Nanomanipulation And Characterization Of Individual Carbon Nanotubes

Rodney S. Ruoff*

*Department of Mechanical Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA, r-ruoff@northwestern.edu

ABSTRACT

A new tool that operates in a scanning electron microscope for measuring the mechanics of nanostructures is briefly presented, and its use to measure the response to tensile loading of carbon nanotubes is outlined.

1 INTRODUCTION

The rapid advancement in miniaturization in the last decade has seen the discovery a variety of nanostructures. Carbon nanotubes (CNT) have received particular attention. Multi-walled carbon nanotubes (MWCNT) were discovered in 1991[1] and single wall carbon nanotubes (SWCNT) in 1993 [2,3], and over 4100 scientific publications have appeared on CNTs to date. The mechanical and electrical properties of CNTs have been the subject of numerous theoretical and experimental studies. CNTs can be considered to be a seamless cylinder (SWCNT), or a set of nested cylinders (MWCNT), of graphene sheet(s), and can have open or capped ends. The properties of a graphene sheet, of quantum confinement in small dimensions, and the detailed geometry including the chirality of the shell structure of CNTs have been studied, and potential applications are likely in materials reinforcement [4,5], field emission panel display [6-8], electronic nanowires [9,10] and devices [11-13], chemical sensors [14], H_2 gas storage [15], as tips for scanning microscopy [16,17], for use in batteries [18], and so on.

CNTs should possess mechanical properties far superior to commercially available carbon fibers, due to their expected structural perfection. Young's modulus (~ 1 TPa) similar to the in-plane modulus value for high quality graphite and high tensile strength (~ 50 to 100 GPa, thus much greater than any other available material) are predicted, and for the modulus experimentally verified, for CNT [19-22]. For comparison, the highest strength carbon fiber in industry has a strength of ~ 7 GPa [23].

The small dimensions of CNTs offers significant challenges for experimental study of their mechanical properties: (i) the challenge of CNT placement in an appropriate testing configuration; (ii) in certain cases the fabrication of appropriate clamps and thus achieving control of the boundary conditions for loading; (iii) successful application of the desired loading; (iv) characterizing and measuring the mechanical deformation at the nanometer and perhaps even the atomic length scale.

High-resolution microscopes allow the characterization of nanostructures, and developments in the new area of "nanomanipulation," based on inserting or adapting new tools to such microscopes, have enhanced our ability to mechanically test nanostructures such as

Here, we briefly summarize our effort in the development of new tools for nanoscale characterization and the study of various mechanical properties of CNTs.

2 A BRIEF REVIEW OF RELATED INSTRUMENTS FOR NANOSCALE MATERIAL CHARACTERIZATION

Scanning probe microscopy and electron microscopy have been the most widely used methods for resolving and characterizing nanoscale objects. We and others have primarily used SPM and EM instruments to study nanotube mechanics. For this reason, we give a brief review of the methods of operation of these types of microscopes.

Electron microscopes (EM) use high-energy electron beams (several keV up to several hundred keV) as a source for scattering and diffraction from a sample, which results in high resolving power down to sub-nanometer resolution because of the extremely short wavelength (a fraction of a nanometer) of high kinetic energy electrons.

In scanning electron microscopy, SEM, a focused electron beam (nanometers in spot size) is rastered across the sample surface and an amplified image of the sample surface is formed by recording the secondary electron signal or the back scattering signal generated from the sample. SEM is limited by the scattering volume of the electrons interacting with sample material, and high end instruments are capable of achieving a resolution of a few nanometers.

Scanning probe microscopes (SPM) use extremely sharp probes (that can have 10 nm or smaller radius of curvature at the tip) controlled by sensitive sensing and actuation feedback electronics for obtaining nanoscale and even atomic scale information. In a typical imaging experiment, the tip is rastered over the sample and the sample geometry is thereby mapped out. SPM can also be used to nanoindent samples, to nanomachine surfaces, and to bend and manipulate nanostructures. Depending on the type of interaction force involved for sensing, an SPM includes a family of microscopes such as the atomic force microscope (AFM), magnetic force microscope, electric force microscope, friction force microscope, and so on. Depending on the mechanism used for measuring the force interaction, the SPM also includes many modes of operation, such as contact mode, tapping mode, force modulation mode and so on. We refer to, for example, references [24-26].

3 NEW TOOLS FOR NANOSCALE MECHANICAL MEASUREMENT

The high resolution and large sample chamber space make SEM a good candidate for inclusion of three

freedom manipulation device inside SEM was developed by Yu et al. to allow handling and characterizing CNTs and thus also other nanostructures [27]. The device can probe a collection of CNTs, isolate an individual CNT, and extract it for study. The manipulator can be used as a testing stage once a CNT has been isolated. The device fits well in the SEM and can be operated without disturbing the SEM's function.

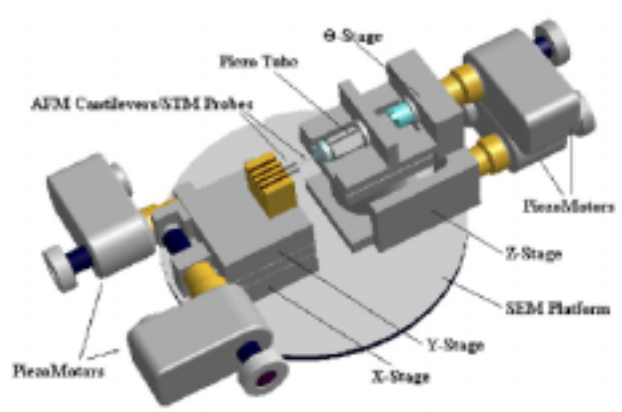

Figure 1: The design of the manipulator is depicted here.

Only the major components are shown in fig. 1. The manipulator was designed with small size, low-cost, wide translation range, reasonable precision, and rapid assembly in mind. The SEM stage manipulator occupies roughly 50 cm^3. Well-controlled lateral and longitudinal motions are necessary for manipulation and in order to measure, for example, strain-induced conductance properties.

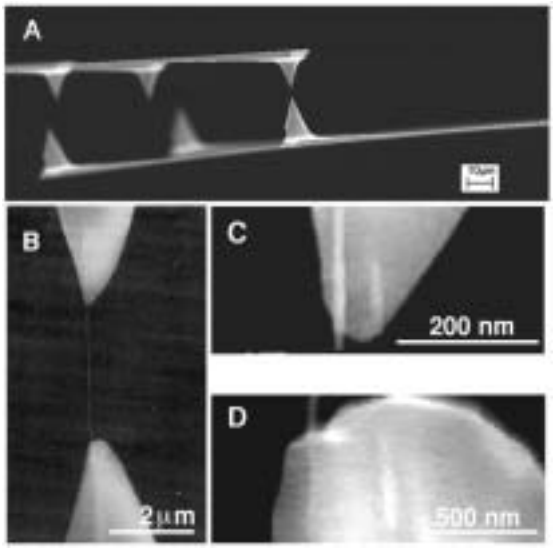

Figure 2: **(**A) An SEM image of two AFM tips holding a MWCNT attached at both ends on the respective AFM silicon tip surfaces by electron beam deposition of carbonaceous material. The lower AFM tip in the image is on a soft cantilever, the deflection of which is imaged to determine the applied force on the MWCNT. The top AFM tip is on a rigid cantilever that is driven upward to apply tensile load to the MWCNT. **(**B) SEM image showing the MWCNT between the two AFM tips. **(**C) SEM image showing the attachment of the MWCNT on MWCNT on the lower AFM tip. The MWCNT section is covered by a square-shaped carbonaceous deposit.

Commercially-available AFM tips (Such as from Digital Instruments) with rigid cantilevers and soft cantilevers were used (Fig. 2) in our work. AFM tips were mounted opposite the rotating tungsten probe tip, which also served as a mount for an AFM cantilever when "dueling" AFM tips were used.

Attaching an individual CNT or CNT bundle to an AFM tip is done by a rather simple process. A visible quantity of purified CNT material is loaded onto a tip and placed into the tip holder on the x-y stage along with three to six other AFM tips that are ready for CNT attachment. The AFM tip on the piezotube can then be brought close to the raw material. When the tip is brought close enough to a protruding CNT, it "jumps" to the tip and is held in place through the van der Waals attraction. This initial jump to the tip could be due to an electrostatic attraction as the CNT and the AFM tip could be unequally charged from the electron beam; or it could simply be from van der Waals forces. The van der Waals forces are then sometimes enough to hold the tube and tip together as the tip is retracted from the bunch. If not, a stronger bond can be made by using the electron beam to perform localized electron impact-induced deposition of carbonaceous materials due to the presence of the gases in the chamber. (Figs. 2C and D.) Attaching CNTs to AFM tips has been previously done by Dai et al. [16] with light microscope observation, and their work involved the first example of a CNT as a tip for AFM, and the first detailed studies of the mechanical performance of such a CNT AFM Tip. Our technique, attachment with simultaneous viewing in the SEM, allows the CNT tip to be inspected at much high spatial resolution, and immediately altered if desired.

Of course, this general approach is not limited to CNTs, and we expect that a large number of different types of nanofilaments, such as metal nanowires, inorganic nanowhiskers, and nanoplatelets of various layered materials, will be "nanoclamped" in various types of testing stages configured to be in SEMs, TEMs, or SPMs, or adapted to various spectroscopic probes, such as Raman. The method of making clamps, and the types of clamps, will likely be sample dependent. For example, "pull-out" experiments of relevance to the understanding of nanocomposites, could be done with such an approach.

4 EXPERIMENTAL RESEARCH ON THE MECHANICS OF INDIVIDUAL CARBON NANOTUBES

The response to axial tensile loading of individual MWCNTs was realized by Yu et al. using a testing stage based on a nanomanipulation tool operating inside an SEM introduced above [28]. The nanomanipulation stage allowed for the three-dimensional manipulation -- picking, positioning, and clamping -- of individual MWCNTs as demonstrated previously [27]. The individual MWCNTs were attached to AFM probes having sharp tips by localized electron beam induced deposition (EBID) of carbonaceous material inside the SEM.

probe, and the applied force was measured at the other end by the cantilever deflection of the other AFM probe. The measured force vs elongation were converted, by SEM measurement of the MWCNT geometry, to a stress versus strain curve and the breaking strength of each MWCNT was obtained by measuring the maximum tensile loading force at break. The experiment also clearly resolved that a MWCNT normally breaks in a sword-in-sheath breaking mechanism, where the MWCNT so attached under tensile load breaks at its outmost layer followed by the sliding out of the inner shells during the continuous pulling.

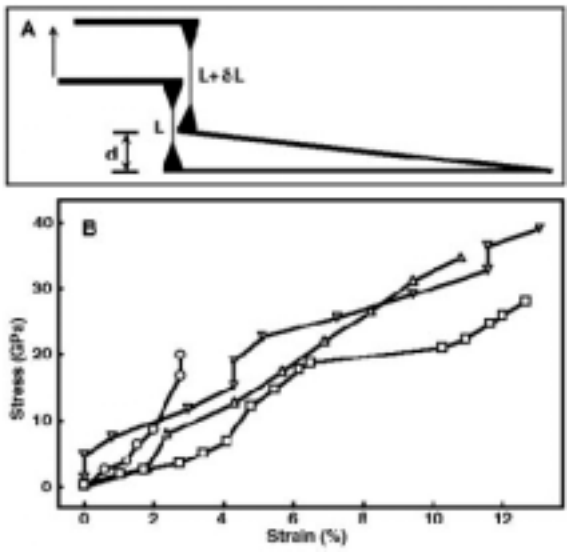

Figure 3: **(**A) Schematic showing the principle of the tensile-loading experiment. When the top cantilever is driven upward, the lower cantilever is bent upward by a distance d, while the nanotube is stretched from its initial length of *L* to *L* + *dL* because of the force exerted on it by the AFM tips. The force is calculated as *k*d, where *k* is the force constant of the lower cantilever. The strain of the nanotube is *d*L/L. **(**B) Plot of stress versus strain curves for individual MWCNTs.

The shear strength between the shells of a MWCNT is also an interesting subject for experimental study. Yu et al. were able to directly measure the friction force between the neighboring layers while pulling the inner shells out of the outer shells of a MWCNT using the same apparatus for measuring the tensile strength of individual MWCNTs [29]. The realization of such measurement was based on the discovery that a tensile-loaded MWCNT normally broke with a sword-in-sheath breaking mechanism. The separated outer shell can still be in contact with the underlying inner shell in certain cases (in other cases, the "snap back" of the loading and force-sensing cantilevers leads to two separated fragments). A model was then developed to include forces such as (i) F_a, the applied force from the deflection of the soft AFM cantilever; (ii) F_s, the static shear interaction force between shells present during the "stick" event; (iii) F_d, the dynamic shear interaction force between shells in the "slip" event; (iv) F_c, the solid-solid surface tension interface force that is due to the creation of a new shell surface area in the pullout event

dangling bonds on the edge of the fractured MWCNT cylinder with the internal shell surface. Shear strength was related to the shear interaction force. The continuous measurement of force and "contact length" (the overlap length between the outer shell and its neighbor) in the pullout process provided then the necessary data for obtaining the dynamic (0.08 MPa) and static shear strength (0.30 MPa in one case and 0.08 MPa in another case) between the shells. Such measurement also allowed the direct estimation of the surface energy of graphite.

5 CONCLUSIONS

The new developments in the area of nanoscale manipulation and measurement as reflected in the studies presented in the last section have certainly helped our understanding of CNT mechanics. Since CNTs possess unique structures that maintain their conformation while being manipulated they represent a "nano-tinker toy" for manipulation on the nanoscale. Therefore, such types of approaches also provide a window on current capabilities for exploring and exploiting the "nano-world," and provide an avenue for future advancement in methods and tools useful in nanotechnology.

But what has the community not yet achieved? We have not yet measured the tensile loading response of an individual SWCNT, nor have we applied a known torque or controlled, and reversible, twist along a CNT. The influence of environment on NT mechanics has not yet been explored in any detail—such as effects of temperature, chemical environment, loading rate, defect density, nor do we have a clear and detailed picture of the nucleation, propagation, and ultimate failure resulting from, defects. From the experimental perspective, such advances will come with new approaches and tools generated by innovative thinking. It is clear that focused effort in developing new measurement tools that can be integrated into high spatial resolution imaging instruments is necessary for further advances in nanostructure mechanics.

6 ACKNOWLEDGEMENTS

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