Sharpened Nanotubes, Nanobearings, and Nanosprings

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Abstract. We demonstrate a method whereby outer nanotube walls or shells can be successively removed near the end of multiwalled carbon nanotubes (MWNTs). This allows "sharpening" of the tubes, and has important implications for power dissipation in current-carrying nanotubes. We further exploit the technique to create low friction MWNT-based linear bearings and constant-force nanosprings. Our experiments are performed in-situ inside a high resolution transmission electron microscope, which allows simultaneous monitoring of atomic-scale mechanical deformation and wear of nanotube bearing surfaces.

Nanotubes are model systems for the study of fundamental physical properties of nanostructures. They also have far-reaching applications potential. Obvious applications include catalysts[1], biological cell electrodes[2], nanoscale electronics[3,4], scanned probe microscope and electron field emission tips[5,6], nanobearings, and nanosprings. For many such applications it would be desirable to control or shape nanotube geometry. For example, the "ideal" scanned probe, field emission, or biological electrode tip would be long, stiff and tapered for optimal mechanical response, and have an electrically conducting tip. Similarly, a constant-force nanospring might be formed from a configuration of concentric nanotubes where the van der Waals force provieds the extention-independent restoring force. Again using MWNTs, linear and rotational[7] bearings might might be achieved by using concentric shells of nanotubes as low-friction sliding surfaces.

We here describe the successful engineering of multiwalled carbon nanotubes into "ideal-geometry" tips for scanned probe microscopy, field emission, or biological insertion applications, as well as the construction of apparently wear-free linear nanobearings and constant-force nanosprings. All three constructions hinge on an initial "sharpening" of the tip of a MWNT, which results in a stepped or tapered nanotube diameter. At the end of the MWNT, the inner core nanotubes then freely protrude. The shaping process involves electrically-driven vaporization of successive layers (i.e. tube walls) of the MWNT. This decortication process can be repeatedly applied to the same MWNT until the very innermost small-diameter tube or tubes are exposed, often with a tip radius of curvature comparable to that of a single, single-walled nanotube.

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Our MWNT "tip engineering" is performed *in-situ* inside a transmission electron microscope (TEM) configured with a home-built mechanical/piezo manipulation stage with electrical feedthroughs to the sample. Fig. 1 shows high resolution TEM images of a conventional arc-grown MWNT at different stages in the tip engineering or peeling

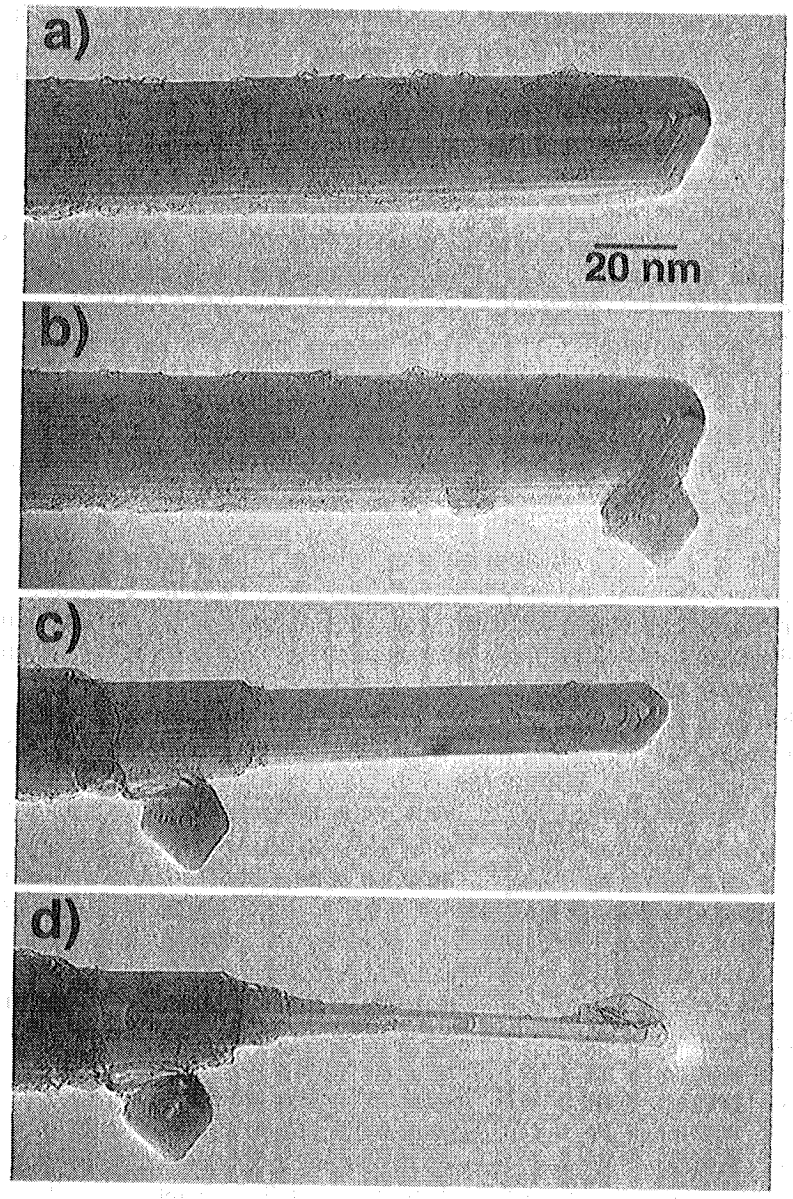

FIGURE 1. TEM images of a multiwall carbon nanotube being peeled and sharpened

process. The left end of the nanotube (beyond the figure border) is attached to a stationary zero-potential gold electrode. To the right (also not shown) is a second nanotube which serves as the "shaping electrode"; it is attached to a manipulator whose potential can be externally controlled. Fig. 1a shows the original MWNT before modification. For Fig. 1b, the shaping electrode has been momentarily brought into contact with the MWNT and a carbon onion has been inadvertantly transferred from the shaping electrode to the MWNT, but no attempt has been made to shape the MWNT. For Fig. 1c, the shaping electrode has been brought into contact with the tip of the MWNT at 2.9V and 200mA; numerous layers of the MWNT have been peeled away near its end and the MWNT now has a stepped diameter and is significantly sharpened. The carbon onion has been displaced further down the tube. Most importantly, the newly exposed tip of the MWNT appears undamaged. For Fig. 1d, the peeling and sharpening process has been repeated, resulting in a MWNT with highly desirable characteristics for many nanotube applications. The dominant protruding segment now consists of a three-walled electrically conducting nanotube with a radius of just 2.5 nm. This sharpened MWNT constitutes, for example, a "near ideal" coducting AFM tip. The physical process by which only the outer MWNT shells are "blown away" by an applied electric current has important implications for charge conduction in MWNT's. It is possible that for the most part MWNTs conduct ballistically[8], but that dissipation does occur at defect sites (such as pentgons, etc). Such defects are most abundant at nanotube ends, which would lead to current-induced end-sharpening as described above.

The nested concentric shells of MWNTs interact primarily via the relatively weak van der Waals force. This suggests that MWNTs might form highly efficient linear and rotational bearings. A major difficulty in actually realizing such a construction is the commonly capped ends which seal in all inner core nanotube cylinders. Even if the MWNT ends are opened by methods such as acid etching, it is difficult to selectively contact just the core tubes and move them with respect to the outer shells. On the other hand, the peeling and sharpening process just described perfectly prepares MWNTs for bearing applications.

Fig. 2 shows schematically the configurations used inside the TEM for bearing and other mechanical experiments. The MWNT is first rigidly mounted (a), and the free end of the MWNT is then sharpened to expose the core tubes (b). In c) a nanomanipulator is brought into contact with the core tubes and, using electrical current, is spot-welded to the core. c) is the common starting point for numerous mechanical experiments. d), e), and f) show three different classes of such experiments. In d) the manipulator is moved right and left, thus telescoping the core out from, or reinserting it into, the outer housing of nanotube shells. The extration/reinsersion process can be repeated numerous times, all the while viewing the MWNT at high TEM resolution to test for atomic-scale nanotube surface wear and fatigue. In e) the manipulator first telescopes out the inner core, then fully disingages, allowing the core to be drawn back into the outer shells by the intertube van der Waals energy-lowering force. A real-time video recording of the core bundle dynamics gives information pertaining to van der Waals and frictional forces. In f), a partially-telescoped nanotube

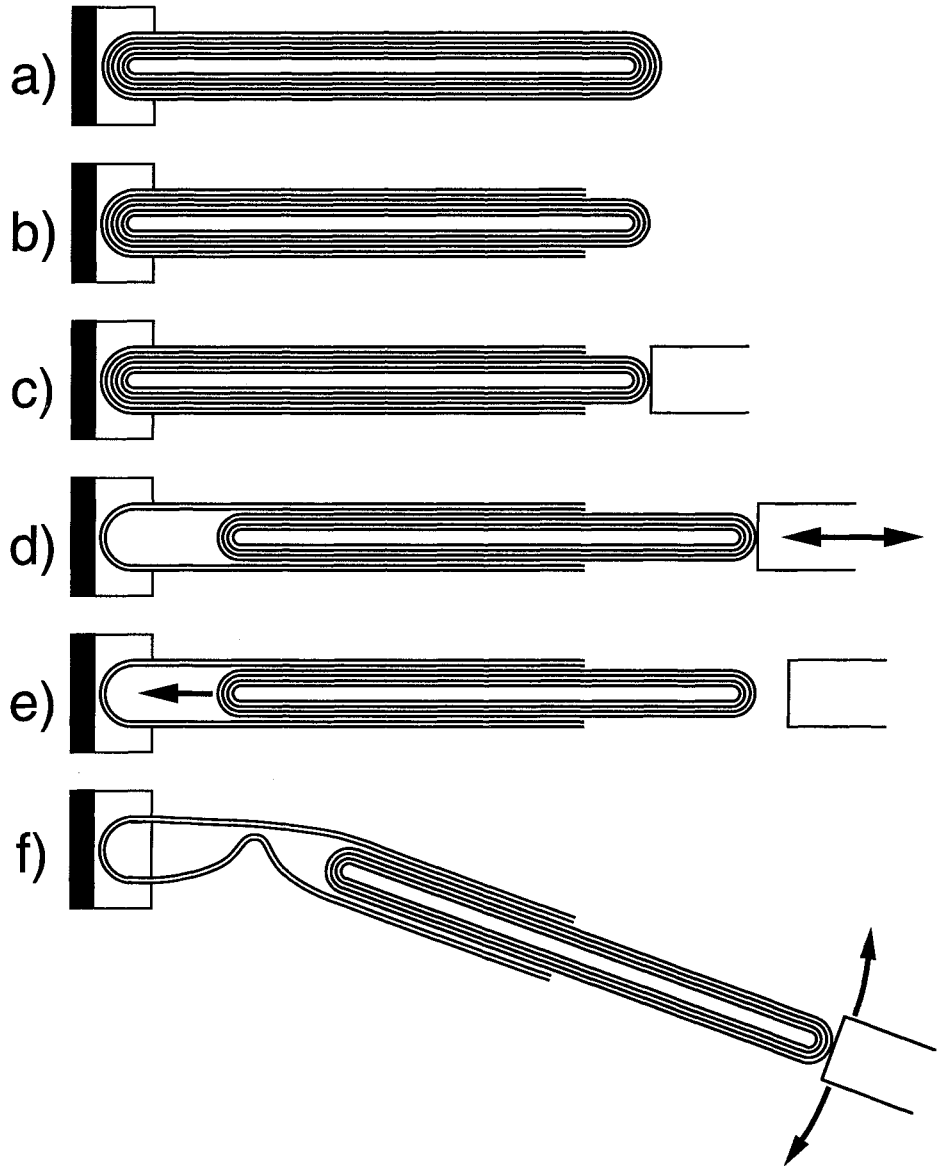

FIGURE 2. A schematic for MWNT processing and mechanical manipulations. A sliding nanobearing is illustrated in d).

is subjected to additional transverse displacements, and reversible mechanical failure modes such as buckling and complete collapse are induced.

Fig. 3 shows a TEM image of a MWNT in a fully telescoped position. Using higher resolution imaging than that used for Fig. 3, we determined that this MWNT

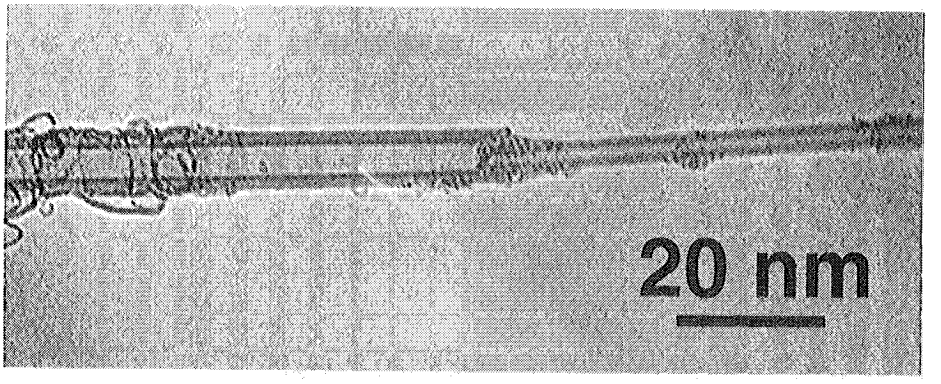

FIGURE 3. A fully telescoped MWNT.

originally had 9 walls, with an outer diameter of 8 nm and an inner diameter of 1.3 nm. After extension, a 4 nm diameter core segment (consiting of 4 concentric walls) has been almost competely extracted from the outer shell structure. The telescoping process was found to be fully reversible, in that the core could be completely pushed back into the outer shells, restoring the MWNT to its original "retracted" condition. The process of extending and retracting the core was repeated many times for several different MWNTs, and in all cases no apparent damage to the "sliding" surfaces, i.e. the outer tube of the core or the inner tube of the shell structure, was observed, even under the highest TEM resolution conditions (~2 Å). The apparent lack of induced defects or other structural changes in the nanotube contact surfaces at the atomic level suggests strongly that these near atomically-perfect nanotube structures may be wear-free and will not fatigue even after a very large number of cycles.

Several internal forces are associated with telescoping MWNTs. To first order these consist of the van der Waals-derived force and possible static and dynamic frictional forces. The van der Waals force is given by

$$F_{vdW} = -\nabla U(x) \qquad (1)$$

where $U(x) = 0.16Cx$ joules with C the circumference of the "active" nanotube bearing cylinders and x the length of the overlap between the core section and the outer walls, both measured in meters. The van der Waals energy lowering gained by increasing the tube-tube contact area tends to retract the extended core of a telescoped MWNT. Interestingly, since the active intertube contact area decreases linearly with core tube extension, this restoring force is independent of contact area, or equivalently, independent of core extension. Hence, a telescoped nanotube with only one active (sliding) surface pair is expected to act as a constant force spring.

To determine experimentally if F_{vdW} dominates nanotube linear bearing dynamics we have used the configuration described in Fig. 1e. The core tubes of a MWNT were first telescoped using the manipulator. Lateral deformations of the manipulator were used to fatigue and eventually break the spot weld, thus releasing the core segment. The resulting accelerated motion of the released core segment was recorded using a

continuous video system tied to the TEM imaging electronics. The core tubes were observed to rapidly and fully retract back into the outer shells. From the dimensions of of the core tubes in one such experiment the FvdW retraction force for the nanotube in is calculated to be 9 nN. From the observation that the core spontaneously retracted, together with the experimentally determined upper bound for the retraction time, we determine that the static friction force is small, with $f_s < 2.3 \times 10^{-14}$ newtons per atom (6.6×10^{-15} newtons per Å^2), and conclude that the dynamic friction $f_k < 1.5 \times 10^{-14}$ newtons per atom (4.3×10^{-15} newtons per Å^2).

We briefly consider lateral deformations of partially telescoped nanotubes. It has been predicted and observed that nanotubes can, upon lateral deformation, form kinks[11] or even fully collapse[12]. MWNTs with large inner diameters and few concentric shells are particularly susceptible to kinking and collapse. Although kinked or fully collapsed nanotubes have been observed experimentally using static TEM[11,12] or atomic force microscopy methods[13], in-situ high-resolution controlled and reversible deformation studies have been difficult. As outlined in Fig. 1f), using partially telescoped nanotubes we can study the kinking and collapse of a controlled nanotube system. We can directly alter the inner diameter and aspect ratio of the hollow nanotube, apply lateral forces, and in real time observe resulting failure modes. As expected, we find that a MWNT will kink and collapse much more readily after the inner core has been removed. One particular nanotube had 60 original layers with an outer diameter of 43 nm, and upon telescoping a 40 layer core was pulled out up to a maximum extension of 150 nm, leaving an outer shell housing of just 20 layers with an inner diamter of 29 nm. The housing was supported at the base and the inner core section of the tube was still engaged in the housing for a length of 200 nm. When the manipulator was driven laterally to approximately ~5° angular displacement the housing shells developed a kink in the middle of large inner diameter section. At ~26° displacement the kink was severe and resembled the schematic in Figure 1f). At any displacement angle, the telescoped core section was still mobile, and could be moved back and forth inside the unkinked portion of the outer shell housing. At small kink angles less than ~10°, the core could be inserted past the kink position, forcing the kink to disappear and reinflating the outer shells to their original circular cross section. At more severe bending angles, in excess of ~20°, the kink blocked the inner core section from being fully inserted. Hence, suitable kinking of the outer shell housing provides an effective motion stop for nanotube core insertion.

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