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Single-shell carbon nanotubes imaged by atomic force microscopy

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Abstract

Single-shell carbon nanotubes, approximately 1 nm in diameter, have been imaged for the first time by atomic force microscopy operating in both the contact and tapping modes. For the contact mode, the height of the imaged nanotubes has been calibrated using the atomic steps of the silicon substrate on which the nanotubes were deposited. For the tapping mode, the calibration was performed using an industry-standard grating. The paper discusses substrate and sample preparation methods for the characterization by scanning probe microscopy of nanotubes deposited on a substrate.

1. Introduction

The discovery of a method for the mass-production of the roughly spherical, nanometer-sized fullerenes (e.g. C_{60} and C_{70} molecules), spawned an extensive effort directed toward the exploration of their physical and chemical properties [1,2]. Following these advances, Iijima [3] and Ebbesen and Ajayan [4] reported on a method for the production of tubular fullerenes, carbon nanotubes that consist of several shells of hollow graphitic tubules. These nanotubes may either be open at the ends or capped by fullerene-like hemispheres, as evidenced by high-resolution transmission electron microscopy. In particular, Iijima observed caps that were curved, polygonal, or cone-shaped, while Ebbesen and Ajayan reported on pentagon-shaped caps. The length of the nanotubes typically extend to several micrometers, while the diameter of these multi-shell structures vary from 2 to 20 nm. Recently, Iijima and Ichihashi [5] and Bethune et al. [6] reported on the production of single-shell nanotubes in the soot from metal-containing carbon arcs. The rapid progress in the synthesis and characterization of these nanotubes arouse much excitement, as theory predicts that their electronic properties may vary from semiconducting to metallic, depending on the diameter of the structure and the degree of helicity in the arrangement of the carbon hexagons [7–11].

Several techniques are available for the direct imaging of single nanotubes, i.e., high resolution transmission electron microscopy (HRTEM),

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scanning electron microscopy (SEM), scanning tunneling microscopy (STM), and atomic force microscopy (AFM). The SEM, with its limited resolution, can provide a three-dimensional topographical image of only multi-shell nanotubes. HRTEM, which can resolve both multi-shell and single-shell nanotubes, reveals only the projection of the structure associated with the position of its carbon atoms. Because of the long depth of focus inherent in this method, it is difficult to identify which nanotubes are at the bottom or at the top of a bundle of nanotubes, and the images appear therefore to be two-dimensional. Scanning tunneling microscopy (STM) and atomic force microscopy (AFM), being proximity probes, are unique in that they have an inherent atomic resolution [12] and at the same time can provide three-dimensional topographic images. These techniques have the advantage of being able to manipulate structures on a small scale, and in addition may be used to characterize the electronic (STM) and elastic (AFM) properties of nanostructures. Indeed, previous work has already demonstrated that the STM and AFM can image, manipulate, and characterize multi-shell nanotubes [13–16]. As an extension of this work, we demonstrate in this paper that the AFM is also capable of imaging single-shell nanotubes whose diameter is approximately 1 nm. Note that this is the diameter of C_{60} and C_{70} molecules that had been imaged with an AFM only in a film structure that had a well-defined periodicity [17,18].

2. Experiments and discussion

We prepared the nanotube samples in an arc generator. Here, two graphite electrodes, a cathode with a 9 mm diameter and an anode with a 6 mm diameter, were arced at 550 Torr, 75 A DC, and 27 V in a helium environment. These conditions favor the synthesis of nanotubes [3–6]. For the purposes of this study, the samples were prepared by two different methods: For the first sample, a solid 6 mm diameter anode was arced against a solid cathode under conditions described above. The cathode deposit was removed

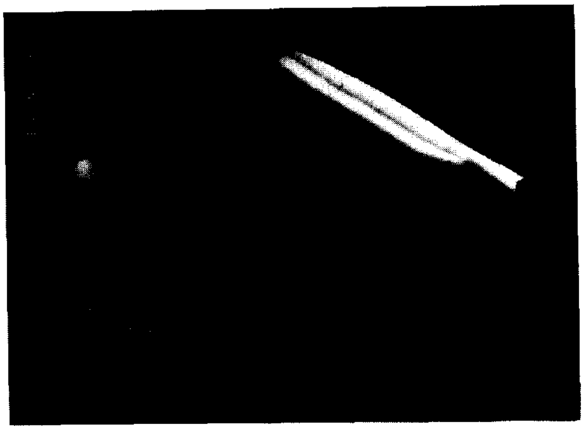

Fig. 1. An atomic force microscope image, obtained in the *contact mode*, of one single-shell (left-hand side) and two adjacent multi-shell nanotubes (right-hand side) on the oxidized Si(111) substrate.

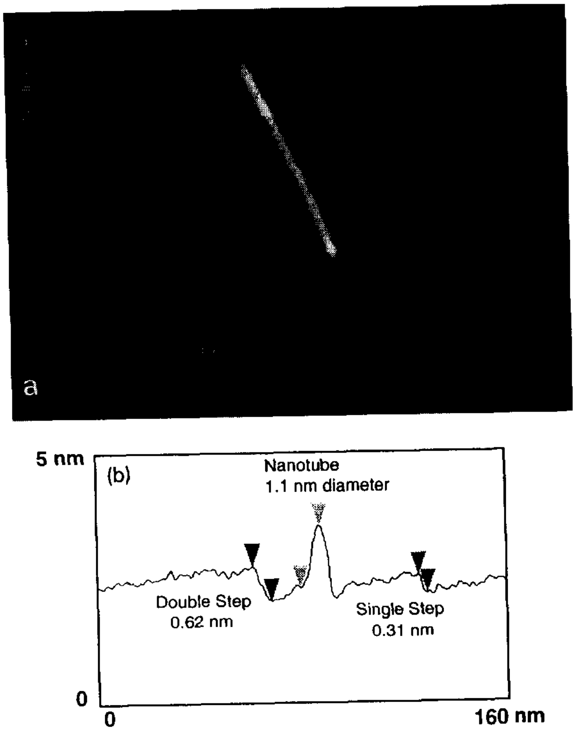

Fig. 2. (a) A second atomic force microscope image, obtained in the *contact mode*, of the same 1.1 nm diameter single-shell nanotube shown in Fig. 1, on the background of the oxidized Si(111) substrate. (b) A cross section of the image showing single and double atomic steps on the silicon substrate.

and crushed into fine powder which was used as one of the samples. For the second sample, we prepared the anode by drilling a 3 mm hole in the 6 mm diameter anode and packed it with Ni powder. The anode was then arced against a solid cathode under the same conditions as for the first sample, and the soot was collected and examined. The samples were separately dispersed in acetone or ethanol and sonicated for several hours. A few drops of the dispersed solution were then deposited and dried on a Si(111) wafer substrate.

For the nanotubes prepared by the first method, the silicon substrate was annealed under ultrahigh vacuum (UHV) conditions to remove the residual contamination as well as the oxide layer. The wafer was then removed from the UHV chamber into air, where a thin native oxide is expected to grow. This surface exhibited well-defined atomic steps which could be resolved with the AFM. For the nanotubes prepared by the second method, we used as a substrate an unannealed, oxidized Si(111) wafer. Imaging was performed in air using a deflection based AFM operating in the contact mode, or a laser diode interferometer based stand-alone AFM operating in the tapping mode [19–23], using a Nanoscope III system [24].

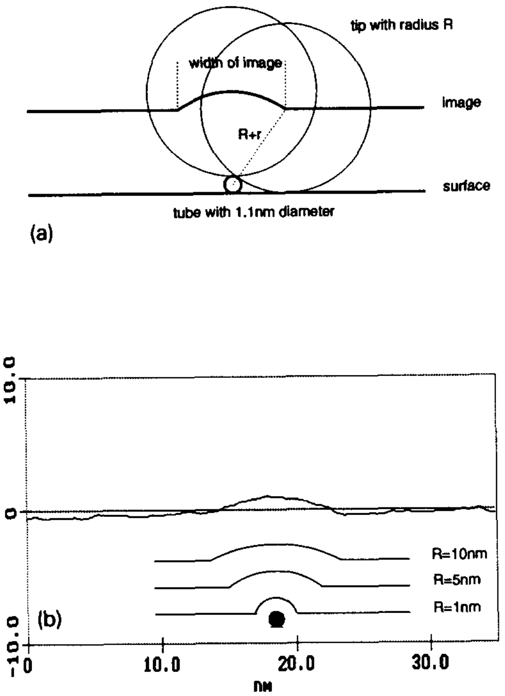

Fig. 3. Schematic diagram of the convolution of the geometries of the AFM tip and the nanotube. (a) A spherical tip with a radius R and a nanotube with radius r. (b) The convoluted shape for $R = 1$, 5 and 10 nm, and an experimental cross section, from Fig. 2.

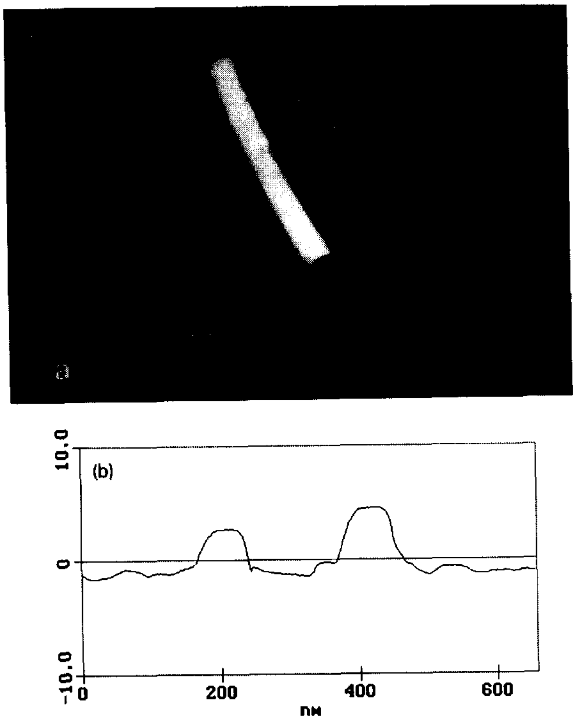

Fig. 4. (a) An atomic force microscope image, obtained in the *contact mode*, of two bundles of nanotubes on the background of the silicon substrate. (b) A cross section of the image. Note the flat top of the imaged bundles.

Shown in Fig. 1 is an image obtained from the sample prepared with the pure graphitic rod used in the arc generator. The image, obtained in the *contact mode*, shows one small nanotube (left-hand side) and two large nanotubes (right-hand side) on the silicon substrate. Note that the small nanotube was moved by the AFM tip during the scanning process. A second image of the small nanotube, on the background of the silicon substrate, is shown in Fig. 2a. A cross section of this image, depicted in Fig. 2b, shows single and double atomic steps on the silicon substrate. From the height of these steps, 0.31 and 0.62 nm, respectively [25], we find that the small nanotube has a height of 1.1 nm. HRTEM experiments indicate that nanotubes having such a small diameter are single shelled [5]. The adjacent larger nanotubes are probably multi-shelled nanotubes, being the prevalent species fabricated when using a pure graphitic rod in an arc generator. Because of the finite size of the AFM tip, the apparent lateral dimensions of the atomic steps and the nanotubes are much larger than their height [26]. Fig. 3a is a schematic of a spherical tip with radius R, a nanotube with radius r, and their

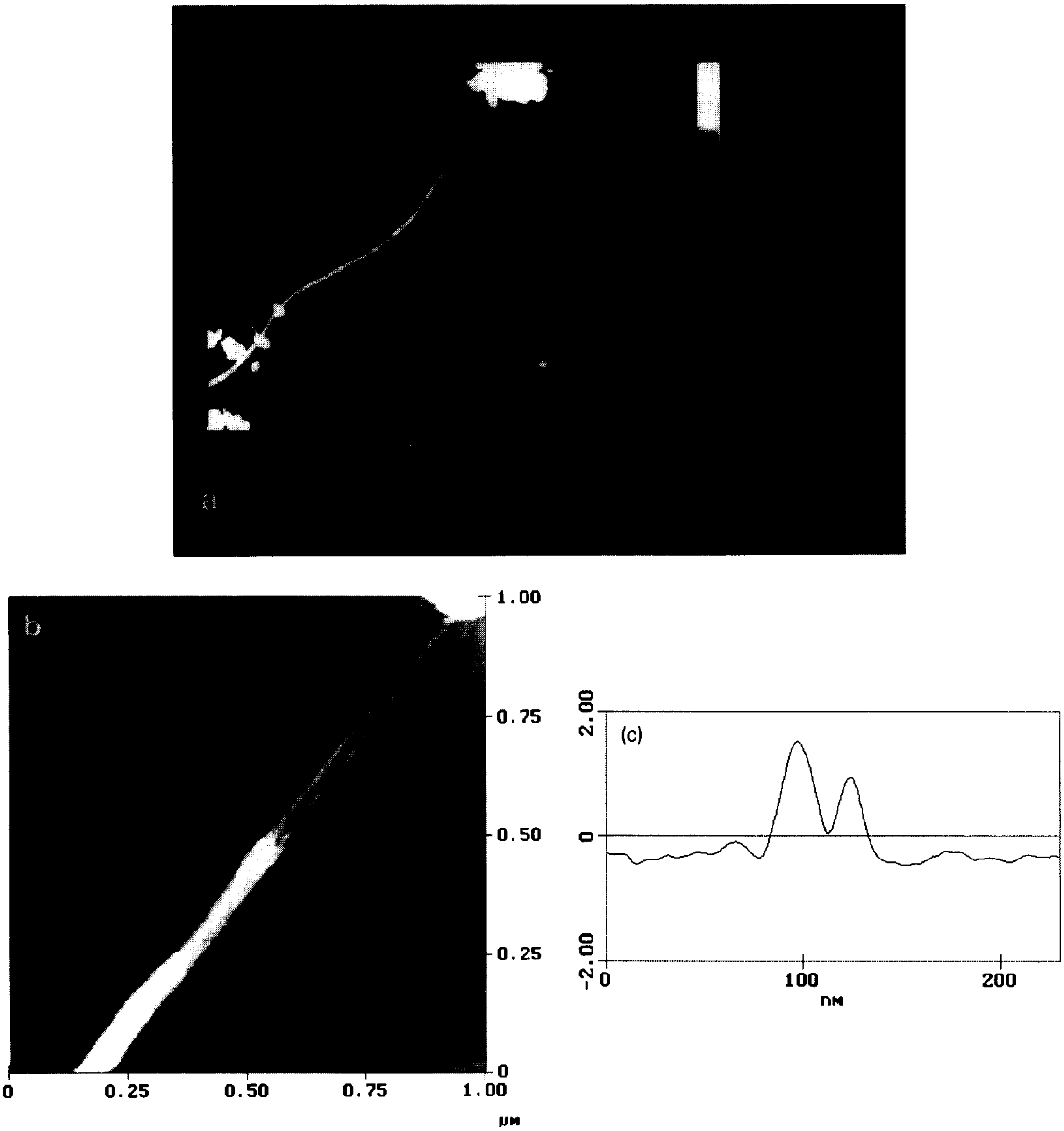

Fig. 5. (a) An atomic force microscope image, obtained in the *tapping mode*, of a 5 μm-long collection of nanotubes attached on both sides to large-scale clusters, on the background of the silicon substrate. (b) A zoomed image. (c) A cross section of the image.

convoluted cross section. Fig. 3b depicts the experimental cross section of the nanotube shown in Fig. 2, together with the calculated cross section using $r = 1.1$ nm, and $R = 1$, 5 and 10 nm. Note that 7 nm seems to be a reasonable radius for the AFM tip.

In the next set of experiments we imaged samples obtained by incorporating Ni in the graphitic rods in the arc generator. It is known that this fabrication method produces both isolated and bundled single-shell nanotubes [5,6]. These samples were then deposited on the unannealed, oxidized silicon substrate. Fig. 4a shows an image, again obtained in the *contact mode*, of two bundles of nanotubes on the background of the silicon substrate. The cross section of the image, Fig. 4b, shows that the top of the imaged bundles is flat, rather than rounded. It is reasonable to assume that the image depicts a non-cylindrical assembly of nanotubes.

One of the difficulties involved in imaging nanotubes with the STM or AFM, is that the tip frequently displaces them as it raster scans across the surface of the sample. To alleviate this problem, we have used a novel mode of operation of the AFM, dubbed the "tapping" mode [22–24]. Here, the AFM tip is vibrated with an amplitude ranging from 20 to 100 nm, and the change in the amplitude of oscillations, as the tip gently touches the surface, is a measure of the topography of the nanostructure. Since the lateral forces in this technique are small, it is expected that the tip will be able to sense the nanotubes without pushing them around, as indeed was the case.

The AFM was calibrated using an industry-standard grating with a step height of 9.3 ± 0.5 nm. Figs. 5a and 5b show a large and a zoomed area, respectively, of a 5 μm-long collection of nanotubes attached on both sides to large-scale clusters, on the background of the silicon substrate.

A cross section of the image in Fig. 5b indicates that the height of these nanotubes is 1.3 and 1.9 nm, respectively. The calibrated tapping-mode AFM image implies, that at least the smaller nanotube may be single shelled. Note that the possibility of a 1.3 nm nanotube being single-shelled is in agreement with Refs. [5,6]. Figs. 6a and 6b show an image and its cross section, respectively, of 1.2 and 2.6 nm diameter nanotubes that cross each other, on the background of the silicon substrate, obtained in the *tapping mode*. The small tube appears to be single shelled on account of its small diameter. Note that the protrusions across the nanotubes have often been observed in HRTEM images [6].

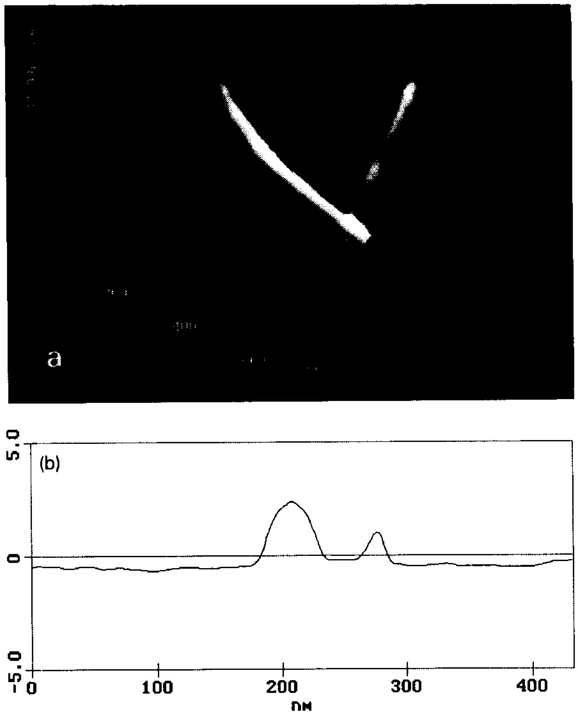

Fig. 6. (a) An atomic force microscope image, obtained in the *tapping mode*, of 1.2 and 2.6 nm diameter nanotubes, on the background of the silicon substrate. (b) A cross section of the image. Note that one of the nanotubes runs across the other one.

3. Conclusion

In summary, we have obtained images of nanotubes, prepared with two different methods, using atomic force microscopy operating in two different modes. Single-shell nanotubes have been observed with samples prepared both with a pure and a Ni doped graphitic rod in the arc generator. The choice of a Si(111) substrate covered with a native oxide was found to be suitable for (a) immobilizing the nanotubes so that the scanning tip does not push them around, and (b) serving as an in-situ calibration of the height of the nanotubes. It is plausible that the reason the AFM could image 1 nm-size nanotubes deposited on the oxidized silicon, but not 1 nm-size C_{60} molecules, is because the latter have a much smaller contact area with the surface of the sample, and therefore could be pushed around more easily by the tip. The results reported in this paper describe sample preparation, choice of substrate, and image analysis. These should be of help in subsequent STM and AFM experiments that characterize the electronic and elastic properties of single-shell nanotubes, respectively.

Acknowledgments

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