PECASE – First Principles Modeling of Mechanics and Chemistry of Materials

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Final Report

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Recent experiments on nanostructured materials, such as nanoparticles, nanowires, nanotubes, nanopillars, thin films, and nanocrystals have revealed a host of “ultra-strength” phenomena, defined by stresses in a material component generally rising up to a significant fraction > 1/10th of its ideal strength – the highest achievable stress of a defect-free crystal at zero temperature. While conventional materials deform or fracture at sample-wide stresses far below the ideal strength, rapid development of nanotechnology has brought about a need to understand ultra-strength phenomena, as nanoscale materials apparently have a larger dynamic range of sustainable stress (“strength”) than conventional materials. Ultra-strength phenomena not only have to do with the shape stability and deformation kinetics of a component, but also the tuning of its physical and chemical properties by stress. Reaching ultrastrength enables “elastic strain engineering”, where by controlling the elastic strain field one achieves desired electronic, magnetic, optical, phononic, catalytic, etc. properties in the component, imparting a new meaning to Feynman’s statement “there’s plenty of room at the bottom”.

15. SUBJECT TERMS
Abstract

Recent experiments on nanostructured materials, such as nanoparticles, nanowires, nanotubes, nanopillars, thin films, and nanocrystals have revealed a host of "ultra-strength" phenomena, defined by stresses in a material component generally rising up to a significant fraction > 1/10th of its ideal strength – the highest achievable stress of a defect-free crystal at zero temperature. While conventional materials deform or fracture at sample-wide stresses far below the ideal strength, rapid development of nanotechnology has brought about a need to understand ultra-strength phenomena, as nanoscale materials apparently have a larger dynamic range of sustainable stress ("strength") than conventional materials. Ultra-strength phenomena not only have to do with the shape stability and deformation kinetics of a component, but also the tuning of its physical and chemical properties by stress. Reaching ultrastrength enables "elastic strain engineering", where by controlling the elastic strain field one achieves desired electronic, magnetic, optical, phononic, catalytic, etc. properties in the component, imparting a new meaning to Feynman's statement "there's plenty of room at the bottom". We are investigating the principal deformation mechanisms of ultra-strength materials. The fundamental defect processes that initiate and sustain plastic flow and fracture, and the mechanics and physics of both displacive and diffusive mechanisms are being modeled at the atomistic and electronic-structure levels. Also, electrochemistry coupled with mechanics dictates the microstructural evolution and service life of many materials, and underlies problems such as stress-corrosion cracking and battery cyclability. While atomistic and first-principles modeling is adept at looking at the finer details of energetics and microstructural evolution, it often needs help from experiments to identity the key performance-limiting microstructural processes. To resolve this bottleneck we have created a nanoscale electrochemical testing platform inside a transmission electron microscope (TEM), and performed direct observations of the electrochemical reactions of the individual nanowires. SnO$_2$, ZnO, Si, Ge, graphene and carbon nanotube anodes and LiFePO$_4$ nanowire cathode have been tested so far. Lithium embrittlement is found to be a persistent issue. These in situ TEM experiments greatly complement our modeling efforts, and together they provide unprecedented details on how materials degrade in service due to combined electrochemical-mechanical actions.

Fundind History

This PECASE award was initially granted to the PI at Ohio State University as FA9550-07-1-0007. Only $25,916 was spent out of the $500,000 budget, before the project was transferred to
the University of Pennsylvania as FA9550-08-1-0325, with a total budget of $474,083, and budget dates of May 1, 2008 - Nov. 30, 2012.

Results

The PI used the PECASE grant to perform a range of research activities on first-principles modeling of mechanics and chemistry of materials, in combination with critical experiments such as in situ electron microscopy. The publications supported by FA9550-08-1-0325 are listed in\(^1\)\textsuperscript{30} in order of relevance for the high-temperature materials program. These work can be roughly categorized into the following:

**Simulation of Coupled Displacive-Diffusional Processes** – In the majority of solid-state processes, coupled displacive-diffusional processes is a rule rather than an exception. Mechanistic studies of these processes require modeling capabilities at atomistic length scales but diffusional time scales, which is beyond the reach of current molecular dynamics (MD) methods. Partially supported by this project, a new computational method called Diffusive Molecular Dynamics (DMD) is being developed\(^1\), which, unlike the MD, captures diffusional and displacive evolution of complex microstructures at the atomic scale by coarse graining over atomic vibrations and evolving a continuous occupational probability of atomic density clouds. Derived in grand canonical ensemble, DMD is a chemical mean-field extension of the variational Gaussian method coupled with the master equation for diffusion solved on a discrete and moving atomic grid. It combines long-range elastic effects and short-range atomic interactions simultaneously with gradient thermodynamics and allows for simultaneous displacive and mass-action dynamics such as lattice diffusion. We are also developing corresponding phase-field descriptions of these transformations, which eventually could seamlessly link to DMD as in the quasi-continuum approach.

**Studying Slow Dynamics** - In order to study the slow dynamics in glassy materials\(^30\) in general, we have developed a Markovian network model to calculate the shear viscosity of deeply supercooled liquids based on sampling of an atomistic energy landscape. Shear stress relaxation is calculated from a master-equation description in which the system follows a transition-state pathway trajectory of hopping among local energy minima separated by activation barriers, which is in turn sampled by accelerated MD-based algorithms\(^6\). Quantitative connection is established between the temperature variation of the calculated viscosity and the underlying potential energy and inherent stress landscape of several glasses\(^11,12\), showing a different landscape topography or 'terrain' is needed for low-temperature viscosity from that associated with high-temperature viscosity\(^11\). We have also developed an accelerated 'strain-boost' MD algorithm\(^6\), inspired by the Eshelby transformation formalism, that could provide more efficient sampling of the shear transformation zone (STZ) event in glasses.
In particular, silica (SiO$_2$) glass is one of the essential materials in human civilization for making household items, window panes, lenses and optical fibers. An important reason for its wide adaptation is its formability near the glass-transition temperature ($T_g > 1100$C). SiO$_2$ glass at room temperature, however, is usually brittle due to fracture instability. But when the “brittle” glass is confined in extremely small dimensions at tens of nanometres, the nature of flow and fracture may change. Newest experiments performed at Sandia Center for Integrated Nanotechnologies (CINT) show that glass nanowires with diameters less than 20 nm can become ductile at room temperature, with surprisingly large tensile plastic elongations up to 18%. Remarkably, these ductile glass nanowires also possess high flow strengths, and are thus much more energy-absorbing and damage-tolerant than expected. Atomistic modeling indicates that the unexpected ductility is due to the development of a surface affected zone in the nanowires, which enhances ductility by producing more bond-switching events per irreversible bond loss.

**Investigating Solid-state Amorphization Processes** - We have studied the solid-state amorphization of phase-change nanowires$^4$ and large shape change of oxide nanowires during electrochemical lithiation, which share certain common characteristics with strain glasses (both solid-state, and both with significant transformation strains). We found that upon electrochemical charging, a reaction front propagated progressively along the nanowire, causing the nanowire to swell, elongate, and spiral. The reaction front contains a high density of mobile dislocations, which are continuously nucleated and absorbed at the moving front. This dislocation cloud indicates large in-plane misfit stresses and is a structural precursor to electrochemically driven solid-state amorphization. Because amorphization-induced volume expansion, plasticity, and pulverization of electrode materials are the major mechanical effects that plague the performance and lifetime of high-capacity anodes in lithium-ion batteries, our observations provide important mechanistic insight for the design of advanced batteries, as well as damage mechanisms in strain glasses. In the modeling effort we have also given a first-principles account of the observed room-temperature lithium diffusivity in amorphous lithium oxide$^5$.

**High-temperature sublimation of graphene** – We have performed in situ transmission electron microscopy (TEM) and modeling of how graphene sublimes at high temperatures. Curvy nanostructures such as carbon nanotubes and fullerenes have extraordinary properties but are difficult to pick up and assemble into devices after synthesis. We have performed experimental and modeling research into how to integrate curvy nanostructures on flat graphene, taking advantage of the fact that graphene bends easily after open edges have been cut on it, which can then fuse with other open edges, like a plumber connecting metal fittings. By applying electrical current heating to few-layer graphene inside an electron microscope, one effectively anneals out the radiation damage and observes the *in situ* creation of many interconnected, curved carbon nanostructures$^7$, such as graphene bilayer edges (BLEs) aka “half nanotubes”, BLE polygons, and nanotube-BLE junctions connecting multiple layers of graphene. A novel piezoelectric effect causes the BLEs to have large permanent electric dipoles of 0.87 and 1.14 Debye/Å for zigzag and armchair inclinations, respectively$^{10}$. Unlike carbon nanotubes which fold graphene by $2\pi$ rotation and are highly poly-disperse in chiralities and radius, BLEs are highly mono-disperse
structures due to the $\pi$ rotation and a lattice orientation constraint during processing$^3$. Further investigations indicate that multiple-layer graphene offers unique opportunities for tailoring carbon-based structures and engineering novel nano-devices with complex topologies. In particular, we show it is possible to create a metal-semiconductor-metal graphene-nanotube junction device with 0.8eV electronic gap$^9$.

**Nanoscale electrochemical tests: in situ TEM experiments and modeling** - Electrochemistry coupled with mechanics dictates the microstructural evolution and service life of many materials in the energy industry and transportation, and underlies problems such as stress-corrosion cracking and battery cyclability. While atomistic and first-principles modeling is adept at looking at the finer details of energetics and microstructural evolution, it often needs help from experiments to identify the key performance-limiting microstructural processes. To resolve this bottleneck we have created a nanoscale electrochemical testing platform$^{2,5}$ inside a transmission electron microscope (TEM), consisting of electron-transparent single nanowire electrodes and an ionic liquid electrolyte, and performed direct observations of the electrochemical reactions of the individual nanowires. SnO$_2$, ZnO, Si, Ge, graphene and carbon nanotube anodes and LiFePO$_4$ nanowire cathode have been tested so far. Lithium embrittlement is found to be a persistent issue. These in situ TEM experiments$^{13,28}$ greatly complement our modeling efforts$^{1,6,9,11}$, and together they provide unprecedented details on how materials degrade in service due to combined electrochemical-mechanical actions.

**Ultra-strength materials** - Recent experiments on nanostructured materials, such as nanoparticles, nanowires, nanotubes, nanopillars, thin films, and nanocrystals have revealed a host of “ultra-strength” phenomena, defined by stresses in a material component generally rising up to a significant fraction $>$ 1/10th of its ideal strength – the highest achievable stress of a defect-free crystal at zero temperature. While conventional materials deform or fracture at sample-wide stresses far below the ideal strength, rapid development of nanotechnology has brought about a need to understand ultra-strength phenomena, as nanoscale materials apparently have a larger dynamic range of sustainable stress (“strength”) than conventional materials. Ultra-strength phenomena not only have to do with the shape stability and deformation kinetics of a component, but also the tuning of its physical and chemical properties by stress. Reaching ultrastrength enables “elastic strain engineering”, where by controlling the elastic strain field one achieves desired electronic, magnetic, optical, phononic, catalytic, etc. properties in the component, imparting a new meaning to Feynman’s statement “there’s plenty of room at the bottom”. We are investigating the principal deformation mechanisms of ultra-strength materials. The fundamental defect processes that initiate and sustain plastic flow and fracture, and the mechanics and physics of both displacive and diffusive mechanisms are being modeled at the atomistic and electronic-structure levels.$^{8,13,28}$

**Elastic Strain Engineering** – An optoelectronic material with a spatially varying bandgap that is tunable is highly desirable for use in photovoltaics, photocatalysis and photodetection. Elastic
strain has the potential to be used to achieve rapid and reversible tuning of the bandgap. However, as a result of plasticity or fracture, conventional materials cannot sustain a high enough elastic strain to create sufficient changes in their physical properties. Recently, an emergent class of materials—named ‘ultrastrength materials’—have been shown to avoid inelastic relaxation up to a significant fraction of their ideal strength. In the paper “Strain-engineered artificial atom as a broad-spectrum solar energy funnel” 29, we illustrate theoretically and computationally that elastic strain is a viable agent for creating a continuously varying bandgap profile in an initially homogeneous, atomically thin membrane. We propose that a photovoltaic device made from a strainengineered MoS$_2$ monolayer will capture a broad range of the solar spectrum and concentrate excitons or charge carriers.

**Acknowledgments/Disclaimer**

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**Awards Received**

TMS Robert Lansing Hardy Award (2009), for "a young person in the broad fields of metallurgy and materials science for exceptional promise of a successful career".


Chinese Ministry of Education and Li Ka Shing Foundation Chang Jiang Scholar Award (2009)

Technology Review TR35 award, for 35 "world's top innovators" under age 35 (2007)


**Presentations**


Invited talk, APS March Meeting, Boston, February 27-March 2, 2012.


Joint MIT ANS Student Chapter / faculty seminar on "Nanoscale electrochemical tests: in situ TEM experiments and modeling", November 21, 2011.

First Annual Richard K. Osborn Lecture, Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Stamps Auditorium, September 23, 2011.

Lee Hsun Young Scientist Lecture Series on Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China, July 18, 2011.


Invited talk, MRS Fall Meeting, Boston, November 29 - December 3, 2010.

Microstructure Modelling symposium, MMM2010, the Fifth Conference on Multiscale Material Modelling, Freiburg, Germany, October 7, 2010.

Invited talk, Physics and Astronomy Colloquium Series at University of Southern California, August 30, 2010.


Invited talk, 17th International Symposium on Metastable, Amorphous and Nanostructured Materials (ISMANAM 2010), Zurich, Switzerland, July 4 - 9, 2010.

Invited talk, Sixth International Conference on Materials Structure & Micromechanics of Fracture (MSMF6), Brno, Czech Republic, June 28 - 30, 2010.

Invited talk, Department Werkstoffwissenschaften, Lehrstuhl WWI: Allgemeine Werkstoffeigenschaften, Universität Erlangen-Nürnberg, Germany, June 24, 2010.


Invited talk, Materials Science and Engineering Seminar, University of Tennessee, Knoxville, April 26, 2010.

Invited talk, Materials Science and Engineering Seminar, Rensselaer Polytechnic Institute, Troy, April 7, 2010.


Keynote talk (40 min), mini-symposium Finite Plasticity & Viscoplasticity of Conventional & Emerging Materials (In celebration of 65 Years of Akhtar Khan), Plasticity 2010, St. Kitts, West Indies, January 3-8, 2010.

Invited talk, MIT Center for Computational Engineering (CCE), December 2, 2009.

Invited talk, Civil Infrastructure Seminar, School of Civil and Environmental Engineering, Cornell University, November 10, 2009.


Invited talk, Department of Mechanical Engineering Seminar, University Of Houston, September 3, 2009.

Invited talk, Workshop on Probing the Limits of Strength, Lawrence Berkeley National Laboratory, Berkeley, California, August 11-12, 2009.

Invited talk, "In-situ Observation of Graphene Sublimation and Edge Reconstructions," mini-symposium Graphene growth and properties through experiments and simulations, tenth U.S. National Congress on Computational Mechanics (USNCCM X), Columbus, July 16-19, 2009.

Invited talk, School of Materials Science and Engineering, Shanghai Jiao Tong University, June 10, 2009.


Invited talk, Othmer-Jacobs Department of Chemical and Biological Engineering, Polytechnic Institute of NYU, Brooklyn, New York, May 4, 2009.


Invited talk, Shanghai Institute of Ceramics, March 10, 2009.


Two invited talks, National Sun Yat-sen University, Kaohsiung, Taiwan, December 13-21, 2008.

Invited talk, Georgia Institute of Technology Woodruff School of Mechanical Engineering Seminar, Oct. 23, 2008.


Two invited lectures, Workshop on Multi-Scale Modeling of Moving Interfaces in Materials, Katholieke Universiteit Leuven, Belgium, July 2-4, 2008.

Invited talk, 2nd International Conference on Heterogeneous Materials Mechanics (ICHMM-2008), HuangShan, China, June 3-8, 2008.


Invited talk, NIST 2008 Diffusion Workshop, Gaithersburg, Maryland, May 12-13, 2008.
Publications acknowledging AFOSR support, ranked in order of relevance for the high-temperature materials program; Li, J. means being a corresponding author


