Direct Growth of Single-Walled Carbon Nanotube Scanning Probe Microscopy Tips

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Herein, we report the first growth of single-walled carbon nanotubes (SWNTs) directly from conventional atomic force microscopy (AFM) cantilever assemblies to create very high-resolution tips for scanning probe microscopies. Metal catalysts were deposited onto the pyramids of microfabricated AFM tips and chemical vapor deposition (CVD) was used to synthesize carbon nanotubes. Scanning and transmission electron microscopies show that nanotubes grow along the surface and reproducibly protrude from the tip apex in the optimal orientation for imaging, and that single SWNT, small SWNT bundle, or very small diameter multi-walled nanotube (MWNT) tips can be controllably made. AFM measurements demonstrate that these new nanotube tips are mechanically robust and can image with very high resolution. We believe that this straightforward growth method will make nanotube tips broadly accessible, and moreover, that the molecular size diameters of these SWNT tips creates unique opportunities for imaging in chemistry and biology.

Carbon nanotubes are ideal structures for the tips used in scanning probe microscopies, such as AFM, since they (i) have intrinsically small diameters, which are comparable to molecules in the case of SWNTs, (ii) have high aspect ratios, (iii) can buckle elastically, and (iv) can be selectively modified at their ends with organic and biological species to create functional probes.[1−6] Mechanical methods have been used to attach nanotube bundles in the fabrication of tips, although we believe that this time-consuming approach has limited the development of nanotube tips.[1−6] To overcome these limitations we have been exploring the direct catalytic growth of nanotubes from conventional tips and recently showed that individual MWNTs could be grown by CVD from the ends of Si tips with controlled orientation.[7] In this first example of the direct growth of nanotube probes, we utilized selective etching of commercial tips to create nanopores, deposited catalyst within these pores, and used the pores to help orient the nanotubes in an ideal direction for imaging.[7] Our present work extends this initial demonstration in two important ways: we show that (1) the pore etching step can be eliminated by using "surface growth" and (2) SWNT tips can be readily prepared by controlling the CVD growth conditions.

Our overall strategy for the growth of SWNT tips is outlined in Figure 1. In this approach, catalyst is first deposited onto the pyramidal tip of a commercial cantilever assembly, and then CVD is used to grow the SWNT probe. The basis for this approach is our observation that SWNTs and small diameter MWNTs prefer

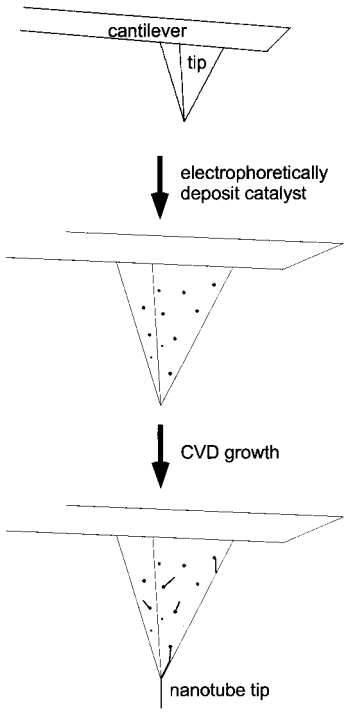

Figure 1. Overview of the approach used to prepare SWNT tips.

to grow along a surface (due to the attractive nanotube−surface interaction[8]), and therefore, will generally bend to stay in contact rather than grow out from the surface when they encounter an edge. Nanotubes prepared from catalyst deposited on a pyramidal AFM tip will grow along the surfaces until they reach the pyramid edges, then some will be directed toward the tip apex along the edges. At the pyramid end the nanotubes will protrude straight from the apex (vs bending) to create an ideal tip, because the strain energy cost of bending the nanotube is not compensated by nanotube−surface interactions. We find that this approach is extremely robust and works readily with a wide range of catalysts.

Well-defined SWNT tips are formed reproducibly after CVD growth with ethylene using electrophoretically deposited supported Fe−Mo[9] and colloidal Fe−oxide[10] catalysts.[11,12] Representative electron microscopy images of a nanotube tip produced from the supported Fe−Mo catalyst after 3 min growth in 1:200:300 C_2H_4:H_2:Ar at 800 °C are shown in Figure 2.[12] These conditions were specifically chosen to favor the growth of SWNTs and very small diameter MWNTs (<10 nm), and it should be noted that well-defined changes in the ratio of C_2H_4:H_2:Ar can be used to tune nanotube tips from SWNTs to large MWNTs.[9] Field-emission scanning electron microscopy (FE-SEM) images demonstrate that nanotube tips prepared in this way protrude from

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(11) The Al_2O_3 supported Fe−Mo and Fe−oxide colloid catalysts were prepared using reported methods.[9,10] The catalysts were electrophoretically deposited onto FESP (force modulation etched silicon probe, $k = 0.5-5$ N/m, Digital Instruments, Santa Barbara, CA) silicon AFM tips from 0.1% ethanol (Al_2O_3 supported Fe−Mo catalyst, −1.8 V) or 0.1% aqueous (1.5−4 nm Fe−oxide, −0.5 V) solutions.
(12) Chemical vapor deposition was carried out with the tips in a 1-in. reactor connected to Ar, H_2, and C_2H_4 sources. The tips were heated at 15 °C/min to 800 °C in a flow of 600 sccm Ar and 400 sccm H_2. At 750 °C, 2 sccm of C_2H_4 was added for 3 min, and then the furnace cooled at 15 °C /min in 1000 sccm Ar.

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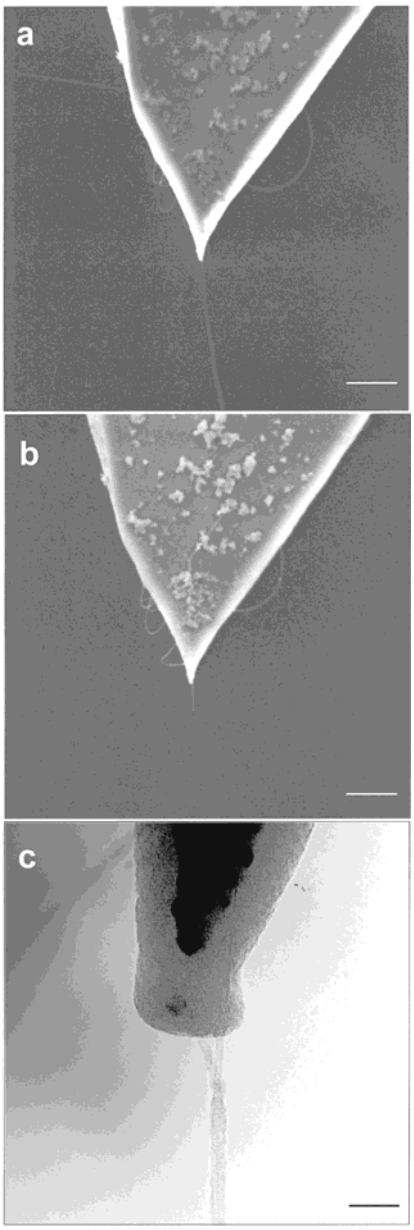

Figure 2. FE-SEM (Leo 982, 1 kV) images of a CVD nanotube tip grown from a Si cantilever/tip assembly (a) before and (b) after shortening. (c) TEM image (Philips EM420, 100 kV) of the pyramid−nanotube region of the tip shown in panel b. The Si-pyramid is in the top-center of the image, and the two nanotubes comprising the tip are in the bottom-center. Amorphous carbon on the nanotubes as deposited during FE-SEM imaging (a, b). The scale bars in panels a−c are 500, 500, and 20 nm, respectively.

the pyramid apex and illustrate the surface guiding effect discussed above. As shown in Figure 2a, nanotubes typically protrude from the edges of the pyramid with a density of approximately one per micron. However, at least 90% of the pyramids have a nanotube protruding directly from the apex. Since the apexes have radii of curvature of 5−20 nm (≪average nanotube spacing), we believe that the surface-growth mechanism must be responsible.

The as-grown nanotube tips are typically too long (i.e., flexible) for high-resolution imaging and are shortened using a straightforward electrical etching method.[2,7,13] Figure 2b shows a FE-SEM image after shortening the nanotube tip shown in Figure 2a. Importantly, the nanotube tip remains attached after this standard procedure and there are no other major changes observed (e.g., transfer of material to the tip apex). The FE-SEM images also indicate that these nanotube tips are very thin but cannot be used to determine quantitatively the tube diameters, and thus we have used transmission electron microscopy (TEM) to define the diameter and structure. A TEM image of this shortened nanotube tip (Figure 2c) demonstrates that it consists of two nanotubes that have come together at the Si apex, and that the nanotubes are SWNTs with diameters of ca. 2.5 nm. This image also serves to highlight the unique resolution advantage of the nanotube probes compared with conventional Si tips.

The two-tube structure of this tip is not surprising since the highly flexible individual nanotubes can line up during the surface growth process described above. We have also observed individual SWNT tips, larger bundles, and small diameter MWNTs, and believe that these can be controlled through variations in the growth conditions.[9] For example, whether the tip is a single SWNT or bundle can be controlled by the density of catalyst and growth time since these factors will determine the probability that single SWNTs encounter each other during surface growth. Second, it is likely that both individual tube and bundle tip structures will be useful for imaging. For example, a single SWNT may provide the ultimate resolution but this will require that the tip be on the order of only 10 nm in length (so that thermally excited vibrations do not limit resolution). Indeed, the enhanced rigidity afforded by the two-nanotube tip of Figure 2, which can still expose a single SWNT at the very tip end, could be more desirable for many applications.

These structurally attractive SWNT tips also function as robust, high-resolution probes in AFM experiments. First, the SWNT tips exhibit reversible buckling similar to mechanically attached SWNTs nanotubes[2b,5b] and CVD MWNT tips.[7] The buckling behavior demonstrates that the CVD SWNT tips have high structural quality and remain attached strongly to the pyramids.[14] Second, we have characterized the resolution of these SWNT tips by imaging 5.7 and 2 nm diameter gold nanoparticles standards.[2,7,15] Significantly, the analysis of nanoparticle image widths using the two-sphere model shows that we can obtain effective tip radii of 3 nm or less. We believe that these results demonstrate quite clearly the uniqueness of SWNT tips for ultrahigh resolution imaging. Last, these nanotube probes, as do any tips, ultimately fail, although we feel it is significant that the CVD process can be repeated at least 5−6 times to provide a new nanotube tip without replacing the catalyst.

In summary, these studies demonstrate a facile and reproducible approach to growth of SWNT probe microscopy tips. Our CVD surface growth method can be carried out using simple low-cost equipment, and we believe could be readily implemented at the wafer level as required for commercial mass production. Moreover, we believe that the molecular scale diameters of these SWNT tips, which can also be coupled with covalent tip-end modification,[5,6] offer the opportunity of revolutionizing probe microscopy imaging in many areas of science and technology.

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(13) All AFM measurements were made with a Nanoscope III or Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) in air. As-grown CVD tips were shortened on a rough niobium sample (GeneraMicro, Hergestellt, Canada) in force-calibration mode with a 5 to 30 V bias applied to the sample and the tip grounded.[2,5,7] Tapping mode images of the rough niobium surface can be used to estimate the sharpness of the tip in situ. The buckling and adhesion properties of the tips were also assessed in the force calibration mode by monitoring the amplitude and cantilever deflection signals, respectively, as a function of tip−sample separation. Images of 5.7 and 2 nm Au nanoparticles (Ted Pella Inc., Redding, CA) deposited on poly-L-lysine coated mica were acquired in tapping mode with a 10−20 nm free oscillation amplitude. Effective tip radii were determined from the analysis of nanoparticle images.[2,7,15]

(14) In addition, these experiments show that the nonspecific adhesion measured with these SWNT tips is typically below the thermal noise level (30 pN) of our cantilevers. The presence of low nonspecific adhesion is important for high-resolution imaging of soft organic and biological samples.

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