

New Methods and Tools for Nanotechnology

NSF Functional Nanostructures Grant 9871874

Principal Investigators:

Rod Ruoff, Department of Mechanical Engineering, Northwestern University

Tomasz Kowalewski, Department of Chemistry, Carnegie Mellon University

James Huettner, Department of Cell Biology and Physiology, Washington University-St. Louis

Collaborators: Mark Dyer and Min-Feng Yu of Zyvex

Focus: on *3-dimensional*, and also *on-surface*, manipulation and structure-properties studies of individual (macro)molecular nanoscale objects.

Free space manipulation and properties: We have invented, designed, fabricated, and used new nano-manipulators that operate inside electron microscopes (SEM and TEM, and in the future in conjunction with scanning probe microscope imaging, SPM) driven by piezoelectric elements. Target materials: nanotubes, whiskers, platelets (graphene sheets). Target properties: mechanical, electromechanical measured with testing stages that are component parts of the nanomanipulators.

Manipulation of objects supported on surfaces: proximal probes (primarily tapping mode AFM) have been employed. Target materials: as above, plus nanoparticles and synthetic and biological polymers. Tapping mode AFM was originally developed in order to minimize tip-sample forces (primarily lateral forces.) Our work has been focused on achieving better understanding of the physics of tapping mode AFM, in particular on controlled reintroduction of tip-sample forces to facilitate mechanical testing and manipulation. We have performed computer simulations and direct measurements of forces in double-cantilever experiments with control of the amplitude and frequency of operation. The average tapping force can now be tuned effectively in the range from piconewtons to micronewtons. Our work in this area led also to the discovery of the improvement of image quality upon operation far below resonance. Maintaining tapping forces in the sub-nanonewton range is critical in all attempts to achieve superior resolution through the use of ultra-sharp probes (e.g. carbon nanotubes or tips formed through mechanochemistry at the apex of conventional AFM probes.) Controlled increase of tapping forces up to the micronewton range facilitates mechanical testing of compressible objects and compliance-based-contrast imaging of materials.

Results achieved:

We have developed and used new tools and approaches for manipulating matter on the nanoscale and for measuring properties, to date publishing 11 papers, submitting 3 more, and in the process of submitting an additional 3, citing this NSF grant. [1-17]

Ruoff conceived of the idea of exploiting localized deformation in nanostructures to drive site-specific chemistry, and in a collaboration with Brenner and Srivastava, and postdoc Kevin Ausman, discussed "Predictions of enhanced chemical reactivity at regions of local conformational strain on carbon nanotubes: Kinky Chemistry." [1, 2]

A new testing stage built in collaboration with industrial affiliate Zyvex, [3] which operates inside of a scanning electron microscope has led to a series of papers on the mechanical properties of nanotubes under tensile load. The first, "Strength and breaking mechanism of multi-walled carbon nanotubes under tensile load," involved the pick up, mounting, and tensile loading to break with measurement of applied load and multi-walled carbon nanotube (MWCNT) elongation, of individual MWCNTs. The breaking mechanism and tensile strength of the outer shell was measured for 19 individual MWCNTs. [4] We then used a modified form of the same device to measure the mechanical response of individual SWCNT ropes, and determined strain at break and strength of these ropes. [5] In a separate and novel experiment, the shear strength of nested and neighboring shells in several MWCNTs was measured, by sliding the (previously broken) outer shell with respect to the inner layers. This paper suggests the possibility, based on such shell sliding, of a nanobearing actuator. [6]

A future goal involves measurement, with a new testing stage we have built and tested (in part with support from this grant), which operates inside of a transmission electron microscope, of individual SWCNTs and other high aspect ratio nanostructures, but in addition also of very thin films/platelets/sheets. For the (ultimate) goal of

measurement on a graphene sheet (one layer of graphite) we have invented and used a new method to create defect-free “pieces” of graphite. The method involves lithographic patterning of freshly cleaved highly oriented pyrolytic graphite and oxygen plasma etching to create graphite islands of small enough dimensions that some are defect-free. [7,8]

In a series of papers involving close collaboration between the Kowalewski and Ruoff groups, we have described the use of new methods for using tapping mode atomic force microscopy (AFM) to study the structure of MWCNTs on surfaces. This has allowed determination of the detailed geometries of either partially or completely flattened MWCNTs (‘NT ribbons’) [9,10] and also the use of tapping-mode to apply known average forces in a study showing remarkable local compression (‘indentation’) of MWCNTs (up to 50% change in height, corresponding to an applied pressure estimated at ~20 GPa, from which full recovery to the relaxed state was seen: nanotubes are remarkably resilient). [11] Yu, who recently obtained his Ph.D. with Ruoff, co-advised by Kowalewski, has accepted a position at our industrial affiliate to this project, Zyvex. He has continued to make discoveries and to collaborate with Ruoff and his colleague Dyer, on projects related to nanotube mechanics, and we have submitted [12] and are soon to submit [13] papers describing further AFM observations on NT ribbons [12], and on intrinsic twisted structures observed with high resolution transmission electron microscopy [13]. Ruoff has begun a new collaboration with the Wing Kam Liu computational mechanics group at Northwestern, and graduate student Dong Qian is currently modeling the case of the twisted NT ribbon structures.

Kowalewski has continued his development of new methods for AFM imaging [14,15] in several new applications in his new position at Carnegie Mellon University (CMU). Variable-force tapping mode AFM was used to characterize novel nanostructured materials with core-shell structures synthesized in collaborating groups: hybrid inorganic-organic nanoparticles and polythiophene nanowires. (a). Hybrid inorganic-organic particles consisting of (co)polymers tethered to polysilsesquioxane cores were synthesized in Matyjaszewski's group at CMU using Atom Transfer Radical Polymerization (ATRP). These particles may find applications in nanocomposites and in specialty coatings and in membrane materials. When the particle shell was composed of a low- T_g polymer, by imaging at variable force we were able to visualize the core-shell morphology. In addition, when the shell consisted of a block copolymer with high and low- T_g blocks, the layered structure of the shell could be visualized.[16] (b). Nanowires formed by the self-assembly of well defined block copolymers of poly(3-hexylthiophene) (PHT), a conjugated, electrically conductive polymer, with polystyrene (PS) were synthesized in McCullough's group at CMU. Well-defined architecture and composition was achieved through a novel combination of regioregular polymerization (PHT block) and ATRP for the addition of PS block. It turned out, that owing to their perfect regioregularity, PHT blocks have an extremely strong tendency to self assemble into nanowires with lengths approaching microns. The nanowire cores are surrounded by PS sheath, and their structure is poorly resolved when imaged with low tapping forces. However, the structure of nanowire cores could be perfectly resolved when imaging was carried out at increased tapping forces, far below resonance. [17]

Huettner and Ruoff have worked on new methods for stimulating growth of nerve cells on silicon wafer surfaces. The concept was to create very sharp chemical gradients of, e.g., nerve growth factor (NGF) and study neurite growth patterns from baby neurons in the presence of such strong gradients. Deep reactive ion etching was used in combination with lithographic patterning to create (in a multi-step process) “pin holes” in a standard Si wafer with diameters as small as 20 nm. These holes are connected to larger holes (the 20-nm hole is through a thin oxide window which is the end surface of a long and wide channel spanning the top and bottom surfaces of the wafer) so that NGF can be distributed from the bottom-side, ultimately through an array of the 20-nm holes. Preliminary results show that the plated baby nerve cells do grow projections as if responding to the local gradients.

Education. Graduate student Min-Feng Yu recently defended his Ph.D. and has accepted a position as a staff scientist at the nanotechnology startup Zyvex. Several postdocs have played an important role as well in the work cited, particularly Kevin Ausman (now at Rice University as a research scientist), Henry Rohrs (now at the Washington University School of Medicine), Xuekun Lu (research scientist with Michael Polanyi, Univ of Toronto), and Oleg Lourie (continuing with the Ruoff group). Several undergraduates have also been supported on this project and performed undergraduate research projects related to the project goals.

References

- 1. Predictions of enhanced chemical reactivity at regions of local conformational strain on carbon nanotubes: Kinky Chemistry.** D. Srivastava, D. W. Brenner, J. D. Schall, K. D. Ausman, M. F. Yu, and R. S. Ruoff, *J. Phys. Chem. B*, **103**, 4330-4337 (1999).
- 2. Nanostressing and mechanochemistry.** K. D. Ausman, H. W. Rohrs, M. F. Yu, and R. S. Ruoff, *Nanotechnology*, **10**, 258 (1999).
- 3. Three-dimensional manipulation of carbon nanotubes under a scanning electron microscope.** M. F. Yu, M. J. Dyer, H. W. Rohrs, X. K. Lu, K. D. Ausman, J. V. Ehr, and R. S. Ruoff, *Nanotechnology*, **10**, 244 (1999).
- 4. Strength and breaking mechanism of multi-walled carbon nanotubes under tensile load.** M-F Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, and R. S. Ruoff, *Science*, **287**, 637 (2000).
- 5. Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties.** M. F. Yu, B. S. Files, S. Arepalli, and R. S. Ruoff *Phys. Rev. Lett.*, **84**, 5552 (2000).
- 6. Controlled sliding and pullout of nested shells in individual multi-walled carbon nanotubes.** M. F. Yu, B. I. Yakobson, and R. S. Ruoff, *J. Phys. Chem. B*, **104**, 8764(2000).
- 7. Patterning of highly oriented pyrolytic graphite by oxygen plasma etching.** X. K. Lu, H. Huang, N. Nemchuk, and R. S. Ruoff, *Appl. Phys. Lett.* **75**, 193 (1999).
- 8. Tailoring graphite with the goal of achieving single sheets.** X. K. Lu, H. Huang, H. Huang, and R. S. Ruoff, *Nanotechnology* **10**, 269 (1999).
- 9. Structural analysis of collapsed, and twisted and collapsed, multiwalled carbon nanotubes by atomic force microscopy.** M. F. Yu, T. Kowalewski, and R. S. Ruoff, *Phys. Rev. Lett.*, **86**(1), 88 (2001).
- 10. Realization and observation of the reversible and irreversible radial deformation of carbon nanotubes by tapping mode atomic force microscopy.** Yu, MinFeng; Ruoff, Rodney S.; Kowalewski, Tomasz; Dyer, Mark J.; Von Ehr, James R.; Faircloth, Brian; Krchnavek, Robert R *Proc.-Electrochem. Soc. (1999)*, **99-12**(Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials), 552-557.
- 11. Investigation of the radial deformability of individual carbon nanotubes under controlled indentation force.** M. F. Yu, T. Kowalewski, and R. S. Ruoff, *Phys. Rev. Lett.*, **85**, 1456 (2000).
- 12. Structure and mechanical flexibility of carbon nanotube ribbons: an atomic force microscopy study.** Min-Feng Yu, Mark J. Dyer, Rodney S. Ruoff, *J. of Applied Physics*, submitted.
- 13. Intrinsic Twists in Multi-walled Carbon Nanotube Ribbons.** Min-Feng Yu, Mark J. Dyer, Jian Chen, Rodney S. Ruoff, to be submitted.
- 14. Determination of tip-sample forces in tapping mode AFM.** T. Kowalewski, M. F. Yu, R.S. Ruoff, to be submitted to *Journal of Applied Physics*.
- 15. Off-resonance tapping mode AFM—towards superior resolution and control of tip-sample forces.** T. Kowalewski, to be submitted to *Appl. Phys. Lett.*
- 16. Synthesis of Well-Defined Block Copolymers Tethered to Polysilsesquioxane Nanoparticles And Their Nanoscale Morphology On Surfaces** J. Pyun, K. Matyjaszewski, T. Kowalewski, D. Savin, G. Patterson, G. Kickelbick, N. Huesing, submitted to *J. Am. Chem. Soc.*
- 17. Self Assembly of Electrically Conductive Polymer Nanostructures: Synthesis and Properties of Well-Defined Regioregular Polythiophene Diblock and Triblock Copolymers** J. Liu, E. Shiena, T. Kowalewski, and R.D.McCullough, submitted to *J. Am. Chem. Soc.*