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LETTERS

High-Yield Assembly of Individual Single-Walled Carbon Nanotube Tips for Scanning Probe Microscopies

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The structural and mechanical properties of single-walled carbon nanotubes (SWNTs) make them ideal tips for scanning probe microscopies such as atomic force microscopy (AFM). However, the ideal nanotube probe, which corresponds to an individual SWNT, has been difficult to produce in high yield. To overcome this difficulty, a straightforward and easily implemented method that enables very high-yield fabrication of individual SWNT probes has been developed. This new method is based upon the observation that microfabricated tips can “pick up” vertically aligned SWNTs grown from planar substrate surfaces. Substrates with isolated, vertically aligned SWNT are first prepared by chemical vapor deposition and then imaged with commercial microfabricated silicon AFM tips. The silicon tips pick up individual SWNTs from the substrate during imaging to create well-aligned SWNT probes. The SWNT tips have been etched using a procedure that allows variation of the nanotube length with 2 nm control. Studies of gold nanocluster standards demonstrate that these individual SWNT tips are capable of high resolution and robust imaging in air and fluids, and thus these tips are expected to open up new opportunities in nanoscale science and technology.

Introduction

Atomic force microscopy (AFM) has greatly impacted many areas of science and technology due to its unique ability to image a number of distinct properties of samples, such as topography, elasticity, and chemical functionality, with nanometer-scale resolution in a vacuum, ambient, and fluid environments.^{1,2} In AFM and other scanning probe microscopies, the probe tip that interacts with a sample is one of the most important and potentially limiting pieces of the overall technology. Most AFM tips are prepared by microfabrication and are pyramidal with ca. 5 nm (silicon) or ca. 50 nm (silicon nitride) radii of curvature at the tip apex, and cone angles of ca. 30 degrees.³ In many imaging applications, especially molecular and biological sciences, sharper and higher aspect ratio tips are needed. In

addition, the atomic structure of commercial tip is not well characterized and typically can change while imaging.⁴

To overcome these limitations and develop improved tips, several techniques have been explored, including FIB etching,⁵ electron beam deposition,⁶ diamond-like film deposition,⁷ and the use of small, naturally occurring asperities.⁸ These approaches represent improvements for specific samples and imaging conditions; however, none provides a tip structure with both high aspect ratio and sub-nanometer radius of curvature, while being chemically stable and mechanically robust. Carbon nanotubes, which are graphene cylinders with diameters ranging from 0.5 to 50 nm and lengths of many microns,⁹ may represent the ultimate AFM tips.¹⁰ They provide a unique combination of high resolution and high aspect ratio imaging due to their exceptionally large Young's modulus.^{11,12} In addition, carbon nanotubes elastically buckle rather than fracture under large loads,¹² which makes them highly robust as AFM probes.

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Previously, nanotube probes have been prepared by manual assembly of preformed nanotube material onto commercial AFM tips by micromanipulation.^{13–15} This approach enabled the early development of nanotube tips, including the observation of nanotube buckling,¹³ high resolution¹⁴ and high aspect ratio¹³ imaging, and covalent modification of the tip ends for chemical force microscopy.¹⁵ This manual assembly process is very time-consuming, which places significant constraints on large scale fabrication, and moreover, the resolution is limited by the larger diameter and/or thick bundles of nanotubes that can be viewed during the micromanipulation process. Although a recent report provides one example of “sharpening” a multiwalled nanotube tip down to the innermost tube in an electric field,¹⁶ the typically large inner diameters of multiwalled nanotubes and the vacuum requirements of this sharpening method suggest that it represents little improvement over the similar in situ etching method reported previously for nanotube AFM tips.^{13–15}

Many of the limitations of manual assembly can be overcome by direct growth of nanotubes at the tip apex by chemical vapor deposition (CVD).^{10,17–20} This process has yielded high-resolution multiwalled nanotube and SWNT tips, and enabled tip fabrication in parallel. The CVD tip growth approach can yield individual SWNT tips, which would represent the ultimate high-resolution probe, by lowering the catalyst density,^{18–20} although this strategy reduces the tip yield.²⁰ Herein, we present a hybrid CVD/assembly method for the facile production of individual SWNT tips with essentially 100% yield. This new method is based upon the observation that microfabricated tips can “pick up” vertically aligned SWNTs from a planar substrate surface. Substrates with isolated, vertically aligned SWNT have been produced by CVD, and then microfabricated silicon tips are used to pick up individual SWNTs from the substrate during imaging to create well-aligned SWNT probes. Studies of gold nanocluster standards demonstrate that these individual SWNT tips are capable of high resolution and robust imaging in air and fluids.

Methods

Nanotubes were grown on oxidized silicon substrates by CVD using an iron catalyst. Briefly, a 150 $\mu\text{g/mL}$ solution of ferric nitrate nonahydrate in 2-propanol was prepared and stirred for 2 min. Silicon substrates were dipped in this solution for 10 s, rinsed in hexane, and dried. These substrates were then placed in a tube furnace and annealed at 700 °C for 15 min under a flow of 600 standard cubic centimeters (sccm) argon and 400 sccm hydrogen. Ethylene was then added at 0.5 sccm for 6 min, and finally, the furnace was cooled under argon.

Nanotube tips were fabricated by imaging the nanotube-covered wafers in tapping mode with silicon tips using a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA). For fluid imaging tips, the microfabricated pyramids were coated with a thin layer of a UV-cure adhesive (Loctite 3105). After a nanotube tip was attached by the “pick up” procedure, the glue was cured in UV for 30 min (UVGL 25 Mineralight lamp, UVP, Inc.). Force calibration curves were recorded on a clean silicon wafer to assess nanotube length, and then 10–20 V, 50–100 μs pulses were applied to the tip while imaging in tapping mode to shorten the tip in approximately 2–5 nm increments per pulse. Force calibration curves were repeated after removing approximately 20 nm from the tip end, and this sequence was repeated until the desired tip length was produced.

Transmission electron microscopy (TEM) experiments were performed with a Philips EM420 (FEI, Hillsboro, OR) operated

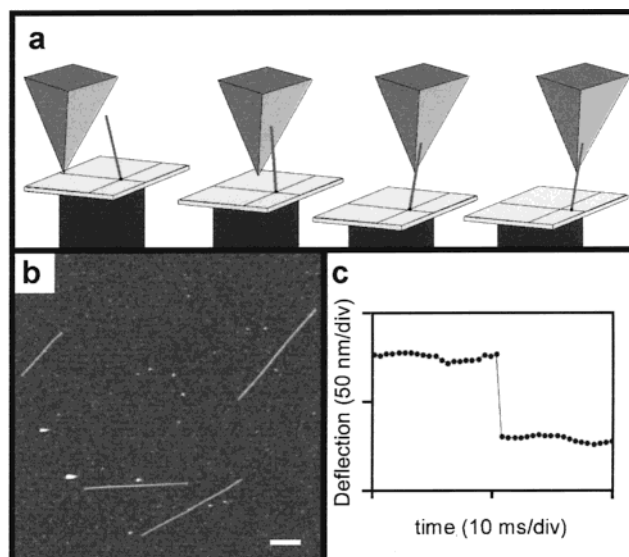


Figure 1. (a) Schematic depicting the process by which a microfabricated pyramidal tip picks up a vertically aligned carbon nanotube. (b) An AFM image of isolated, SWNTs on the substrate surface. The scale bar is 100 nm. (c) A plot of the z -piezo position versus time for a single pick-up event.

at 100 kV. The entire cantilever/tip assembly with nanotube tip was mounted on a custom TEM holder for imaging.

Results and Discussion

In our new method for SWNT probe fabrication, conventional AFM tips are used to “pick up” nanotubes from substrates on which vertically aligned nanotubes have been grown by CVD (Figure 1a). Significantly, metal-catalyzed CVD growth enables control of the nanotube tip diameter by varying the catalyst size and growth conditions.^{19–21} In these studies, we have focused on the growth of isolated SWNTs since these can lead to ultrahigh resolution, individual SWNT probe tips. A typical AFM image of a substrate following CVD growth (Figure 1b) reveals very straight and isolated SWNTs with lengths of several hundred nanometers. The average diameter of the SWNTs determined from AFM height measurements for this sample is 2.2 ± 0.5 nm and typically ranges from 0.7 to 3 nm depending on catalyst and growth conditions.

Significantly, while imaging samples prepared in this way, the sample z -position often jumps to a lower value with a step size on the order of 10–100 nm (Figure 1c). This jump corresponds to an increase in the AFM tip length, and can be explained by a SWNT becoming attached to the tip as shown schematically in Figure 1a. These observed events, which occur approximately once per $8 \times 8 \mu\text{m}^2$ scan, and our suggestion that they correspond to the attachment of SWNT at the tip apex are consistent with observations showing that nanotubes also protrude in a near vertical orientation from the substrate surfaces.²²

Definitive proof that the observed z -position jumps correspond to the attachment of individual SWNTs to the AFM tip apexes was obtained from TEM investigations (e.g., Figures 2a, 2b). These TEM studies clearly show that (1) individual SWNTs are attached to the silicon tip apexes, (2) the nanotube tips fabricated in this way are remarkably well aligned, and (3) the nanotube lengths extending from the tip apexes are similar to the z -position height steps. The range of SWNT diameters measured by TEM is also in good agreement with that measured by AFM for the nanotubes lying flat on the surface; that is,

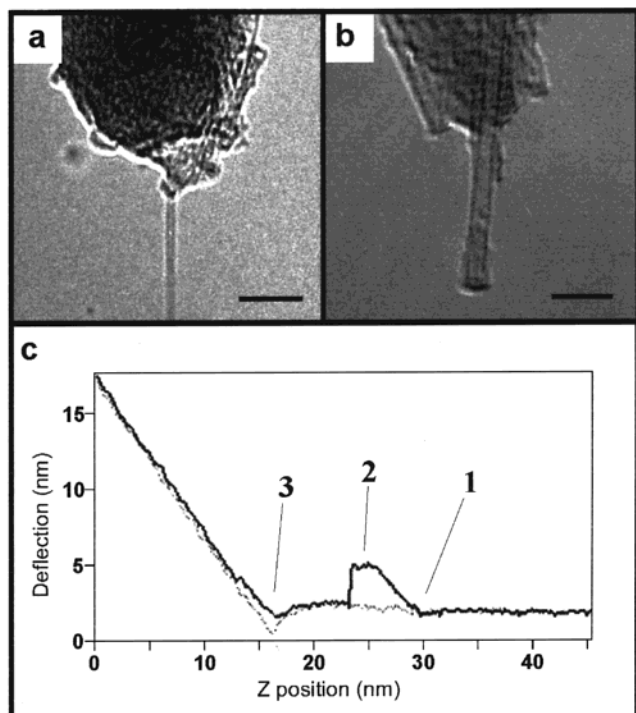


Figure 2. TEM images of (a) a 0.9 nm diameter nanotube tip and (b) a 2.8 nm diameter nanotube tip. The scale bars are 10 nm. (c) Cantilever deflection versus z -position. The difference between points 1 and 3 corresponds to 12 nm; the deflection decrease at point 2 corresponds to nanotube buckling.

from 0.7 to 3 nm. The SWNT tips shown in Figure 2a and Figure 2b illustrate this range with diameters of 0.9 and 2.8 nm, respectively.

To assess the properties of the SWNT tip in-situ, we have measured the deflection versus tip-sample separation (Figure 2c). When the nanotube first comes into contact with the sample, the tip is deflected (point 1). As the tip-sample separation is further reduced, the applied force will exceed the nanotubes buckling force. At this point (point 2), the deflection saturates and often drops to zero as the nanotube is deformed. Ultimately, the silicon pyramid contacts the sample (point 3) and the deflection increases again. The nanotube length corresponds to the separation between points 1 and 3, and is ca. 12 nm for the tip measured in Figure 2c. The fact that the deflection-separation curves can be repeated multiple times demonstrates that these nanotube tips are highly robust and have a sufficiently large nanotube/silicon adhesion for routine imaging.

The assembled nanotube tips are capable of imaging immediately after pick-up attachment, although they are usually too long for high-resolution studies due to excessive thermal noise. The thermal vibration amplitude, X_{tip} , can be approximated by equating $\frac{1}{2}k_B T$ with the potential energy of lateral nanotube bending:¹²

$$X_{\text{tip}} = \sqrt{\frac{k_B T}{k_{\text{nt}}}} \quad (1)$$

where k_B is Boltzmann's constant and T is the temperature in Kelvin. The nanotube force constant for lateral bending, k_{nt} , can be approximated from the continuum formula:

$$k = \frac{3\pi r^4 Y}{4l^3} \quad (2)$$

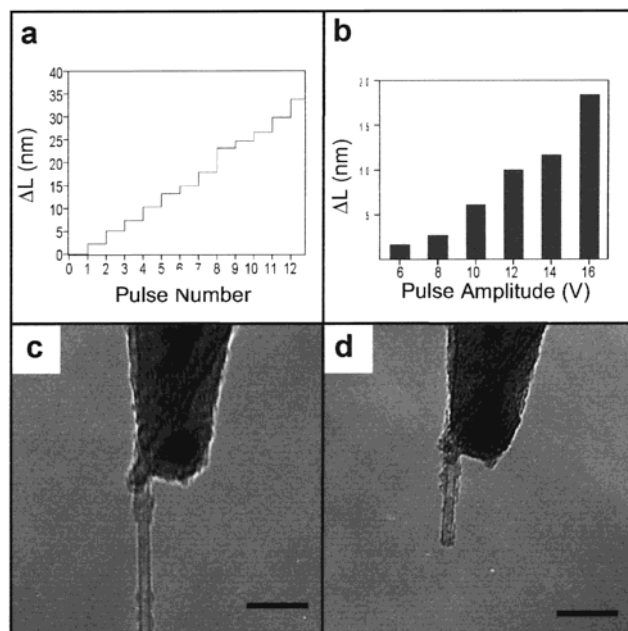


Figure 3. (a) The change in nanotube length measured from the sample z position after consecutive 6 V pulses. (b) The average etched length per pulse as a function of the pulse amplitude in volts. TEM images of a nanotube tip (c) before and (d) after etching. The scale bars are 20 nm.

where r is the nanotube radius, l is the length, and Y is the Young's modulus. Using these equations and setting an upper limit of 0.5 nm on the vibration amplitude, we estimate that a 3 nm diameter nanotube tip should be no more than 90 nm long, while a 0.8 nm diameter nanotube tip should be no longer than 15 nm. This analysis suggests that ultrahigh-resolution imaging with the smallest diameter SWNTs will require the nanotube length be controlled with 2–5 nm precision.

Previously, multiwalled nanotube tips and SWNT bundle tips, which can be much longer due to their large diameters, were etched by applying a DC bias between the tip and sample with the end of the nanotube probe near a conducting surface. This method typically removes about 50 nm of tip, and is thus inadequate for etching the individual SWNT tips described here. To achieve the much greater control required for these smaller diameter individual SWNT tips, we have developed a modified etching technique in which 10–20 V, 50–100 μs pulses are applied to the tip while imaging a conducting substrate (n^+ -doped silicon). In this procedure we monitor the sample z -position to assess removal of material from the tip end. Significantly, this method allows 2 nm lengths per pulse to be consistently removed from the tip end as shown in Figure 3a. In addition, the pulse amplitude may be adjusted to control the length etched per pulse (Figure 3b). Reproducible etching of 2 to 20 nm per pulse can be achieved in this way. A typical series of TEM micrographs corresponding to before and after etching of an individual SWNT tip are shown in Figure 3c and Figure 3d, respectively. These data show that short individual SWNT tips can be produced by our etching procedure and that the ends of the shortened tips are clean.

We have assessed the lateral resolution of these individual SWNT tips by analyzing images recorded on gold colloid standards deposited on mica.²³ The full width at half-maximum height (fwhm) of the particle image provides an estimate of the tip radius and represents a measure of the resolution.¹⁹ Figure 4a shows a tapping mode image of 5.2 nm gold colloid particles imaged with an individual SWNT pick up tip. Significantly,

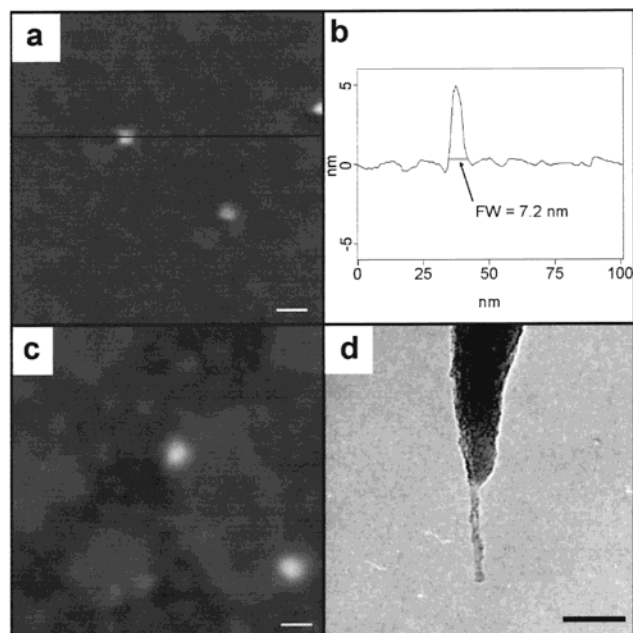


Figure 4. (a) Tapping mode AFM image of 5.2 nm gold colloids recorded in air. The scale bar is 10 nm. (b) A cross section from (a) demonstrates that the full width of the colloid is 7.2 nm. (c) Tapping mode AFM image of 5.2 nm gold colloids recorded in water. The scale bar is 10 nm. (d) TEM image of a glued nanotube tip capable of being used in fluid imaging. The scale bar is 25 nm.

the cross section (Figure 4b) reveals that the *full width* of the particle image (FW) is only 7.2 nm, which implies a tip radius of 1 nm for the entire 5.2 nm particle height (vs more typical half-height). This impressive resolution on a relatively tall structure can be readily explained in terms of the small diameter and high aspect ratio cylindrical geometry of the single SWNT tip. In previous studies, manually assembled multiwalled and SWNT tips were shown to have radii as low as 6 and 3.4 nm, respectively,¹⁴ while direct growth CVD SWNT tips exhibited typical radii of 1.5–4 nm.¹⁸ Hence, the present pick-up SWNT tips exhibit a significant improvement in resolution, and do so in a highly reproducible manner.

Last, these new ultrahigh resolution nanotube tips can be used for imaging in fluid solution. For reliable operation in fluids we have improved the SWNT-Si pyramid contact by coating the pyramids with a thin layer of UV-curable adhesive prior to SWNT pick up. The adhesive layer is then cured after the nanotube is attached. Individual SWNT tips prepared in this way could be etched and used for extended imaging in fluid solutions. A typical image of gold nanoparticles acquired in water with a glued nanotube tip is shown in Figure 4c. TEM images (Figure 4d) and deflection–separation curves verify unambiguously that the tips remain attached in aqueous solution and can be used for extended high-resolution imaging. The images of gold colloid particles recorded in fluid exhibit high resolution but do not have as well defined edges as those recorded in air (e.g., Figure 4a). We believe that this difference may be due to long-range interactions between the tip and sample supported by the fluid and/or motion of the particles in fluid, and are currently pursuing approaches to improve the resolution further.

Conclusions

We have demonstrated a simple and high yield means of producing individual nanometer and sub-nanometer diameter

SWNT tips for AFM and other scanning probe microscopies. This straightforward method for preparing SWNT tips will enable widespread application of these ultrahigh resolution probes, in which the tip is essentially a single fullerene-like molecule, in many areas of science and technology. For example, these SWNT tips offer significant advantages for AFM applications in structural biology, and when modified at their ends,¹⁵ could enable spatially resolved functional imaging and single molecule force spectroscopy in which the reaction coordinate is well-defined. In addition, this method could also be used to assemble SWNTs on advanced cantilever structures, which may not survive high CVD temperatures, such as those used for thermal sensing,²⁴ to enable other types of experiments at unprecedented resolution.

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