3 nm. (c) Ultrahigh vacuum STM image of a SWNT rope deposited on a Au(111) substrate. The image was recorded in the constant-current mode with a bias voltage of 150 mV and a tunneling current of 150 pA. (Inset) height cross section along the solid line shown in (c). The x axis of the inset increases from bottom to top along this line.

In conclusion, we have demonstrated that SWNT probes significantly improve the lateral resolution obtainable in AFM compared to conventional tips. We have been able to image gold nanostructures with a 70% improvement in resolution using SWNT tips with respect to Si tips. SWNT tips were capable of imaging substructure within dispersed SWNTs on surfaces, and thus showed that the features observed in low-resolution AFM images correspond to several SWNTs aligned within a raft-like structure and not individual SWNTs. Finally, we find that SWNT tips provide significant improvement in lateral resolution when imaging

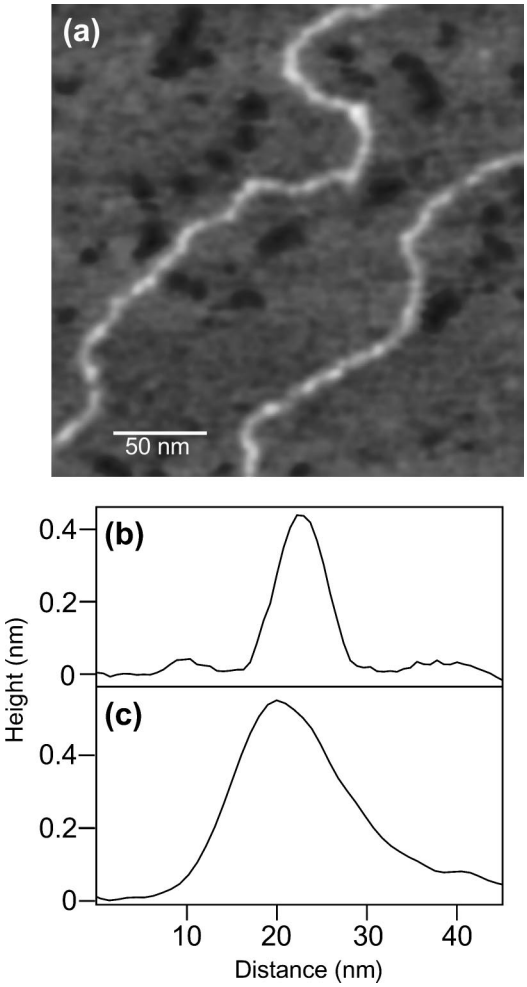

FIG. 2. (a) Height image obtained with a SWNT tip of double-stranded DNA adsorbed on mica. (b) Typical height cross section from the image in (a). The FWHM is 5.6 nm. (c) Typical height cross section from an image of the lambda-DNA obtained with a conventional Si tip. The FWHM is 14.4 nm.

double-stranded DNA. We believe that the use and further development of these tips is especially promising, since the observed radii are still much larger than the 0.5 nm radius that would be produced by exposing an individual SWNT. The development of improved methods to expose individual nanotubes at the tip ends should enable true molecular-resolution AFM imaging in the future.

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