

Nanostressing and mechanochemistry

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Abstract. Experimental evidence supporting the heightened chemical reactivity of highly conformationally strained carbon sites in multi-walled carbon nanotubes is reported. The strain is introduced by two methods, van der Waals attractions to nonplanar surfaces and ultrasonic cavitation. Oxidative acid attack was observed in both cases, in the former by etching of the nanotubes' kinked sites, and in the latter by peptide coupling to polystyrene spheres that are large enough to be visible by SEM imaging. A novel single-axis straining stage for nanometre-scale objects is also described.

1. Introduction

The remarkable mechanical and electrical properties of carbon nanotubes make them nearly ideal candidates for components in molecular machines and electronics (Wong *et al* 1997, Treacy *et al* 1996, Cornwell and Wille 1998, Iijima *et al* 1996, Falvo *et al* 1997, Charlier and Issi 1998, Frank *et al* 1998, Kasumov *et al* 1998). Integration of these components into working devices, however, will require robust, well-defined connections, for which little is better than covalent functionalization. In addition, derivitization of carbon nanotubes has the potential to locally modify the intrinsic properties of the nanotubes (Brenner *et al* submitted).

It has been observed that pristine carbon nanotubes are preferentially reactive at pentagonal defect sites, such as are commonly found at the tube end caps (Yao *et al* 1998, Satishkumar *et al* 1996, Ajayan *et al* 1993, Tsang *et al* 1993, Sloan *et al* 1998, Tsang *et al* 1994). This can be easily explained by the curvature effects introduced by these pentagons on the atomic orbital configuration of the carbon atoms (Chen *et al* 1998a, Haddon and Raghavachari 1996, Haddon 1993). Not only does this introduced curvature shift the hybridization of the atoms to a higher energy state, it also causes a decrease in the p-orbital overlap that causes conjugation. These effects are directly along the reaction coordinate for an addition reaction across an unstrained olefin, in which the carbon atom hybridization changes from sp^2 to sp^3 . Thus the chemical reactivity of carbons at these strained sites is expected to be enhanced relative to unstrained, planar sp^2 carbon.

For these reasons, the functionalization of carbon nanotubes is easiest at the end caps (Wong *et al* 1998, Liu *et al* 1998, Satishkumar *et al* 1996). Although end cap derivitization will be necessary for the construction of nanotube-based devices, controlled, selective side wall derivitization would lead more easily to t-joint scaffolding and three-lead electronics devices. In addition, the end cap reactions explored to date, primarily oxidation, also lead to

a small, uncontrolled degree of reaction along the side walls (Lago *et al* 1995, Ebbesen 1996, Yu *et al* 1998, Chen *et al* 1998a). Although there has been a report of a designed carbon nanotube side-wall reaction, it was performed on nanotubes that had already been opened by oxidation, thus the relative reactivity between side wall sites and end cap sites was not explored (Chen *et al* 1998a, b).

Thus, a more selective scheme for carbon nanotube derivitization that allows controlled reaction at specific sites along the otherwise undifferentiated side walls would be extremely useful. The introduction of local strain through conformational deformations, such as by kinking or twisting, will have similar effects on the atomic orbitals of carbon atoms as pentagonal defects, but to a degree that is controlled by the amount of local bending. This effect, observed fortuitously or by design in high-resolution transmission electron micrographs (Iijima *et al* 1996, Ruoff *et al* 1995, Subramoney *et al* 1995, Kuzumaki *et al* 1998), will boost local reactivity at the kink sites significantly above that of the rest of the side walls (Srivastava *et al* 1999). Unlike the strain introduced by pentagonal defects, however, the local strain is elastically introduced by reversible conformational distortions (Wong *et al* 1997, Falvo *et al* 1997). Thus, after reaction, the nanotube could be straightened, leaving behind nanotubes selectively functionalized on the side wall.

In this paper we report the results of experiments aimed at exploring this proposed conformational-strain heightened reactivity of carbon nanotubes. In particular, we report results of reactions on nanotubes dispersed across a patterned surface that introduces conformational distortions in the tubes, and of reactions on nanotubes kinked in liquid suspension by ultrasonic waves.

Controlled mechanical manipulation and testing of nanostructures will be essential to the development and refinement of components for nanotechnology applications. In this paper we propose a design for a one-axis transmission electron microscope (TEM) compatible straining stage for nanometre-scale objects. When applying tensile stress, this stage will allow determination of elasticity, yield-point, and tensile strength of nanoscale components or

materials. Some of these properties have been measured for multi-walled carbon nanotubes by other methods involving thermal vibrations (Treacy *et al* 1996) or lateral bending (Wong *et al* 1997), but for geometric reasons the off-axis mechanical properties are likely to be different from the on-axis properties. When the proposed stressing stage is used to apply compressive stress, bending, kinking, and buckling may be observed. Furthermore, this stage may be used to pre-stress nanotubes for controlled kink-promoted chemistry experiments.

2. Experimental details

2.1. Nanotubes on a V-ridged substrate

A dilute suspension of multi-walled carbon nanotubes (donated by R Smalley) was made in 2-butanol and then air-dried on a V-ridged silicon substrate (K-Tek TGG01). The peaks are $3.0\ \mu\text{m}$ apart and $1.7\ \mu\text{m}$ tall with a peak angle of 70° . The substrate was then exposed to nitric acid vapor at room temperature for 15 h. Images of the tubes before and after the reaction were taken on a Hitachi S-4500 field emission gun scanning electron microscope (SEM).

2.2. Sonomechanicochemistry

Multi-walled carbon nanotubes in surfactant/water solution were donated by S Roth. These tubes had been purified and length-selected by size exclusion chromatography (SEC) (Duesberg *et al* 1998). SEC is the only carbon nanotube purification method in the literature that does not depend upon exposure to oxidative acids, which have the side effect of reacting somewhat with the nanotubes, leaving carboxylic functionality at the reaction sites. The nanotubes were redispersed in dimethylformamide (DMF) by repeated centrifugation, decanting, and sonication. Then one aliquot was reacted with concentrated nitric acid under reflux for 30 min. A second aliquot was reacted with concentrated nitric acid at room temperature in an ultrasonic bath for 30 min. Both samples were centrifuged, decanted, resuspended in DMF, and then reacted with thionyl chloride at 100°C for 30 min. They were then centrifuged, decanted, washed with DMF, and then resuspended in a diluted solution of primary amine-functionalized polystyrene microspheres (Bangs Laboratories, PA02N Lot 3427, mean diameter $100\ \text{nm}$). The resulting solution was then placed on silicon wafers, dried, and imaged by SEM.

3. Results and discussions

3.1. Nanotubes on a V-ridged substrate

Before reaction, the dispersed multi-walled nanotubes followed the surfaces of the V-ridged substrate closely, as shown in figure 1. After extended room-temperature reaction with nitric acid vapor, the kink sites at the peaks of the ridges are observed to be selectively etched, as shown in figure 2. The upper portions of the tubes are etched away, though the bottom portion directly in contact with the surface may be intact.

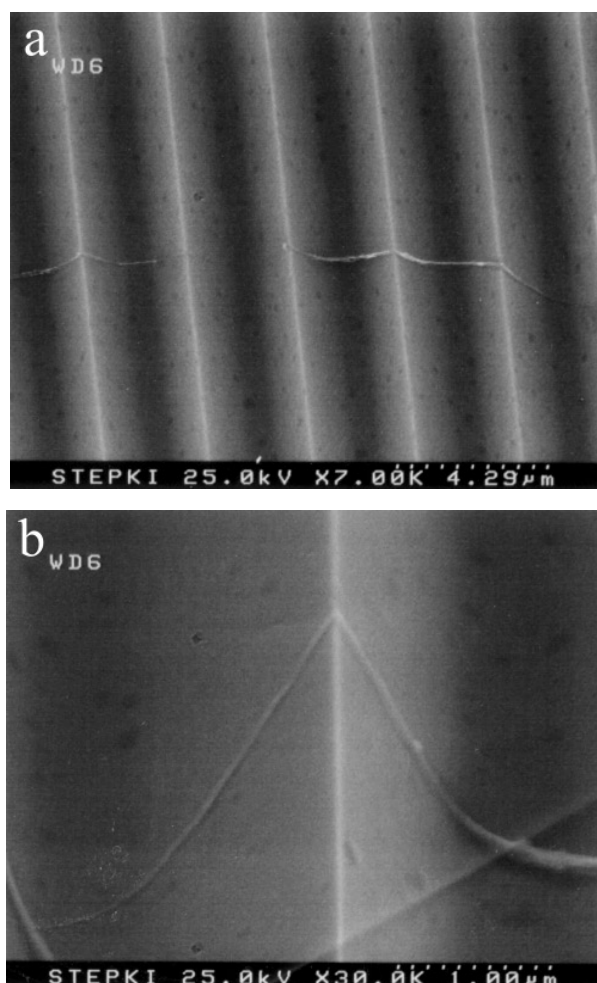


Figure 1. SEM images of multi-walled nanotubes dispersed on a V-ridge substrate.

3.2. Sonomechanicochemistry

In these experiments, the oxidation by nitric acid should leave carboxylic acid functionality at the sites of attack. The reaction with thionyl chloride converts the carboxylic acid to an acid chloride, which then is attacked by amines to form peptide linkages to the polystyrene microspheres. These spheres were chosen to be an SEM visible tag to identify the sites of oxidation.

As expected, the multi-walled nanotubes oxidized under reflux were thinned and then end-cap coupled through peptide linkages to the amine-functionalized polystyrene microspheres, as shown in figure 3. On the other hand, the multi-walled nanotubes exposed only to room temperature nitric acid under sonication exhibited less thinning and little amide coupling at the end caps (figure 4). Instead, the polystyrene spheres attached to the nanotubes at various points along their side walls. The simplest interpretation of these data are that whereas refluxing nitric acid is sufficient to attack nanotube end caps and etch away at the side walls once attacked, room temperature nitric acid is too mild to do so. However, the cavitation bubbles induced by sonication are likely to compress and kink the nanotubes, locally creating regions of high curvature and thus heightened reactivity.

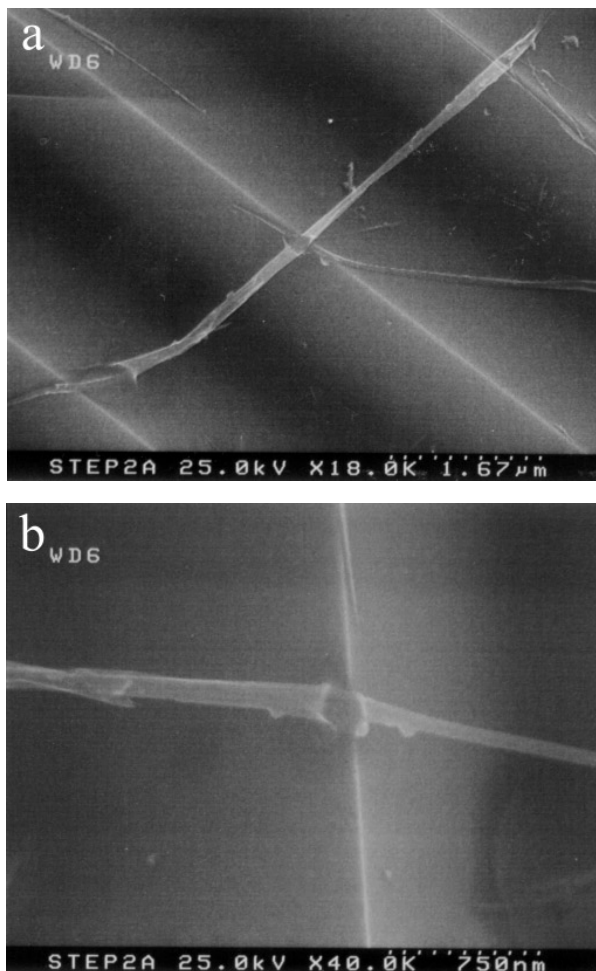


Figure 2. SEM images of multi-walled nanotubes dispersed on a V-ridge substrate after extended exposure to nitric acid vapour.

These results strongly suggest that reversible conformational deformations can heighten nanotube reactivity beyond that observed at pentagonal defects, such as that which is observed at end caps. Individual nanotubes kinked by scanning probe manipulation or by interactions with irregular surfaces should allow controlled promotion of reactions at defined locations along otherwise undifferentiated nanotube side walls. In bulk samples, side wall reactivity can be heightened in a non-site-specific manner by sonication.

3.3. Straining stage for nanometre-scale objects

One would like to measure the mechanical properties of nanometre-scale objects directly. In the device shown in figure 5, we take a step in that direction. This stage will be used to strain small objects while observing their behaviour in a TEM. Measurement of applied force will be incorporated later. The stage will fit into probes manufactured by Gatan. The key component of the device derives from an etched silicon wafer. The chip shown in figure 5 is $10\text{ mm} \times 10\text{ mm} \times 0.5\text{ mm}$. The pattern shown consists of trenches and holes between 20 and $150\text{ }\mu\text{m}$ wide. These will be etched through the wafer from the backside using deep reactive ion etching. The size of the features makes the patterning amenable to

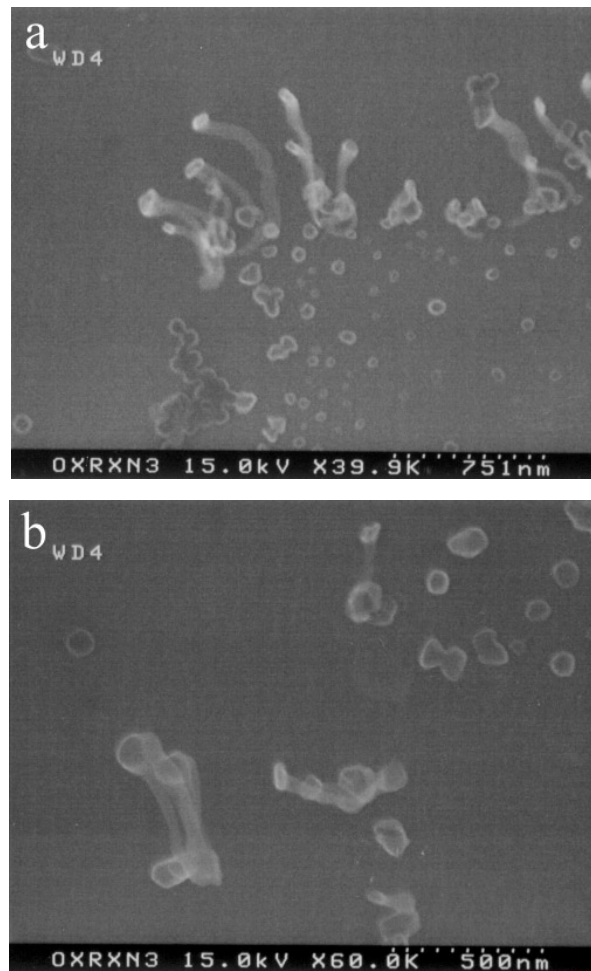


Figure 3. Multi-walled nanotubes linked to polystyrene spheres by peptide bonds.

standard photolithography. In addition, the highly polished silicon wafer will provide coplanar surfaces to which the test specimens will be attached. Note that the overall height of the test stage in the vicinity of the pole pieces of the TEM is only 0.5 mm. Although this is not shown in the drawing, the entire device will mount on a TEM probe or an SEM holder.

The silicon piece consists of a spring and a stage. The spring allows the stage to move. When a force is applied at the contact, the teeth of the stage will be brought closer together. The gap between the teeth is decreased until it is small enough for the desired test. For example, if one wants to probe the behaviour of a 20 nm section of a carbon nanotube under a compressive or tensile stress, the gap would be closed to this distance. The most difficult part of any experiment conducted with this stage will be setting the gap. We will use a fine screw (000–120) for this and will monitor the gap using TEM and SEM. Such a screw moves about $210\text{ }\mu\text{m}$ per revolution and the lever shown will reduce that by approximately one-half. Since many of these will fit on a wafer, we hope to make several stages with varying gaps. Thus, we would bring the teeth together until we had a gap of 100 nm or less then set that stage aside and close the gap on another one. In this way we hope to create stages to test objects between 10 and 100 nm.

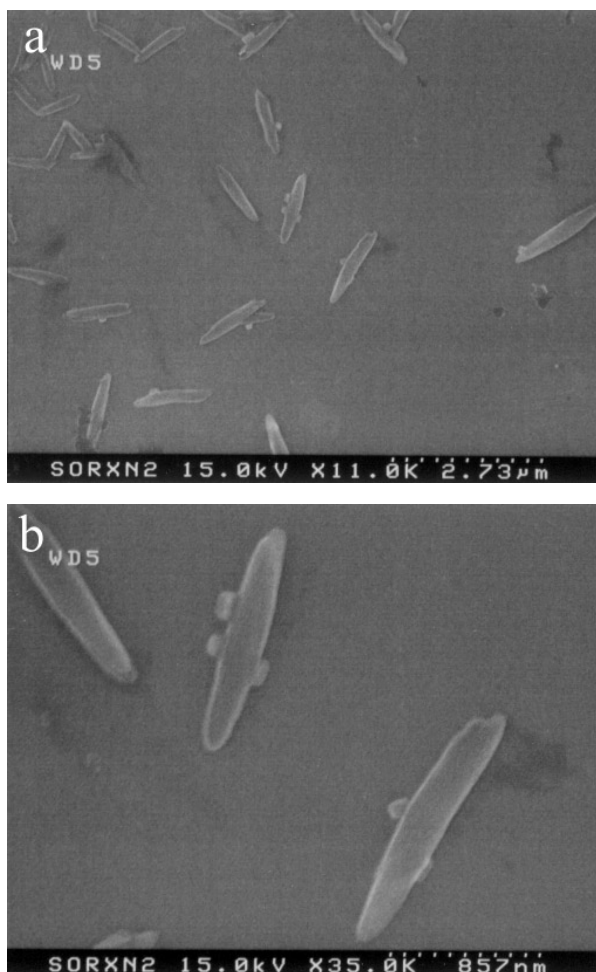


Figure 4. Sonomechanically oxidized multi-walled nanotubes linked to polystyrene spheres by peptide bonds.

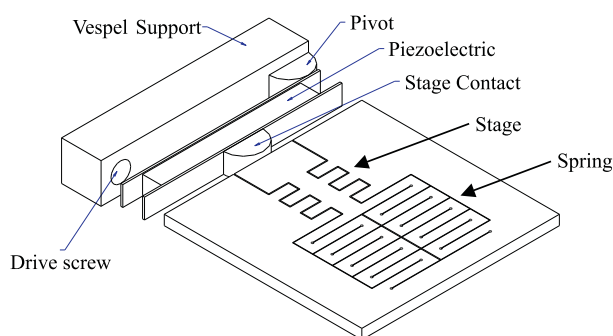


Figure 5. Proposed straining stage for nanometre-scale objects.

Once the gap is set, the object of interest will be positioned across it by dispersing the sample across the surface and manipulating the test specimen using AFM or other means. Once in place and inside the TEM, the specimen will be controllably strained by the expansion or contraction of the PZT crystal. The plates that contact the PZT can be used to hold a capacitive feedback device to monitor the movement of the crystal. The test object will be continuously monitored with the TEM.

The TEM can be used to map out the behaviour of

a particular nanotube versus strain and the tube can be subject to the same forces outside the TEM. Reagents for mechanochemistry can be placed directly on the stage in the form of a drop or the stage could be dipped into a vial. After rinsing and drying, the stage can be replaced in the TEM to observe the effects of the chemical reaction.

4. Conclusions

Conformational strain heightened reactivity has been observed experimentally on two samples of multi-walled carbon nanotubes. In one case, the conformational strain was introduced by van der Waals attractions to a non-planar surface, and the heightened reactivity was observed by oxidative etching. In the other, the conformational strain was a result of the high-pressure collapse of cavitation bubbles in an ultrasonic bath, and the heightened reactivity was observed by coupling polystyrene spheres through peptide linkages to sites of oxidative attack. A design for a TEM compatible straining stage for nanometre-scale objects was also described.

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