ADVANCED MATERIALS

Manipulation and Imaging of Individual Single-Walled Carbon Nanotubes with an Atomic Force Microscope**

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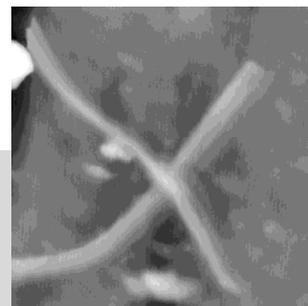
The tip of an atomic force microscope is used to create carbon nanotube junctions by changing the position and shape of individual single-walled carbon nanotubes on a SiO₂ surface. With this manipulation technique, we are able to bend, buckle, cross (see Figure), and break nanotubes, and to unravel a nanotube "crop circle" into a single tube. Tapping-mode atomic force microscopy measurements of the height of a carbon nanotube on the surface always yield values smaller than the nanotube diameter. Variation of the scan parameters shows that this is due to a tapping deformation by the tip. The tapping deformation of manipulated nanotube crossings and buckles is discussed as well.

Carbon nanotubes[1] have attracted a lot of interest because of their unprecedented electronic and mechanical properties on a molecular scale (for a review, see e.g., Dekker[2]). The interplay of these properties, for example, the effect of mechanical deformations on the electron transport properties, seems to be of particular interest.[3–8] While atomic force microscopy (AFM) manipulation experiments have been reported on multi-walled nanotubes,[3–5] the prototype single-walled tubes are much more difficult to study since their diameter is more than an order of magnitude smaller. In this paper, we explore the mechanical properties of individual single-walled carbon nanotubes and nanotube junctions by AFM. We present manipulation experiments on individual single-walled carbon nanotubes, where the tip of an AFM is used to change the nanotube position and shape on a SiO₂ substrate. We show examples where we have used this manipulation technique to locally bend, buckle, break, and cross nanotubes, and where we have unraveled a nanotube "crop circle".[9] We also present tapping-mode AFM measurements of the apparent height as a function of the feedback parameters. These measurements show that in typical AFM imaging, nanotubes always appear lower than expected, due to a local and reversible compression of the nanotube by the tapping tip. Height measurements of a manipulated buckle show that buckles are equally rigid as non-manipulated tubes, whereas manipulated nanotube crossings appear to be more rigid than individual tubes.

In tapping-mode AFM, a stiff cantilever with a sharp tip attached to the end is oscillated near its resonant frequency resulting in an oscillation amplitude in free air in the range of 1 to 10 nm. When this tip is brought into contact with a sample surface, the amplitude of oscillation is reduced. While scanning the surface, the amplitude of the cantilever oscillation will change whenever a change in the height of the sample surface is encountered. A feedback loop then changes the height of the cantilever over the surface to maintain a constant setpoint amplitude. Since the tip is only intermittently in contact with the sample, the lateral forces acting on the sample while scanning are negligible. This enables one to image individual single-walled nanotubes lying on a surface without moving them. If, by contrast, the feedback is turned off, the cantilever is pressed down onto the substrate, and dragged along a predefined path over the surface, one can shift the nanotubes laterally. This is the basis of our manipulation technique. We use a commercial AFM mounted with stiff cantilevers with a force constant of about 50 N/m and a resonant frequency of about 300 kHz. The carbon nanotubes, with an average diameter of 1.4 nm, were synthesized by a laser vaporization technique by Smalley and coworkers at Rice University, USA. They were deposited by spin coating a drop of

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nanotube suspension on a thermally grown SiO$_2$ surface. The experiments were performed in air at room temperature.

In Figure 1 we present several intermediate steps of a typical manipulation experiment of a carbon nanotube. The arrows in the image show the path that the AFM tip has travelled in each manipulation step. The initial configuration of a nanotube with an apparent AFM height of 1.8 nm is shown in Figure 1a. The result of the first manipulation step is shown in Figure 1b. The tube has been successfully dragged from its original position and is strongly bent. The tube is held in this strained configuration by attractive van der Waals binding to the substrate. As the tube has shifted sideways, the lower end of the nanotube has been dragged along its original path (indicated by the white line in Fig. 1b). Apparently, the nanotube is pinned more strongly at the upper part than at the lower part, consistent with the fact that the upper part is longer and thus experiences a larger binding force. At the original position of the nanotube, traces of debris have become visible. These traces are presumably due to amorphous carbon particles from the suspension of nanotubes. The height of the manipulated piece of nanotube is 1.2 nm, which indicates that the initially measured height appeared higher due to the amorphous carbon. Figure 1c shows an enlarged scan of the strongly bent piece. By pushing the nanotube from the lower side, we make the nanotube fold onto itself, as shown in Figure 1d. The next manipulation involved pushing against the upper side. In Figure 1e it is clearly visible that the nanotube has been broken at the point of the sharp end in Figure 1d, and is now crossing itself. The height of the crossing is discussed below. The image in Figure 1f shows a larger image of the manipulation site. Starting from a single nanotube, we have succeeded in fabricating an intermolecular junction.

Figure 2 shows several intermediate stages of the unraveling of a "fullerene crop circle", a nanotube which is circularly folded onto itself.[9] The initial configuration is shown in Figure 2a. The crop circle has a diameter of 520 nm. Several linear manipulation paths have been used to indent the circle. In Figure 2b the result of these operations shows a nanotube which has been shifted locally while leaving behind a trace of amorphous carbon. The next manipulation step shows the appearance of a single tube (Fig. 2c). By pushing the lower right side, we unravel the crop circle to reveal a single tube in Figure 2d. After several further manipulation steps (not shown), the nanotube has been rearranged considerably and has shifted along the surface (Fig. 2e). The length of the nanotube in the final configuration is 2.6 $\pm$ 0.1 μm, while the height is 0.9 nm. After the discovery of these crop circles, it was discussed whether both ends of the nanotube could grow together to form a seamless toroid. We conclude, however, that the crop circle studied here consisted of a single nanotube wrapped almost twice onto itself.

In all of the previous figures, the AFM height of a single nanotube lying on a SiO$_2$ surface always appears to be lower than expected. Figure 3 shows a typical example of height measurements of a nanotube (black dots) as a function of drive amplitude. The height measurements show values for the apparent height of a nanotube of 0.6 to 1.1 nm, i.e., much smaller than the expected value of 1.7 nm, which is the sum of the nanotube diameter of 1.4 nm and the van der Waals separation between nanotube and surface of about 0.3 nm.[10] The height decreases with increasing drive amplitude. At the highest drive amplitudes, the height appears to level off at a value of 0.6 nm. Note that this is close to the sum of the graphite interlayer spacing and the separation between nanotube and substrate.

The dependence of the nanotube height, as recorded in tapping-mode AFM, on the drive amplitude can be understood as follows. In free air, the cantilever amplitude is proportional to the drive amplitude. When performing tapping-mode imaging, the cantilever is lowered towards the sample surface to re-
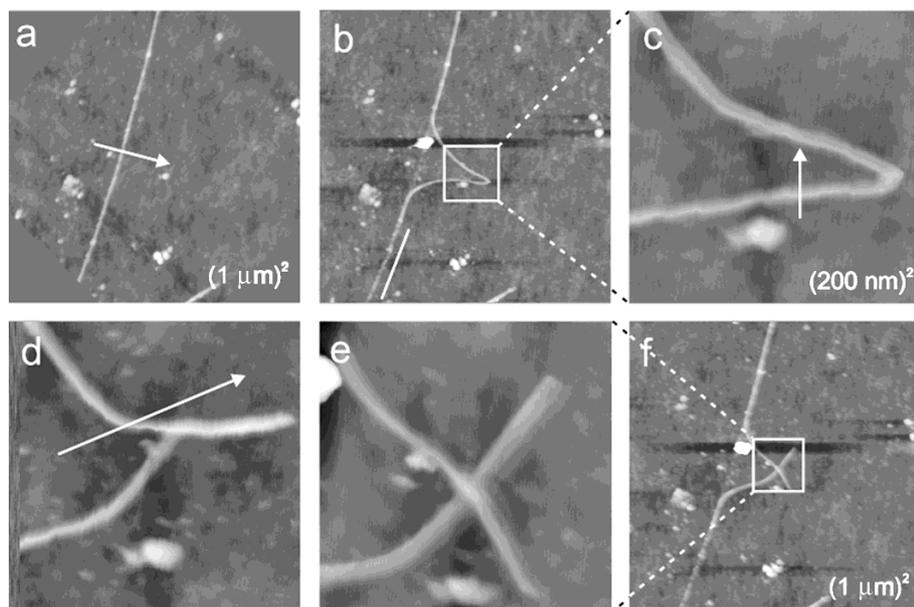

Fig. 1. Tapping-mode AFM height images of intermediate stages of a typical manipulation experiment. Before each manipulation step, the height profile of the surface is recorded. Then the tip is lowered towards the surface and moved across the surface along a predefined path, indicated in the image with arrows. The nanotube is then imaged again. The sequence (a–f) shows how a nanotube crossing is formed from an individual single-walled nanotube.
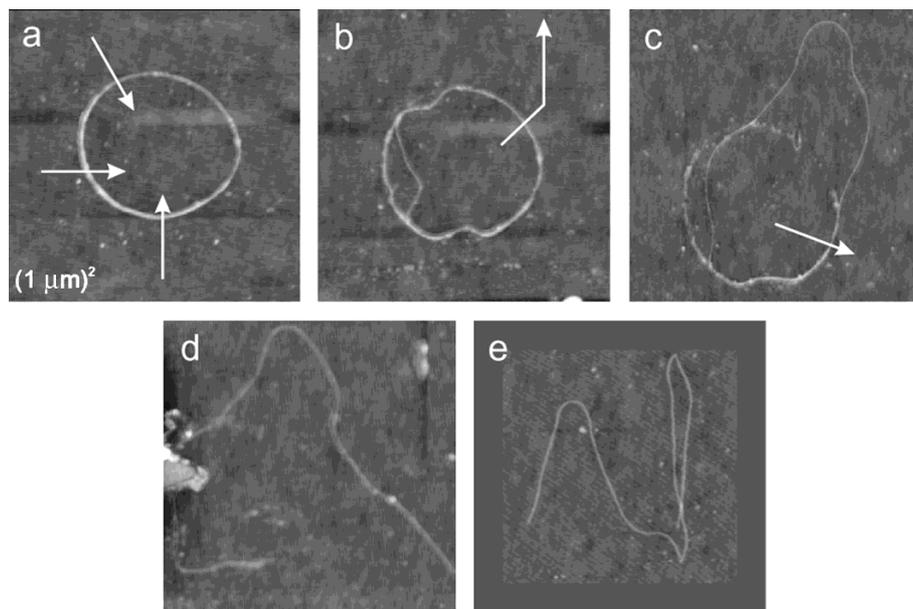
Fig. 2. Tapping-mode AFM height images of intermediate stages in the unraveling of a fullerene crop circle. The arrows indicate the paths the AFM tip has travelled in each manipulation step. The large structure on the left side of d) is material that was deposited from the tip onto the substrate during the previous manipulation step. To move the nanotube away from this spot, several manipulation steps (not shown) have been performed, shifting the nanotube to the entire right (e). All images are 1 μm².
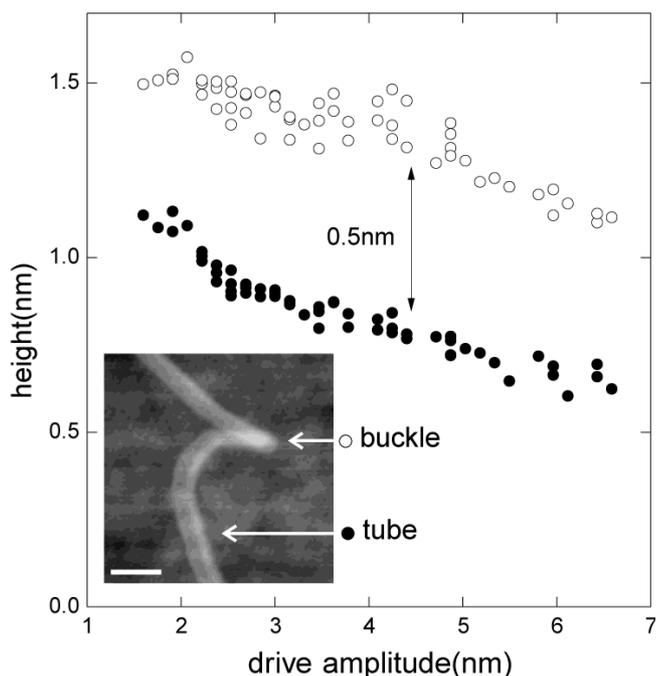

Fig. 3. Tapping-mode AFM height of a nanotube and a manipulated nanotube buckle as a function of the drive amplitude for setpoints from 2 to 6 nm. Below this range the feedback of the AFM does not function properly. For these measurements, the nanotube has been shifted lateraly such that the height measurements are not affected by any amorphous carbon traces. The inset shows a height image; the white scale bar is 50 nm.

the substrate is thus much smaller than over the nanotube. This leads to a decrease of the apparent nanotube height when increasing the drive amplitude due to an inelastic, reversible, and local indentation of the nanotube. This is consistent with the data presented here.

The nanotube crossing presented in Figure 1 has an apparent AFM height of 2.8 nm, whereas the individual nanotube pieces appear to be 1.2 nm high. The expected height of a nanotube crossing consists of twice the nanotube diameter, the spacing between the crossing nanotubes, and the separation between nanotube and substrate. For our nanotubes, this yields an expected crossing height of 3.4 nm. In this crossing configuration, both nanotubes are thus each compressed by 0.3 nm by the tapping tip. The straight segments of the non-manipulated individual nanotube, however, are compressed by 0.5 nm by the tapping tip. This difference is a result of the fact that the nanotubes in the crossing configuration share the tapping deformation. This makes this configuration more rigid than a single tube, leading to a smaller compression of each nanotube at the crossing compared to an individual nanotube. The same effect can be observed in Figure 1d, where the folded piece of tube appears significantly higher than the individual parts. This is a result of the fact that both pieces are lying so close together, that they are indented simultaneously by the tapping tip. Therefore, they share the tapping deformation, leading to a smaller compression and a larger apparent height.

We have also studied the height of manipulated nanotube buckles as a function of the scan parameters. A typical example of such a manipulated buckle is shown in the inset of Figure 3. The buckle has been obtained by AFM manipulation similar to Figure 1a–c. Buckle formation has been studied before for multi-walled nanotubes.[3–5] In that case, the presence of multiple walls inside the outer shell modifies the characteristics of the buckling, as compared to the theoretical models

duce the amplitude to the setpoint value. The degree of reduction is a monotonic function of the average height of the cantilever over the surface. If the drive amplitude is increased, the tip has to be lowered further towards the sample surface in order to maintain the same setpoint amplitude. The necessary tip-height reduction depends on the compressibility of the sample. In our experiments, the SiO₂ surface is much less compressible than the nanotube. The height reduction over

for single-walled tubes.[11] Here, however, we experimentally study buckling in single-walled nanotubes. The expected degree of bending necessary to form a buckle for the nanotubes used in our experiments is 0.08 rad/nm.[11] From the AFM image, we estimate that the buckle is at least localized within a nanotube length equal to the width of the tip, about 20 nm, and that the angle is π rad. This yields a lower limit for the degree of curvature of about 0.16 rad/nm, which is well above the theoretical minimum. The expected height of a buckle is $\pi/2$ times the diameter of a nanotube, plus the separation between nanotube and substrate. This amounts to 2.5 nm. The measurements presented in Figure 3 ($\bigcirc$) show that the buckle indeed appears higher than a non-manipulated nanotube, by about 0.5 nm. Similar to the case of nonmanipulated tubes, the buckle height of 1.1 to 1.6 nm is again smaller than expected theoretically and it decreases with increasing drive amplitude. The trends of the buckle and nanotube heights as a function of drive amplitude appear very similar, which indicates that the rigidity of buckles and straight nanotubes are similar. Height measurements on other buckles in air as well as under an atmosphere of N_2 gas show similar behavior.

The present work shows that artificial nanotube junctions can be created by manipulation of individual single-walled nanotubes. The formation of structures such as nanotube buckles, bends, and crossings opens a route towards transport studies of junctions within nanotubes. First transport studies of a naturally occurring crossing of nanotube ropes[7] and nanotube kink junctions[8] show that molecular junctions can indeed have interesting properties. Transport measurements on our manipulated junctions made from individual single-walled nanotubes show a 4-terminal room-temperature resistance of nanotube buckles and crossings of approximately 1–10 MΩ, which is much higher than the typical value of order 10 kΩ for non-manipulated nanotubes. A detailed study of the transport characteristics of these junctions will be reported elsewhere.[12]

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