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FABRICATION AND CHARACTERIZATION OF A CARBON NANOTUBE-BASED NANOKNIFE

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Abstract

We demonstrate construction and testing of a prototype microtome knife for cutting ~100 nm thick slices of frozen-hydrated biological samples based on a multiwalled carbon nanotube (MWCNT). A piezoelectric-based 3-D manipulator was used inside a scanning electron microscope (SEM) to select and position individual MWCNTs, which were subsequently welded in place using electron beam-induced deposition (EBID). The knife is built on a pair of tungsten needles with provision to adjust the distance between the needle tips, accommodating various lengths of MWCNTs. We performed experiments to test the mechanical strength of MWCNT in the completed device using an atomic force microscope (AFM) tip. An increasing force was applied at the midpoint of nanotube until failure, which was observed *in situ* in the SEM. The maximum breaking force was approximately (8×10^{-7}) N which corresponds well with the typical microtome cutting forces reported in the literature. In situ cutting experiments were performed on a cell biological embedding plastic (epoxy) by pushing it against the nanotube. Initial experiments show indentation marks on the epoxy surface. Quantitative analysis is currently limited by the surface asperities which have the same dimensions as the nanotube.

INTRODUCTION

Three dimensional (3-D) cryo-electron microscopy (cryo-EM) of frozen hydrated samples is important for structural and functional studies of cells. For this work, samples are frozen quickly to minimize crystallization damage; the result is cellular material embedded in vitreous ice. Frozen-hydrated cell samples are sliced in a microtome and subsequently examined in the cryo-EM, using a low temperature specimen holder. When compared with conventionally prepared samples, the frozen hydrated samples have a greater likelihood of displaying cellular structures in their native state [1]. However there is a problem intrinsic to cutting sections of frozen-hydrated samples with conventional diamond or glass knives. The angle included at the knife's cutting edge bends the sections sharply away from the block face, inducing compressive stresses on the upper surface of the section relative to the bottom, which leads to cracking of the sample surface when it is laid flat [2]. A possible solution to this problem is to use a MWCNT in place of a conventional diamond knife. This device would reduce the angle by which the sample is bent during cutting, due to the small diameter of a carbon nanotube.

Carbon nanotubes (CNTs) are promising materials for building nanoscale mechanical structures. Ever since their discovery in 1991, they have received much attention, due to their extraordinary mechanical and electronic properties. Their high tensile strength and well-defined cylindrical geometry offer an attractive means to overcome the problem associated with sectioning thin vitreous cell samples. A CNT should be able to act as an effective compression-cutting tool that could slice through a block of vitreous cells in a manner similar to that of a steel wire cutting a block of cheese [3]. CNTs are flexible and can have very high aspect ratios which make them suitable for 3-D manipulation and the fabrication of nano-devices using a probe type manipulator. There have been a growing number of measurements of their mechanical strength. Wong *et al.* [4] measured the bending strength of a MWCNT using an AFM tip to be 28.5 GPa while Falvo *et al.* [5] reported 100 to 150 GPa for tensile strength. In a direct tensile test by Yu *et al.* [6] the tensile strength of MWCNT was reported to be (11 to 63) GPa. In spite of the significant progress in experiments on CNTs, there is still considerable ambiguity and scatter in these mechanical data, due to the technical difficulties involved in manipulations at nanometer scale; moreover, they are so small that there is no standard testing device that can be used to calibrate such measurements [7,8]. Applications that use CNTs are now being realized in devices such as nano tweezers, nano-bearings and nano-oscillators that have been fabricated by manipulation of CNTs inside an SEM [9,10]. In this paper, we describe initial steps towards the development of a CNT based knife we call a *nano-knife*. This device is formed by welding a CNT across two tungsten needles inside the SEM. Before using it as an actual cutting device we performed tests to investigate its mechanical strength and to identify the failure points of individual nano-knives.

EXPERIMENTAL

FABRICATION OF THE DEVICE

The device consists of two electrochemically sharpened tungsten needles that extend over the edge of a glass support (Fig. 1). The needles, placed at an angle to each other, are glued on a glass substrate (20×15) mm² using a 1:1 mixture of insulating varnish and n-propanol, which sustains high vacuum without out-gassing. The distance between the needle tips is manipulated under an optical microscope. Once the desired tip distance is obtained, the varnish is cured in an oven at 80°C for 30 minutes. The tips of the tungsten needles have a radius of curvature of approximately 100 nm. The device is observed occasionally under the optical microscope as it cures, to see if varnish contraction has had any noticeable effect on tip distance.

Manipulation and attachment of the MWCNT to the device was a step-wise process achieved by using a 3-axis micromanipulator that moved an electrically isolated tungsten probe. The manipulator sits on a custom-made aluminum platform that fits on the SEM stage (Model: JEOL™ 6480 LV) allowing large linear movement of the manipulator and alignment with respect to the sample. In the first step, MWCNTs were fabricated using thermal chemical vapor deposition (CVD) at 725 °C using Fe as catalyst source, the synthesized NT powder was then dried from toluene into a thick mat. The MWCNT mat was cut into small pieces, and one piece was gently rubbed over double-sided acrylic adhesive tape attached to the edge of a sample block. This positioned the nanotubes with their ends overhanging the edge from which they were readily accessible to the manipulator probe [11].

The block edge was aligned with respect to the manipulator, then the probe was brought into contact with the exposed end of the nanotube of interest. The electron beam was focused, and the image magnified at the point of contact. The electron beam irradiated residual hydrocarbons (usually present in the SEM on the sample surface) that decompose and then deposited on the sample, forming a weld. This process is called electron beam induced deposition (EBID) [12, 13]. The CNT was then pulled and separated from the bundle by retracting the probe slowly back to its original position as shown in Fig. 2 (a).

The next step involved replacing the CNT sample block with the glass slide device and realigning the manipulator arm with respect to the two tungsten needles on the glass slide [14]. The CNT on the manipulator probe was then moved so the free end of the nanotube touched the tip of one of the needles on the glass slide. It was subsequently welded to that needle using EBID. The manipulator arm was then moved at the slowest possible speed (step size = 5 nm) to make the CNT touch near the tip of other needle, where it was also welded, so it would bridge the gap. Thus, the CNT was welded at three different points (two on needles mounted on glass and one on the manipulator probe). The manipulator arm was then moved laterally, breaking the CNT from the manipulator probe but, leaving it connected to the needles on the glass substrate as shown in Fig. 2 (b). More details on nano-knife are provided in the attached video file which is a collection of SEM images at each fabrication step.

MECHANICAL CHARACTERIZATION

The first step towards evaluating the nano-knife as an effective compression-cutting tool was to assess its mechanical strength with forces comparable to those required for preparing actual samples. We have performed *in situ* mechanical tests on individual nano-knives in the SEM by loading them in a transverse direction, similar to a rigidly supported beam with the load acting at the center of the beam.

To determine the breaking force at maximum CNT deflection, we employed an AFM tip with a nominal force constant value of 2.8 N/m (as provided by the manufacturer). The AFM tip was glued to a tungsten probe connected to the manipulator. The AFM tip was then aligned with the nanoknife in a manner such that the tip touched the center of the nanotube as shown in Fig. 3 (a). Prior to testing, the AFM tip was slightly blunted by rubbing it against a zirconia substrate; this helped to prevent the AFM tip from slipping past the nanotube. Once the AFM tip was in contact with the CNT, the manipulator was set at its lowest speed with a step size of 5 nm. The AFM tip then moved horizontally (in the field of view of the SEM), pushing against the nanotube and deflecting it.

This deflection was recorded every ~400 nm of manipulator movement by stopping the manipulator and taking an image (Fig. 3b and c). The load on the nanotube was increased until it failed, which in this case occurred at the weld. The AFM tip deflection at failure was measured by image correlation, using commercial software (analySIS™ and stored SEM images. Figure 3(a)-(c) shows the load tests being performed on different nano-knives fabricated in this study. The data corresponding to these load tests are enlisted in Table 1.0. In all of the tests we performed the welds failed, implying that the weld strength is weaker than the strength of MWCNT. The total nanotube deflection for these tests ranged from (3 to 5) μm and there was no visible damage to the CNT after the welds broke. Data from our most successful test showed a maximum deflection of the AFM tip at failure to be 0.29 μm (where the most successful test corresponds to the test in which we observed maximum tip deflection at the point of failure).

The maximum force exerted by tip before weld breakage is given by:

$$F_{\max} = K\delta_{\max} \quad (1)$$

Where, $F_{\max}$ represents the maximum force exerted by the AFM tip, K corresponds to the nominal force constant of the AFM tip (N/m) and $\delta_{\max}$ is the maximum deflection of the AFM tip (μm). The weld area was approximated to be the area scanned by the beam during deposition (roughly the same as the cross section of nanotube in this case) [15,16]. Assuming the welds failure mode to be shear, the maximum weld strength is obtained for test 3 as;

$$\tau = F/2A = 0.145 \text{ GPa} \quad (2)$$

This value represents a weld strength that is less than the tensile strength of MWCNTs reported by Yu *et al.* [6], in which study the tensile testing of MWCNTs was accomplished without breaking the welds.

CUTTING EXPERIMENT ON EPON RESIN

Epon resin is commonly used to embed cell biological samples that have been fixed and dehydrated in preparation for microtomy and then transmission electron microscopy [17]. This resin had several advantages over vitreous ice for the testing a nanoknife based cutting process; (a) Epon can be polymerized so it is reasonably soft, and its mechanical properties are fairly well known; (b) the sectioning of vitreous ice would have required a cryo-environment, which was not attainable in our SEM. Moreover, ultra microtome cutting experiments on Epon resin by Asakura *et al.* [18] have suggested that the cutting force depends on section size and section thickness. Based on their measurements, cutting a section 100 nm thick from a block of polymer whose face is $(30 \times 30) \mu\text{m}$, would require a force of $\sim 1.8 \mu\text{N}$. This value is comparable with the force required to break a nanoknife. Hence we had good reason to try this resin for our first cutting experiments with the nanoknife. A block of Epon resin was trimmed to fit the cutting length of nanoknife. However, this polymeric material tends to become charged under the beam of the SEM, blurring any images acquired. To reduce this problem and improve imaging at higher magnification, the sample was coated with a layer of Au a few nanometers thick. Hence, the optimum conditions to obtain high resolution and larger working distance for our experiments were (15- 30) kV acceleration voltage and minimum Au thickness value of ~ 20 nm. Lower acceleration voltage has other disadvantage; a recent study on CNTs has shown that the maximum physical damage to the nanotube is caused at lower SEM acceleration voltages (close to 1 kV) [19]. This Epon specimen was fixed to a tungsten probe, which in turn was connected to the manipulator arm. Fig. 4 (I) shows side view of the chamber obtained with an infra red camera as the specimen was being aligned with respect to the nanotube inside the SEM. The block was pushed against the nanotube at an angle oblique to the electron gun to allow better view of the nanotube as it made contact with the specimen surface. Fig. 4 (II-IV) is a collection of images showing the stepwise movement of the resin block into the nanoknife. Images of the block surface before and after the tests showed indentation marks from the CNT. It appears that the force exerted by the nanoknife is just sufficient to leave a mark on the Au-coated surface of the block as shown in Fig. 5 (a). The indentation marks on the block are most likely due to plastic deformation of the Epon under the thin Au film. Since the gold coating is only a few nanometers thick, the CNT must pierce or deform the Au film to produce a mark that is visible in our SEM. However, it is impossible to make quantitative statements about the magnitude of the indentations in the plastic. Surface roughness and the imaging characteristics of these specimens in our electron microscope limited the clarity of the before/after differences, which hindered our interpretation of the results from these experiments as highlighted in Fig. 5 (b) and (c).

SUMMARY AND CONCLUSION

We have demonstrated the feasibility of fabricating a nanoknife (compression cutting tool) based on an individual CNT. A nanotube was stretched between two tungsten needles in a manner that allowed us to test the mechanical strength of the assembled device. A force test on the prototype nanoknife indicated that failure was at the weld, while the CNT was unaffected by the force we applied. *In-situ* load tests on the nanoknife indicated maximum device strength of 0.145 GPa, corresponding to a weld breaking force of $0.81 \pm 0.8 \mu\text{N}$.

Cutting experiments performed on a sharp, Au-coated Epon block showed indentation marks due to forces exerted by the nanotube. Characterization of the cutting process has been limited by the lack of high resolution imaging of the polymeric specimen in our SEM, which made it difficult to locate a small cut or mark. The surface roughness of specimen, which is of the same order as nanotube diameter, also contributes to the problem.

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Figure 1.

Schematic of the device that was used for mechanical characterization of MWCNTs and the proposed nanoknife. Two tungsten needles were used to support the MWCNT. The gap between the needles, where the nanotube is to be welded, was typically half the length of the nanotube, approximately 20 μm . Inset is an SEM image of the aligned tungsten needles.

Figure 2.

(a) SEM micrograph of MWCNTs on acrylic tape, hanging from the edge of the SEM A1 block. (b) The nanotube has been welded to the tungsten probe, and is now being taken away from the bundle to be later welded to the needles on the glass substrate.

Figure 3.

(a), (b) and (c) SEM micrographs showing the mechanical testing of the nanotube being pushed by the AFM tip for tests 1, 2 and 3 respectively. Insets in the images are at the same magnification as the main images and correspond to the maximum deflection of the NT as well as the AFM tip before breakage. The images are taken at faster scan rate to avoid creep effects.

Figure 4.

(I) Infra red camera view of the chamber showing arrangement used for cutting experiments with the nanoknife. Fig. 4 (II) – (IV) SEM micrographs of the cutting process being carried out at an oblique angle to the electron beam, providing easier alignment and greater visibility. Nano-welding (EBID) was performed using the SEM in spot-mode, and in this experiment it is clearly seen that the weld survives while nanotube breaks near the weld.

Figure 5.

(a) Top view of the Au-coated resin block just after the test. Indentations made by marks from the CNT and the tungsten needles are visible. No deep or obviously visible cut was observed. (b) and (c) SEM images of the top surface of the Au coated Epon resin showing the artifacts and surface roughness at the edge, which makes, it difficult to quantify any cutting or indentation marks from the nanoknife.

Test data from mechanical testing of three Nano-knives. The diameter of nanotubes and AFM tip deflection was measured in the SEM and a cumulative 10 % percent error is assumed in their value because of nanotube vibration at higher magnifications. Weld area is assumed to be same as the crosssection of the NT; variation arises in locating the exact size of the deposit. For test 1, the load test could not be conducted till the breakage point as the AFM tip started touching the tungsten needles on the support structure.

TABLE 1

Number	d (nm)	δ_{max} (nm)	A (μm^2) ($\times 10^{-3}$)	F _{max} (nominal) N ($\times 10^{-9}$)	τ (GPa)
1	200±20	150±10	31±6.2	420±42	0.013±0.004
2	110±11	200±20	9.5±1.9	560±56	0.029±0.008
3	60±6	290±29	2.8±0.5	812±81.2	0.145±0.043