Future Science Needs and Opportunities for Electron Scattering: Next Generation Instrumentation and Beyond

A U.S. Department of Energy (DOE)
Office of Basic Energy Sciences (BES) Workshop

Hilton Washington DC North
Gaithersburg, MD _ March 1-2, 2007

Instructions to Participants

Dear Workshop Participant:

Please find attached copies of "grand challenge" slides contributed by all participants as of 27 Feb 2007. The slides are in alphabetical order by contributor. A supplement will likely be available during the course of the meeting for slides received or revised past this time.

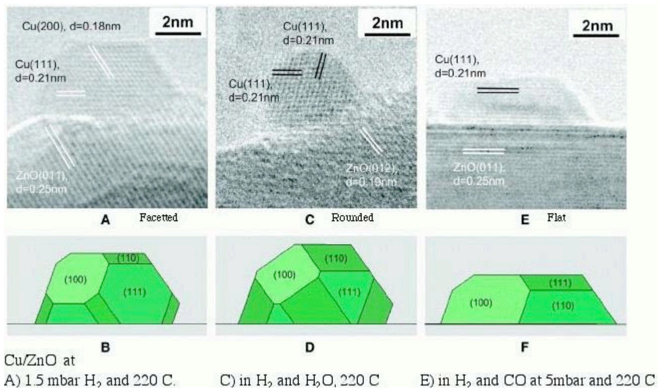
Please use this copy of the slides to record additional information, revisions, etc. that you feel should be considered by the organizers in the drafting of the report. In particular:

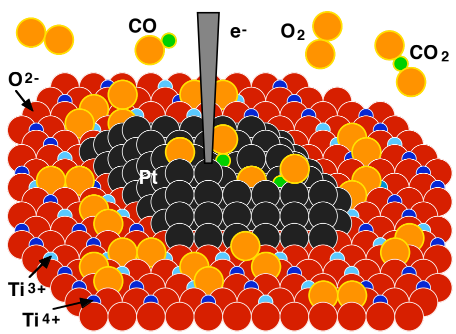
- Are there key words or concepts that could usefully be added to the "scientific questions" or "technical challenges" listings for a given highlight?
- Are there key references that should be cited in the report?
- Are there important issues or concepts that have not been captured that you would like to add?

Please make sure that these ideas, concepts, and references are captured by the workshop organizers.

Thank you for helping to make this a stimulating and successful workshop!

Grand Challenge: Atomic-scale Mechanisms of CO Oxidation Reaction via Heterogeneous Catalysis





Above: Fuel cell Cu/ZnO catalyst particles changing shape in response to gaseous environment; Hansen et al., Science 295, 2055 (2002).

Below: Schematic representation of atomic-scale analysis of Pt/TiO_2 catalyst system

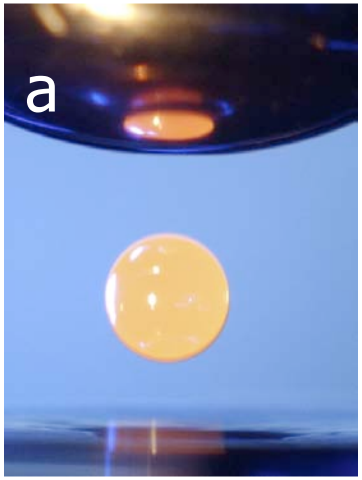
Key Scientific Questions:

- How does 3D morphology of catalyst particle and its wetting to oxide support vary with T, $\{p_i\}$, i = O_2, CO, CO_2, etc.?
- How is oxygen transported to particles to effect redox reaction (e.g., CO to CO_2)?
- What is physical extent of chemically reduced area of substrate in vicinity of active metal particle?

Key Technical Challenges:

- Miniaturization of environmental cell to minimize electron optical path through operating atmosphere
- Can we model a bulk system with an electron-transparent substrate / active particle combo?
  - E.g., 1 nm particle on 20 nm thick oxide support?
- How to control / measure T, $\{p_i\}$ in a miniaturized volume

Grand Challenge: Transient Phenomena



a) Metallic sample levitated electrostatically heated by laser

b) Oscillating droplet

Photos courtesy of Ken Kelton, Washington University

Key Scientific Questions:

- Phase transitions and nucleation
  - approach to the glass transition
- Catalysis
  - Intermediates in reversible reactions
- Photochemically induced reactions
- Structure changes induced by mechanical stresses, electric or magnetic fields

Key Technical Challenges:

- Combined simultaneous probes
  - Neutron, X-ray, Electrons,
- Combination of Sophisticated Environments
  - Temperature, Pressure, Field
- Analysis Software and Infrastructure
  - Shared data bases, Grid computing

Grand Challenge: Spatially Resolved Soft X-ray Emission Spectroscopy to Complement EELS

Key Scientific Questions:

- Valence Band Structure at atomic resolution?
- Site, symmetry, momentum partitioned

Key Technical Challenges:

- Count rate is very low, requiring high collection
- Energy resolution has to be sub-eV: microcalorimetry?

1074 M. Terauchi, M. Kawana / Ultramicroscopy 106 (2006) 1069–1075

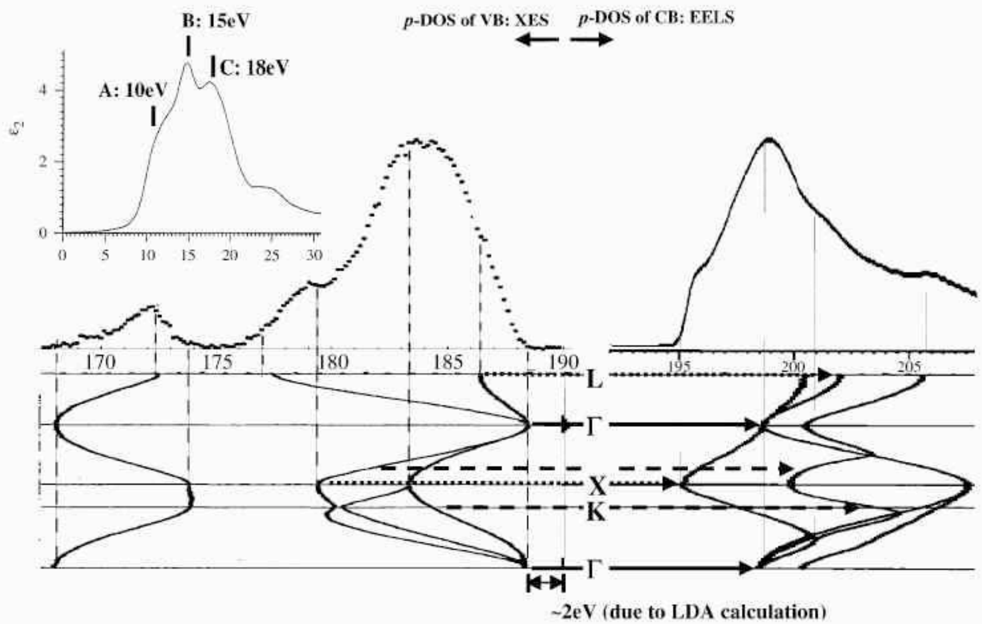
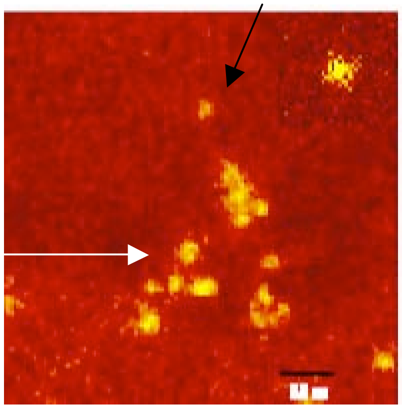


Fig. 8. Combination of a B K-edge EELS spectrum and a B K-emission spectrum of c-BN. Calculated energy band diagrams are also shown for comparison. Dotted vertical lines show correspondence between the peak and/or shoulder structures of the experimental data and special symmetry points of the calculated band diagram. The imaginary part of the dielectric function ε_2 derived from a valence electron excitation spectrum is shown as an inset.

Grand Challenge: Atomic Level Dynamic Studies



P.E. Batson, IBM

Au atoms on amorphous carbon move under the STEM probe, forming and dissolving clusters of atoms. (white arrow) FFT in upper right occasionally shows Au crystal lattice distances. Atoms explore possible bonding sites, sometimes very rapidly. In this sequence, a single atom may be showing a double image because it moves rapidly between two sites. (black arrow)

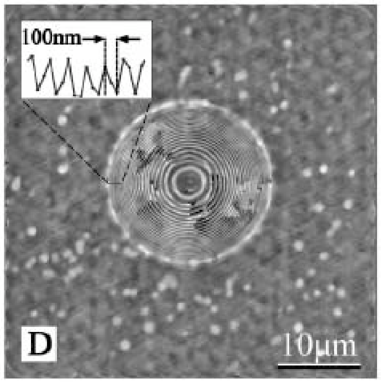
Key Scientific Questions:

- Beam-specimen interaction
  - Atomic impact parameter dependence
  - Decay paths for deposited energy
- Energetics of atom-surface, atom-atom interaction
  - Multiple, near degenerate structures
  - 3-d nature of structures and binding sites
  - Site dependent chemistry

Key Technical Challenges:

- Fast data acquisition
- Sub-Angstrom probe with 0.1-1nA current
- Deep Sub-Angstrom accuracy and stability
- Stereo pairs using two fixed tilt beams?
- EELS with meV energy resolution
- May require low temperature stage

Grand Challenge:
Count Every Electron & Make Every Electron Count



Diffractive imaging reconstruction using hard X-rays in a case where conventional point resolution would be about 5microns. (From Rodenburg et al., PRL **98**, 034801 (2007)) An example where current detectors limit prospects for electrons.

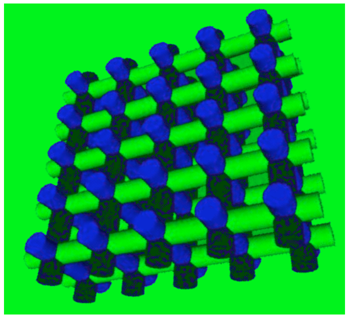
Key Scientific Questions:

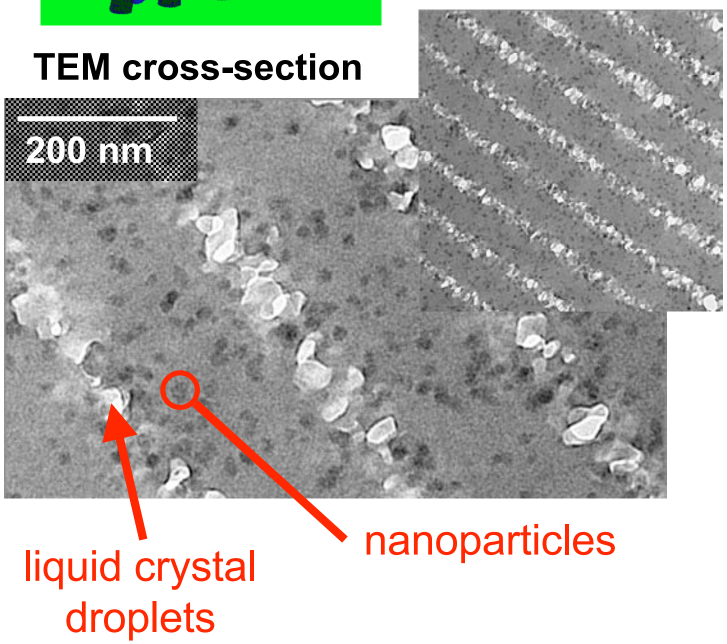
- Damage provides the ultimate limit to many current and future experiments the more so with aberration correction and bright sources.
- Electrons are predicted to be the most fruitful source of information in many cases (e.g. cf. hard X-rays) provided we collect them efficiently!
- Radical new detectors could enable:
  - Diffractive imaging of atomic arrangements in individual proteins.
  - Simultaneous imaging and spectroscopy of single atoms
  - New imaging modes as yet undiscovered

Key Technical Challenge:

- Detection of position/angle <u>and</u> energy of all scattered electrons.
- By simple time-of-flight this would require 50femtoseconds/eV resolution.
  - Time information would be a bonus.

Grand Challenge: Observing Assembly Processes in Solution Based Nanosystems





Holographically defined polymer nanocomposite. Evolution from the starting homogeneous system to final material not known.

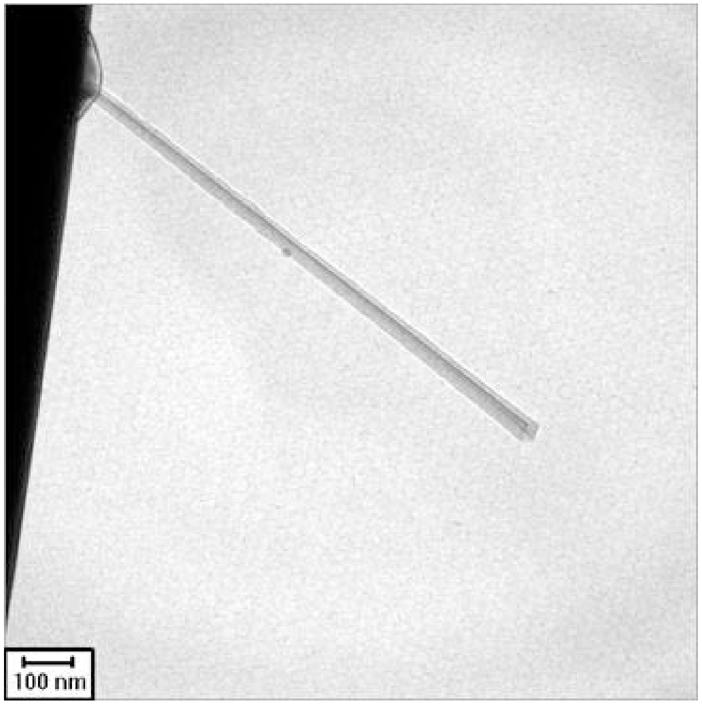
Key Scientific Questions:

- Imaging of nanoparticle synthesis in solution
  - Visualization of nucleation event
  - Direct imaging of chemical ligands
- Nature of the glass transition, which can be studied through a model nanoparticle system
- Nanoparticle assembly in solution
  - Nanoparticle crystallization
  - Polymer nanocomposites
  - Diffusion and transport in multicomponent systems

Key Technical Challenges:

- Minimize electron beam induced damage
- Signal to noise when imaging through solvent
- Enhancing contrast in organic systems
- Electron beam induced artifacts
- Design of sample holders to enable application of external driving forces for assembly (e-field, light, chemical potential)

Imaging Atomic Motion on its Natural Timescale



A Si nanowire with a <111> growth direction, produced by laser ablation of a <111> Si substrate inside the dynamic TEM at LLNL. The Si surface had 4nm of Au deposited on the surface to act as a catalyst and there was no ambient gas present.

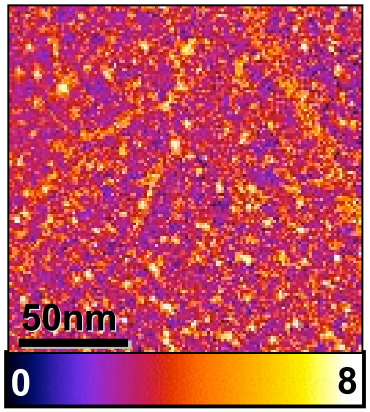
Key Scientific Questions:

- How do nanostructures nucleate and grow?
- What are the specific active sites in all catalysts?
- How can point defects at interfaces engineer better mechanical, electrical and optical properties?
- How do surfaces/defects modulate ionic diffusion?
- How does corrosion and radiation damage proceed in complex systems?

Key Technical Challenges:

- Construction of a coherent ultrafast electron gun to enhance time resolution to ns/ps timescales
- Optimized electron-optical system for in-situ analysis at atomic spatial resolution
- Understanding the effect of the beam on atom motion – particularly for intense C_s/C_c corrected beams
- In-situ control of the specimen temperature, ambient pressure, electrical bias, and strain allowing a full range of tilt

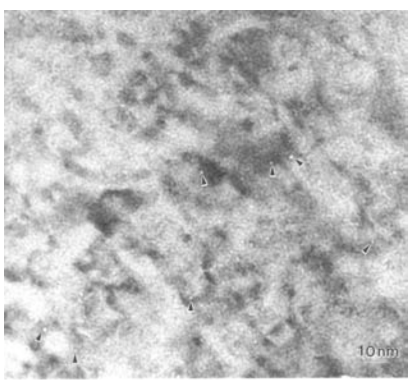
Grand Challenge: Materials Development for Power Generation Applications



wt% Ni

Solute-enriched nanoprecipitates in irradiated steel detectable via FEG-STEM XEDS (Ni map). It is only possible to detect solute-enriched clusters via 3DAP.

Nanocavities formed in irradiated Type 316 stainless steel.



Key Scientific Questions:

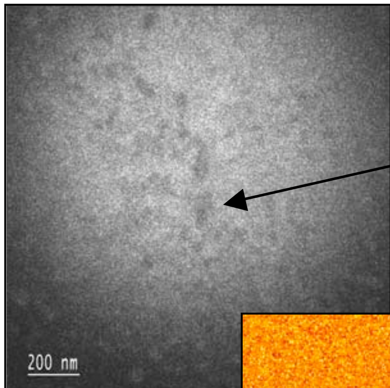
- Can electron-optic techniques effectively detect irradiation-induced microstructural / microchemical changes that affect mechanical performance?
- How does the presence of diffuse nanometer-sized irradiation-induced “features” lead to a reduction in material toughness?
- What is the mechanism of crack advance in stress corrosion cracking/environment-sensitive fracture?
- What is (are) the microstructural change(s) induced by stress-relief treatment?

Key Technical Challenges:

- Ability to image solute-enriched clusters (no change in crystal structure) containing vacancies in steels/alloys; can vacancies be identified? Must avoid inducing electron irradiation damage in material
- In situ straining of radioactive specimens to examine dislocation-cluster interactions
- Ability to detect solute segregation to dislocations (improved spectroscopy capability)
- Amenable/suitable specimens!

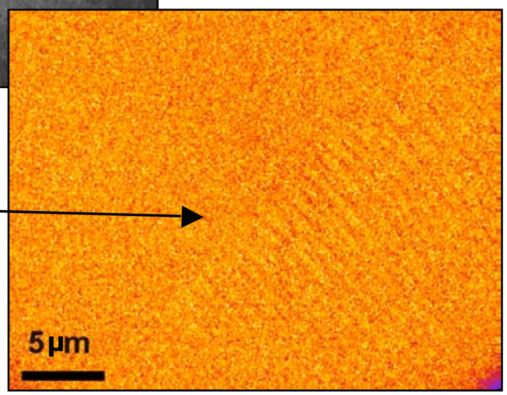
Femtosecond Materials Science in Irreversible Systems: Experiment at the Scale of Simulation

Early Results from DTEM



Growing martensite grains in Ti

Reaction front in a reactive multilayer film moving at 13 m/s



High-time resolution, *in situ* electron microscopic imaging opens a new frontier in materials science

Key Scientific Questions:

- Can predicted melting, amorphization, and disordering in displacement cascades be confirmed experimentally?
- Can we make direct comparison of defect structure evolution with atomistic or dislocation dynamics simulations?
- What are the role of defects in electronic transitions in the GHz regime?
- Does the structure of a moving interface determine its velocity and hence transformation kinetics?
- What are the mechanisms for phase transformations in materials under extreme conditions?

Key Technical Challenges:

- Single-shot femtosecond/nm imaging
- Optimized design of a high spatial resolution/high time resolution electron microscope
- High time resolution atomic movies

Table Top Analysis

Table-top portable TEM. Can it become the next generation of "optical" microscopes for routine characterization of structures in every lab?

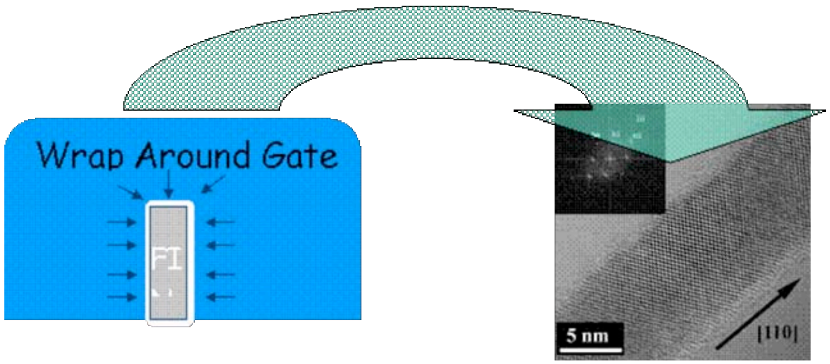
Key Scientific Questions:

- Routine characterization of nano-/bio-materials
  - Small particles science
  - Growth of complex nanostructures
  - Characterization of new materials

Key Technical Challenges:

- Easy access to portable high resolution microscopes both very versatile and user friendly (analogue to an optical microscope today)
  - fully equipped with analytical tools for several different in situ testing (EDX, EELS, nanoprobes, etc.)
- Sample preparation:
  - Development of a tool for automated sample preparation to thin to electron transparency large areas of bulk specimens in one single step

Grand Challenge: Methods for Characterizing Nanoelectronic Materials and Structures

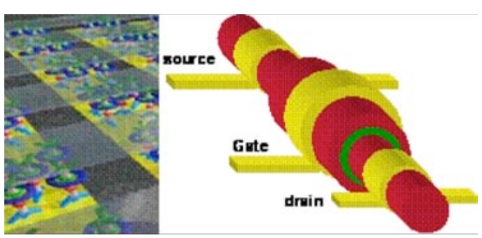


Ge nanowire

Key Scientific Questions:

- Crystal structure and strain in new epitactic structures at atomic dimensions
- Morphology of nanoscale amorphous and nanocrystalline materials with interface specificity
- Atomic-scale diffusion during processing
- The interface between soft materials and traditional semiconductor structures

Beyond CMOS

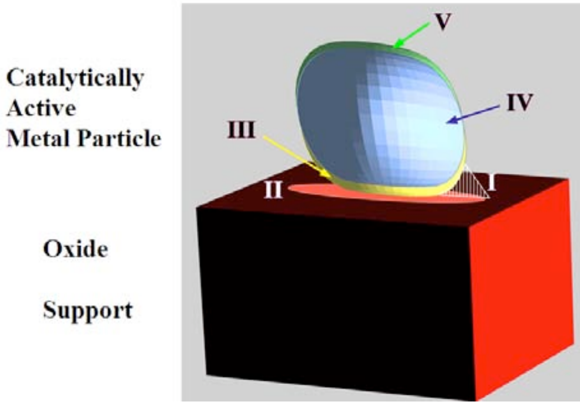


Molecular Switches ?
Nanowire Transistor ?

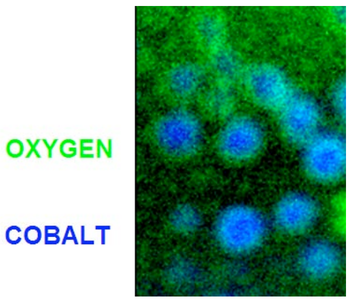
Key Technical Challenges:

- Near atomic-resolution characterization in materials other than single crystals
- Robust sample preparation methods for ultra-thin cross sections (50 nm and below)
- 3D imaging with near-atomic-resolution in incident beam direction
- Quantifiable diffraction techniques for sub-0.5-nm lateral spatial resolution

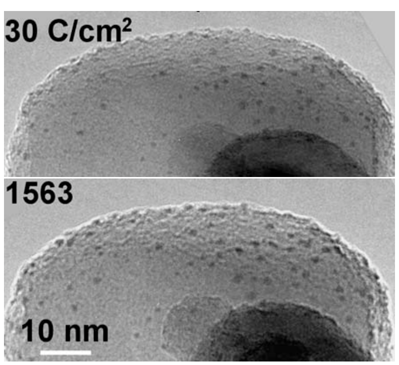
Grand Challenge: Chemistry and Structure of Active Sites for Catalysis



Light element EELS imaging: chemical state of "Support"



Beam effects present critical challenge for step-out in site+reactant info



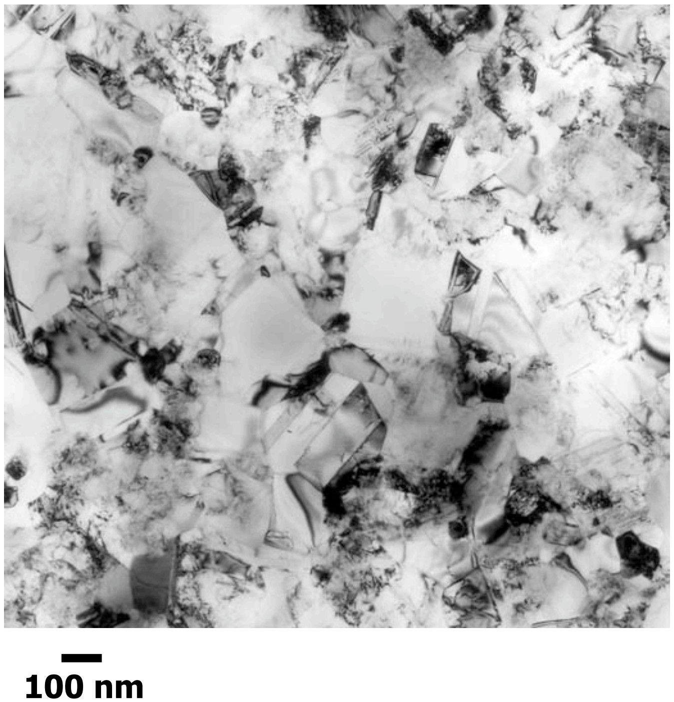
Key Scientific Questions:

- Detection and analysis of active sites and reactants
- 3D particle shapes under / near reaction conditions
- Surface structures in presence of reactants
  - # of surface sites of particular type
- Dynamics (structure and chemistry) of metal-support interactions
  - Effects of key actors (e.g. Sulfur)

Key Technical Challenges:

- Dynamic EELS experiments located by enhanced low atomic # contrast STEM or EELS imaging
  - Oxygen and carbon imaging challenge
  - Methods for 'imaging', 'detecting' and 'tracking' active species and deactivation products
  - In-situ probes and sample preparation critical

Grand Challenge: Relating Nano/Micro Structure and Chemistry to Macro in Complex Eng. Materials



Microstructure of a Ni-base superalloy (TEM).

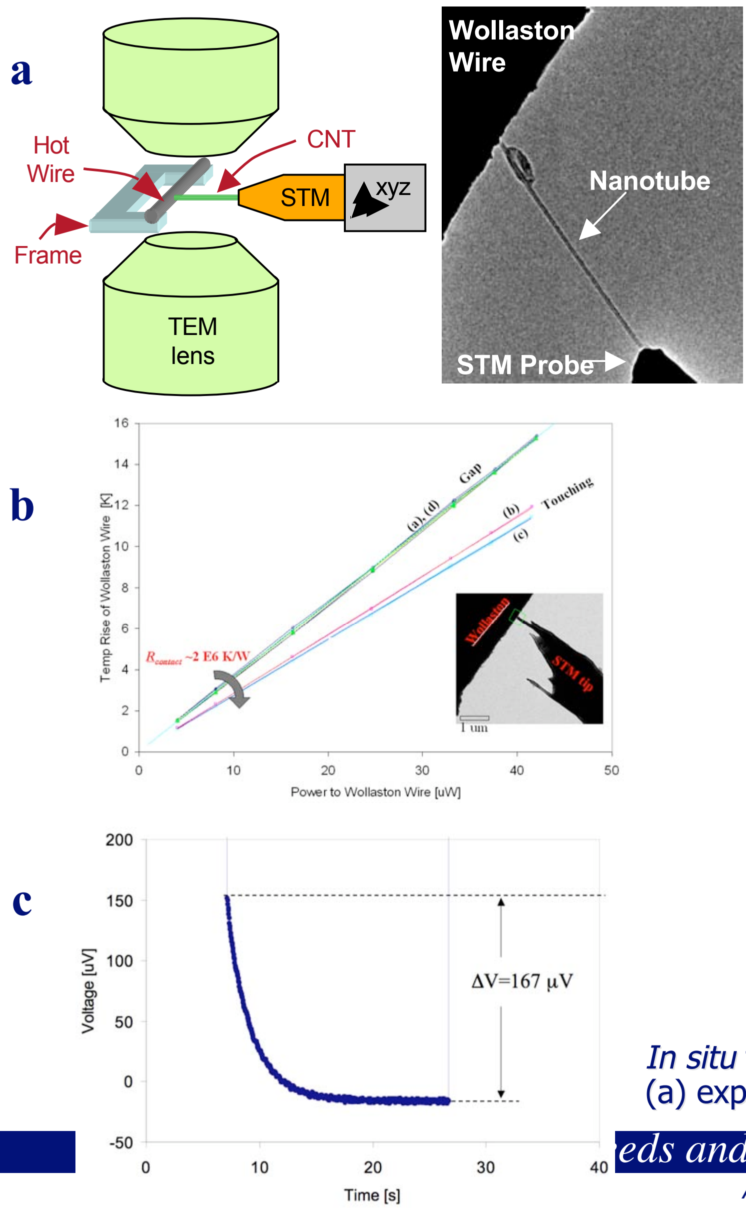
Key Scientific Questions:

- Need high-efficiency methods for collecting structure and chemistry data at atomic, nano, and micro scales with sufficient statistical rigor and over large area(s) to unambiguously relate to macro processing and properties.
- Can we extend capabilities to include dislocation structure, residual stress, other microstructural defects?

Key Technical Challenges:

- Combine high-current FE electron probe with novel detectors for all signals: emitted and scattered electrons (including Auger, photoelectrons) with single electron sensitivity and energy spectrometry; x-rays; light.
- FIB-type capabilities for site-selection, 3D analysis, thin section preparation
- Appropriate user interface for fast analysis, data combination and rendering, information extraction.

Energy Conversion and Transport at the Nanoscale



Key Scientific Questions:

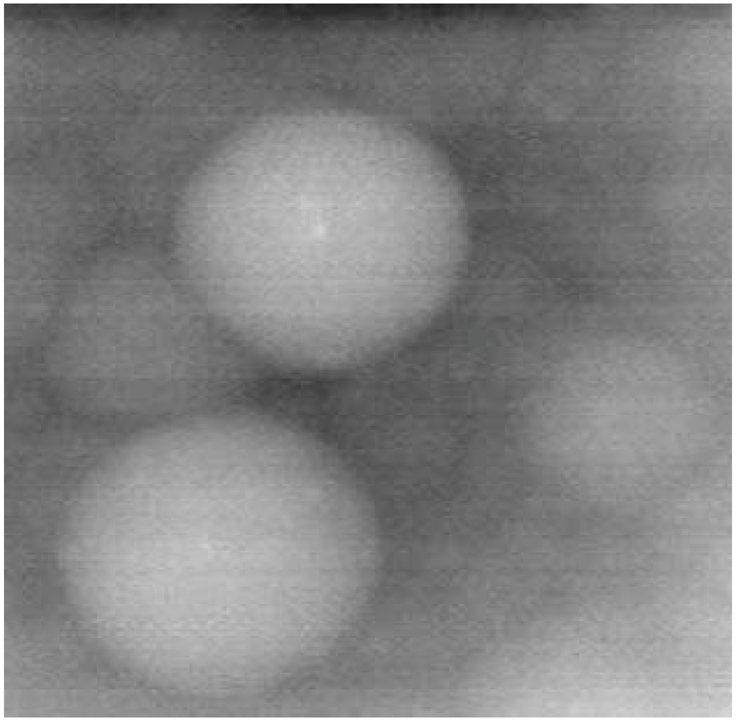
- Direct observation of elementary processes of energy conversion:
  - Charge transport / transfer
  - Molecular rearrangement
  - Chemical reactions
- Direct measurement of fundamental coefficients of nanoscale structures

Key Technical Challenges:

- Spatially and temporally resolved characterization of structure, composition, and spin state
- *In situ* imaging and analysis in real synthesis and operating environments
  - Relevant temperatures
  - Reactive gas or liquid environments

In situ thermal / thermoelectric studies of nanotubes and nanowires (Jianyu Huang): (a) experimental setup; (b) thermal resistance measurement; (c) Seebeck coefficient.

Grand Challenge: Atomic Imaging of Physiologically Viable Biological and Nano-Bio Materials



STEM-HAADF at 200 keV of <100nm gold spheres imaged in 8μm of water

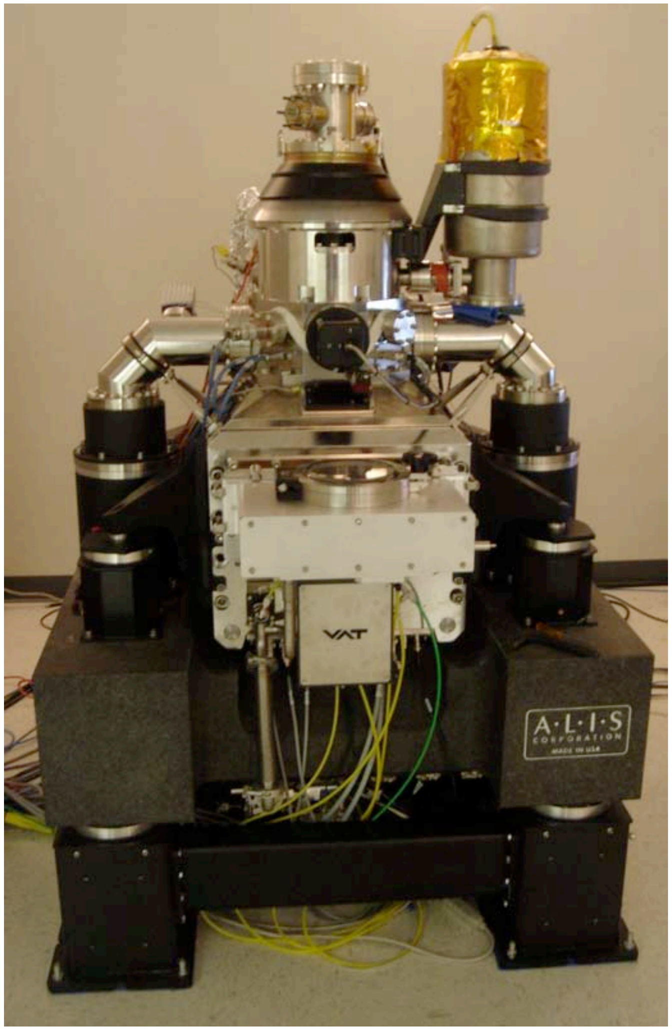
Key Scientific Questions:

- Can proteins, cells, viruses, nano-bio composites etc. be imaged at the atomic level while maintaining their natural state and their physiological viability?
- Is water the best environment or are there better options?

Key Technical Challenges:

- Designing and building liquid (and gaseous) environmental cells capable of atomic level resolution
- Reducing the effects of radiolysis damage
- Minimizing, and correcting for, the effects of electron scatter in the liquid (or gas) environment

The Sensible Alternative to Electrons - Ion Beams for Imaging and Analysis



ALIS ORION He^{+} ion SIM

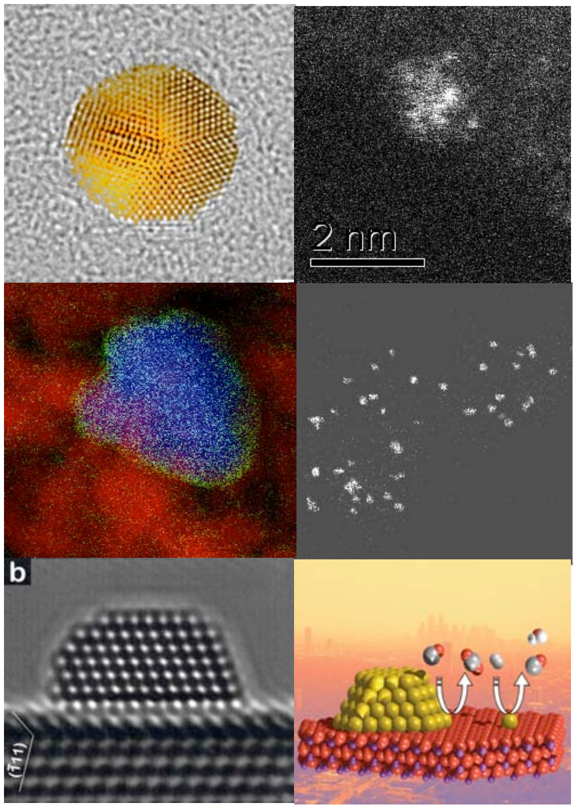
Key Scientific Questions:

- Can the enhanced strength of interactions, the reduced penetration, and the short wavelength of ion beams be exploited to achieve image details at the sub-atomic level?
- Can low energy ion scattering spectrometry be combined with this new imaging capability to perform 'top atomic layer' microanalysis with near angstrom lateral resolution?

Key Technical Challenges:

- Developing high brightness, mono-energetic, noble gas ion sources
- Improving ion optics to a level comparable with the best electron systems
- Developing and implementing microanalytical methods for use with ion beams
- Limiting sample damage resulting from ion implantation and ablation

Grand Challenge: Characterization of Supported Metal Catalyst Systems



(*Top left*) HREM of multiply twinned Au NP; (*Top right*) HAADF of Ru_5PtSn clusters; (*Middle left*) XEDS analysis of Pd surface segregation in AuPd bimetallic; (*Middle right*) STEM-XEDS map showing Au catalyst distribution; (*Bottom left*) Rhodius simulation of Rh/CeO_2; (*Bottom right*) CO oxidation over supported Au species.

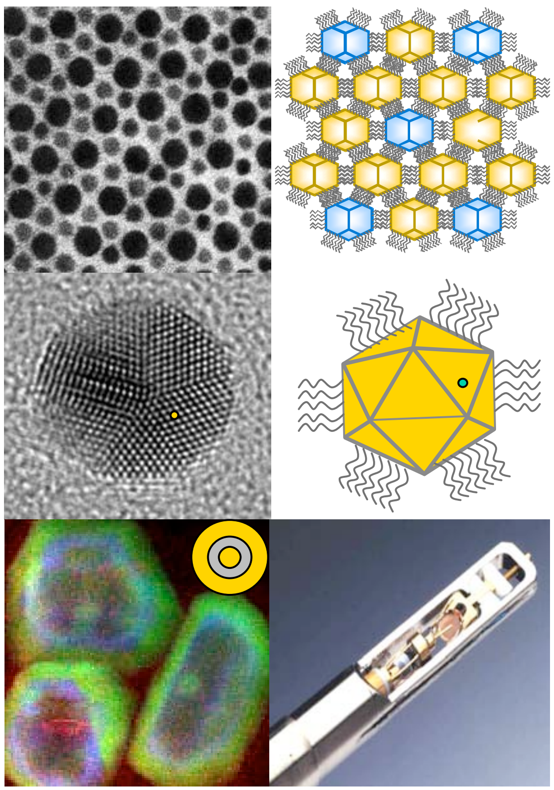
Key Scientific Questions:

- What is the valence state of metal atoms within the catalyst particle directly adjacent to the oxide support?
- What is the precise elemental distribution within a bi- or tri-metallic catalyst nanoparticle?
- Do any components of the support ingress into/onto the metal catalyst particle or is the metal surface oxidized?
- What is the state (*i.e.* dispersion, morphology, valence state) of the supported particles under catalytically *relevant* redox cycles?
- In multi-component metallic (*e.g.* Ru_5PtSn) clusters which atom type preferentially anchors to the oxide support?

Key Technical Challenges:

- Noise reduction methods and quantification protocols in XEDS/EELS spectrum images from facetted ultra-small bi- or tri-metallic particles.
- Single atom sensitivity and atomically resolved depth information in HAADF/EELS/XEDS datasets.
- Overcoming serious beam damage limitations in catalysts.
- Development of usable *in-situ* and *ex-situ* reaction cell systems for high-end aberration corrected instruments.

Grand Challenge: Characterization of Complex Nanoparticles and Self-Assembled Metamaterials



Self-assembled ordered metamaterials (top)

Can we identify the number and location of dopant atoms in a single nanoparticle? (middle)

Concentric shell nanoparticles (bottom left)

Integrated transport-TEM stage (bottom right)

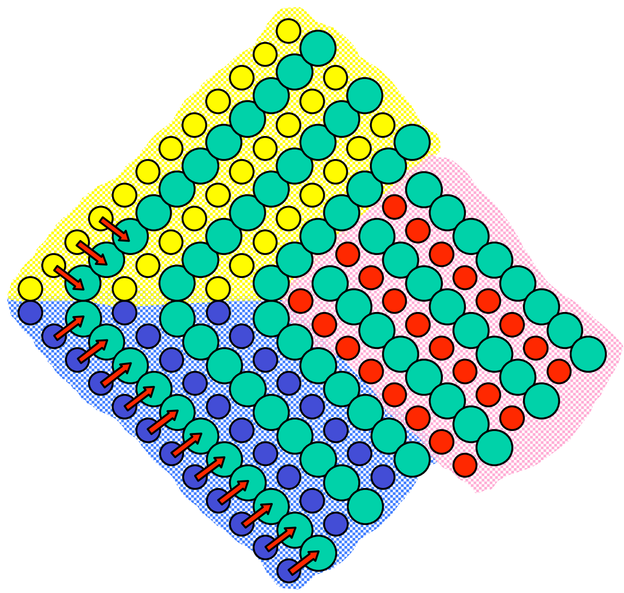
Key Scientific Questions:

- How do we characterize the soft (ligand) component of a metamaterial?
- How do we study the structure of multi-component metamaterials which are thicker than a few monolayers?
- How do we measure the electrical, thermal and magnetic properties of metamaterials with sub-μm^2 areas?
- How do we quantify compositional variations in concentric multi-shell (*i.e.* A@B@A@B) nanoparticles?
- Can we identify the number and precise location of dopant or impurity atoms in an individual nanoparticle?

Key Technical Challenges:

- The development of specialized TEM stages with in-built probes for physical property measurement.
- Overcoming beam damage limitations and developing methods for characterizing the ligands in metamaterials.
- Noise reduction methods and quantification protocols in XEDS/EELS spectrum images from ultra-small particles.
- Single atom sensitivity and atomically resolved depth information in HAADF/EELS/XEDS datasets.

Grand Challenge: Atoms and Fields in Solids



Key Scientific Questions:

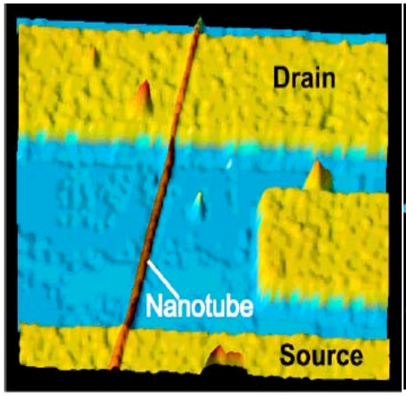
- Which atoms are where?
- Which are the bonds?
- Which are the fields?
    - o Electric
    - o Magnetic
    - o Mechanic
- Quantization of signals
- Find Limits: Information per electron / radiation damage
- Set up Figures of Merit: Guidelines for optimization
- 3D-analysis (tomography)
- Modeling by ab-initio calculations
- Interpretation in terms of structure-properties relation

Key Technical Challenges:

- Resolution
    - o Lateral Resolution
    - o Signal Resolution
- Signal / Noise limits
    - o Brightness of gun
    - o Stability for extended exposure time
    - o Detectors
- In-situ methods
- Preparation of specimen
    - o thickness, orientation
    - o surface structure
    - o dead layers
    - o artifacts

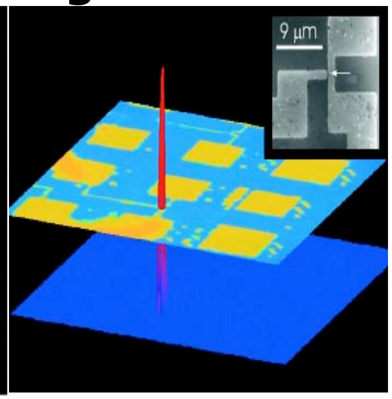
Grand Challenge: Emergence of Carbon Nanotube Based Device Structures

Transistor



S. J. Tans et.al,Nature **393**, 49 (1998); R. Martel et.al, Appl. Phys. Lett. **73**, 2447 (1998).

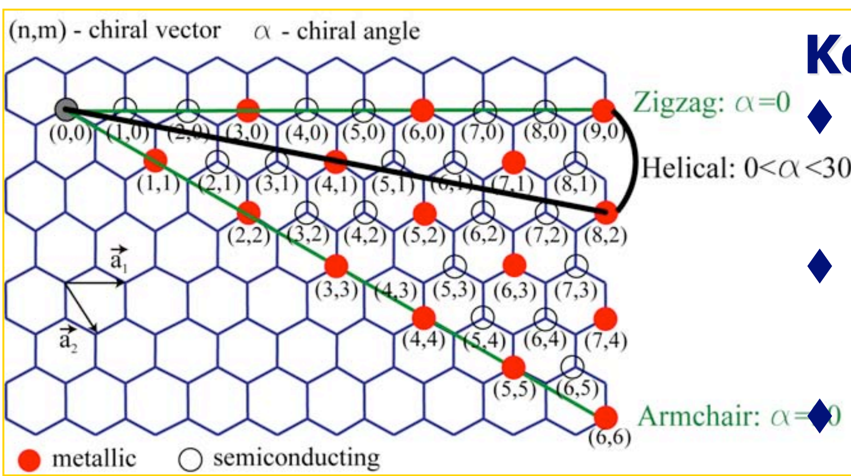
Light Emission



J. A. Misewich et. al, Science **300**, 783 (2003).

Key Scientific Questions:

- Harnessing quasi-1D properties of nanotubes
  - Ballistic transport of charge carriers
  - Confinement effects
- Understanding physical property diversity of synthesized nanotubes
  - Structure and semiconducting / metallic nature
  - Single ad-atom effects
- Synthesis strategies to enable narrower distribution of structures / behavior



Key Technical Challenges:

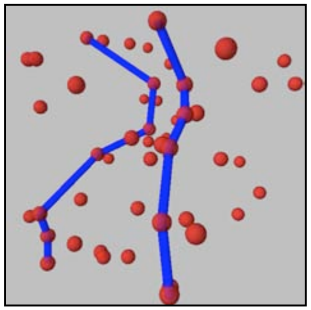
- Correlative measurement of structure, composition, and physical properties of individual nanotubes and nanotube device structures
- Rapid characterization with high sensitivity to enable statistical characterization of synthesized structures and correlation with processing conditions
- In situ characterization during nanotube / device synthesis and operation

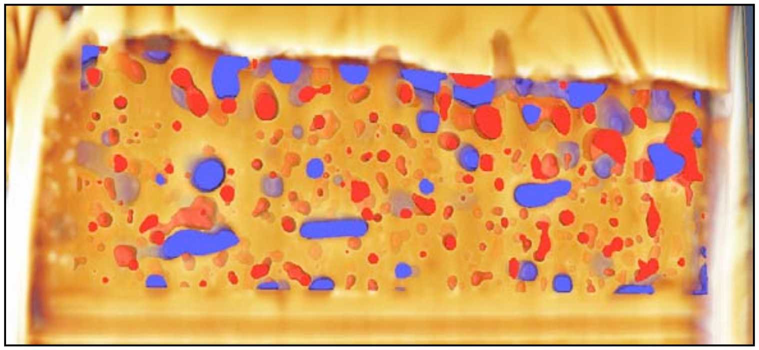
Grand Challenge: Dynamical imaging of vortex-defect interactions in superconductors

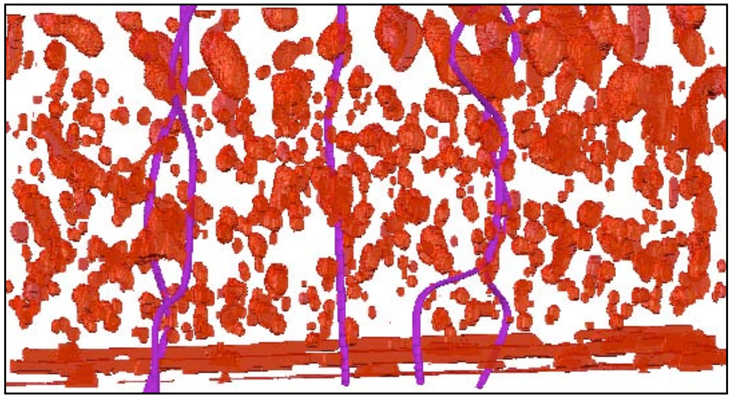
Schematic representation of vortex pinning. (top)

3-D reconstruction of pinning landscape by FIB-based tomography. (middle)

Grand challenge: Schematic representation of simultaneous vortex-defect imaging. (bottom)







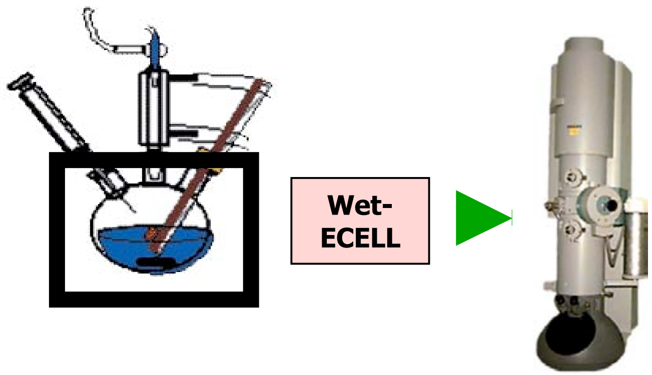
Key Scientific Questions:

- What defects are most effective at pinning vortex lines?
- How do vortices de-pin from a single defect?
- How do vortex-vortex interactions influence pinning in a given “pinning landscape.”

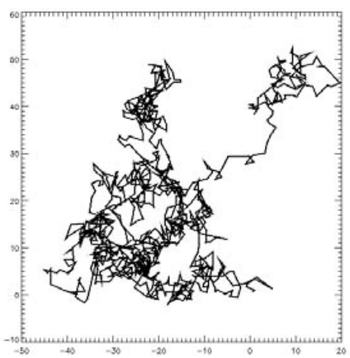
Key Technical Challenges:

- Quantification of microstructure and the “pinning landscape” in 3-D
- Simultaneous crystallographic and vortex imaging (high-resolution structure and Lorentz or holography)
- Imaging of point defects, especially in concert with vortices
- Low temperature and very high fields - uncoupled from rest of microscope
- High-resolution, 3-D, & “lateral-view” imaging of vortices

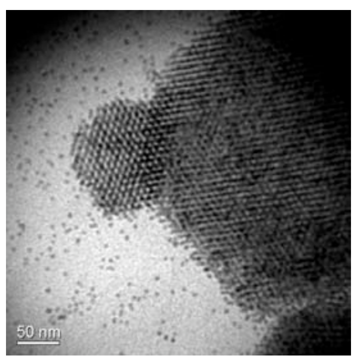
Grand Challenge: Wet Cell TEM- *In Situ* Studies in a Liquid Environment



Electron microscopy has only begun to address the processes that occur in solution



Brownian motion limits our ability to observe nanoparticle growth/interaction in solution



Self-organization of PbSe nanoparticles in wet cell (dried).

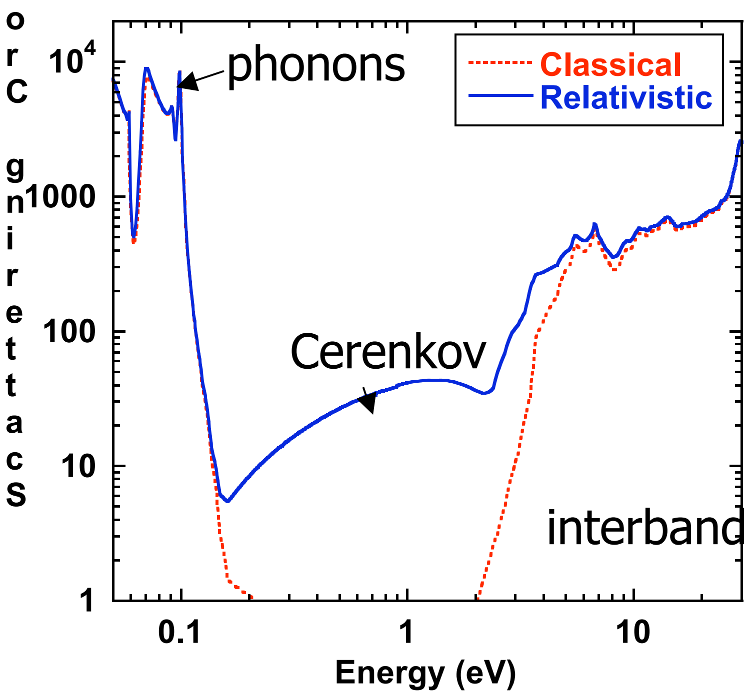
Key Scientific Questions:

- How do nanoparticles grow, interact in solution?
  - Branching of nanorods, self-organization of particles
- Mobility of ions in hydrated polymer electrolytes
  - What governs the flow of ions through channels?
- Environmental/biological interactions mostly occur in hydrated conditions
  - Materials behave differently when hydrated

Key Technical Challenges:

- Miniaturization of wet cell technology
  - Mechanical/electrical/chemical probing in solution
- Signal/noise limits imaging through wet cells
  - 100-200 nm of water full of nanoparticles is "thick"- > are higher voltages needed?
  - New imaging techniques and capabilities needed
  - C_c correction at higher voltages becomes difficult
- Brownian motion of nanoparticles in liquid
  - The mean free path of a 10 nm nanoparticle in water at room temp is ~300 nm/s, too fast to capture motion on a normal ccd/video rate camera-> better detectors?

Grand Challenge:
Imaging Phonons at the Nanoscale



EELS cross sections for phonons are much larger than for interband transitions and are not complicated by the Cerenkov and guided modes present at higher energies

Key Scientific Questions:

- Structural properties
  - Are elastic constants at an interface or crack tip different to the bulk material?
  - How are phonons confined in nanostructures?
  - Vibrational spectra from individual nanoparticles?
- Electronic Properties of strongly correlated systems
  - How does the superconducting gap vary across a grain boundary or interface?
  - Can we image spin and charge waves in bulk materials, not just at free surfaces?

Key Technical Challenges:

- Electron energy loss spectroscopy with better than
  - 10 meV resolution
  - 1-2 nm spatial resolution
  - 100 pA - 1 nA of beam current
- Low drift, low temperature stages

Grand Challenge: Detection, Identification and Quantification of Soft Nanobio Material in Tissue

Key Scientific Questions:

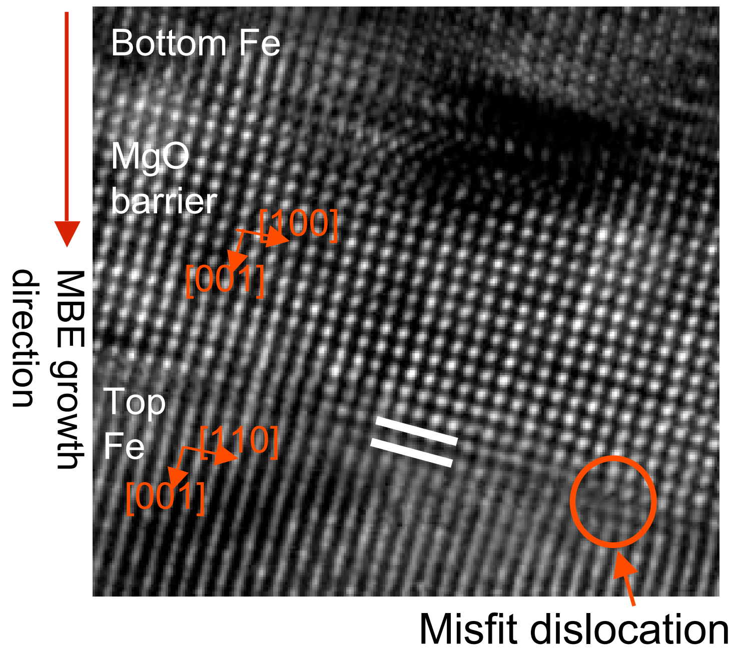
- How to detect, identify, and quantify functional components attached to nanoparticles
- Can we detect, identify and quantify 'soft' multifunctional nanoparticles (organic) loaded with drugs, targeting agents, and imaging agents in cells and tissue
- Can we obtain 3D conformational information of nanoparticles using EM to aid in the computational modeling studies on multifunctional nanomaterial

Key Technical Challenges:

- List in bullet form
  - Sub-bullets listed below

Place figure(s) above.
Figure caption in this box.

Grand Challenge: Fundamental Quantum Mechanical Behavior of Ferroic Nanostructures



MBE-grown Fe/MgO/Fe tunnel junction.
Image courtesy of Chao Wang, U Oxford.

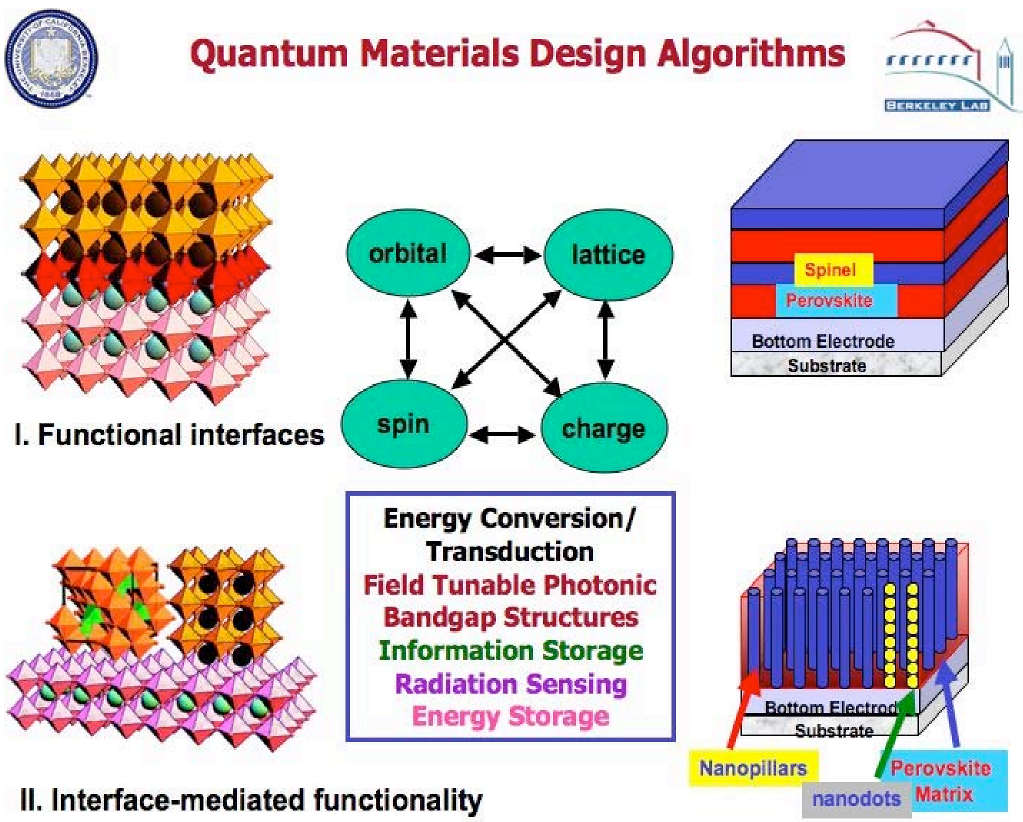
Key Scientific Questions:

- How does microstructure influence quantum confinement/proximity effects e.g. exchange biasing, tunnelling phenomena, magnetotransport, spin injection, spin torque
- What are the dynamics of magnetic/ferroelectric switching at the nanoscale: domains, vortex structure, current-induced switching, spin waves
- What is the antiferromagnetic domain structure in polycrystalline films

Key Technical Challenges:

- Temporal resolution (sub-ns to ps)
- Improved spatial resolution for magnetic imaging
  - Aberration-corrected phase imaging
- External stimuli: magnetic fields, electrical contacts, temperature

Grand Challenge: Coupling/Decoupling Phenomena



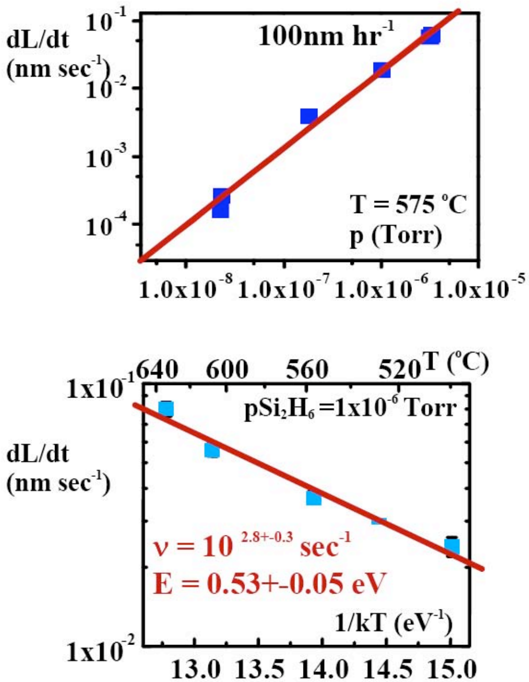
Key Scientific Questions:

- Coupling of order parameters
  - Ferroelectricity and magnetism
- Energy Conversion
  - Thermoelectrics and Photovoltaics
- Probing Dynamics
  - Lattice vs. electron vs. spin
- Order parameters at the atomic scale??

Key Technical Challenges:

- Combination of probes
  - Neutron, X-ray, Electrons,
- Thermodynamic Environments
  - Temperature, Pressure, Fields
- Making Materials and Probing
  - Crystals, Thin Films, Nanostructures

Grand Challenge: Control and Quantification of Thermodynamic Variables for *In Situ* TEM Studies



Pressure and temperature dependence of Si nanowire growth rate measured in situ on individual wires

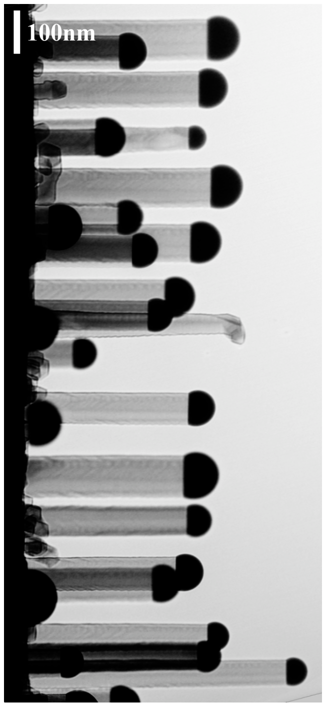
Key Scientific Questions:

- Can we construct generalized phase diagrams for nanoscale structures as a function of T, P, $\{p_i\}$, **E**, **H**, [[_ij]], etc. ?
- Can we use *in situ* characterization of individual structures to quantitatively measure thermodynamic parameters and effects?
  - E.g., activation energies, size effects
- Measurement of growth kinetics and behavior of nanoscale structures during perturbation / activation
  - E.g., optical excitation, electrochemical biasing
  - How does a nanostructure respond to a single spin or charge?

Key Technical Challenges:

- Sufficient homogeneity, control, and measurement of external thermodynamic variables and stimuli
- Interfacing of in situ diagnostics
  - Mass spectrometers, pressure gauges, thickness monitors, MEMS-based sensors, etc.

Grand Challenge: Integration of In Situ TEM Studies with Advanced Imaging Techniques



Nanowires grown in situ… the 3d shape and the composition of the catalyst and wire have not been determined during growth.

Key Scientific Questions:

- For in-situ experiments, there is very little utilization of advanced techniques such as elemental mapping, tomography, holography, etc.
- There is also relatively little combination of techniques (heating/straining is one of the few)
- Opportunities include:
  - Dynamic observation of mass transport
  - Correlation of nanostructure behavior with applied fields
  - Correlation of nanostructure structure and composition with induced fields

Key Technical Challenges:

- Interfacing analytical techniques and high tilt holders with in situ experiments
- Efficient collection of weak signals during time-resolved experiments
  - Even dark field imaging is a challenge

Magnetism/Spin Imaging at High-Resolution

Key Scientific Questions:

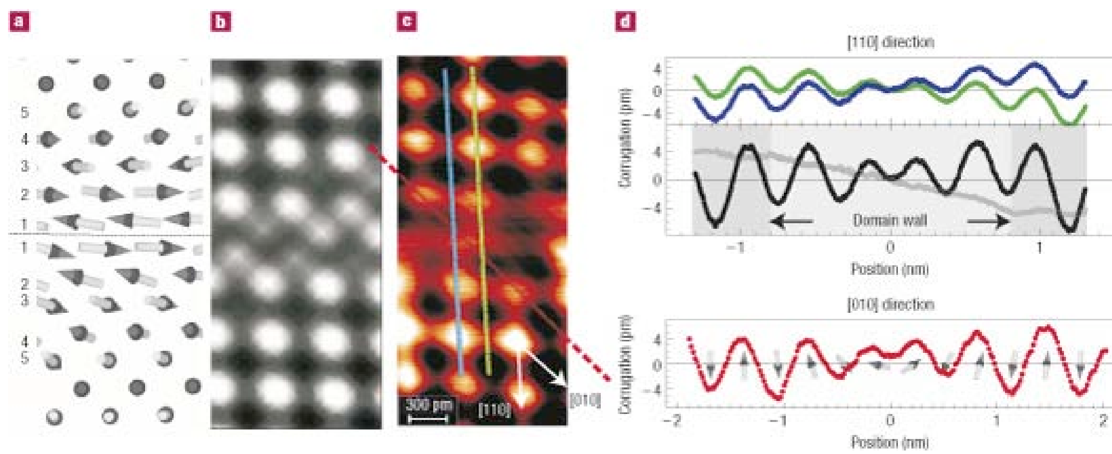
- Magnetic microstructure is governed by exchange interaction. Length scale of this force is of the order of **1 nanometer**. Up to now, magnetism has never been imaged on this length scale by electron scattering methods.
  - resolve spin-structure inside domain-walls?
  - antiphase defects in antiferromagnets?
  - **atomic-resolution spin detection?**

Key Technical Challenges:

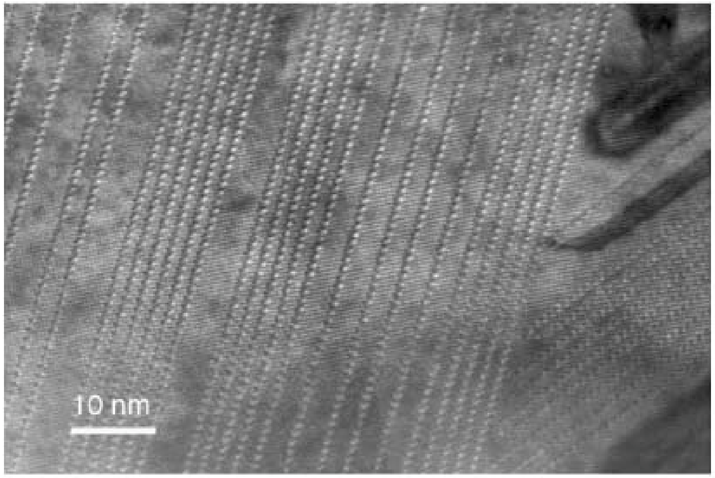
- Implement and optimize aberration-correction on
  - spin-polarized low-energy electron microscope
  - photoemission microscope
  - Lorentz-TEM, holography?
- Why do we not install a spin-polarized electron source on a high-resolution TEM? Can we hope to find interesting contrast mechanisms if we try this?

At surfaces, atomic-resolution imaging of spin is reality [M. Bode et al., Nature Mat. 5, 477 (2006)].

Can we achieve high-resolution magnetic imaging of bulk material?



Grand Challenge: Characterisation and Design of Materials for Gen III+ & IV Reactor Applications



TEM image of reduced rutile (Magneli phase) in a ceramic waste form.

Extended planar defects may facilitate elemental transport during crystallisation and cooling once the buffering capacity of the oxygen is exceeded. In this case, re-oxidation of Ti^{3+} to Ti^{4+} is compensated by uptake of Ca^{2+} and Al^{3+}. The Ca may reside on large sites located on the planar defects.

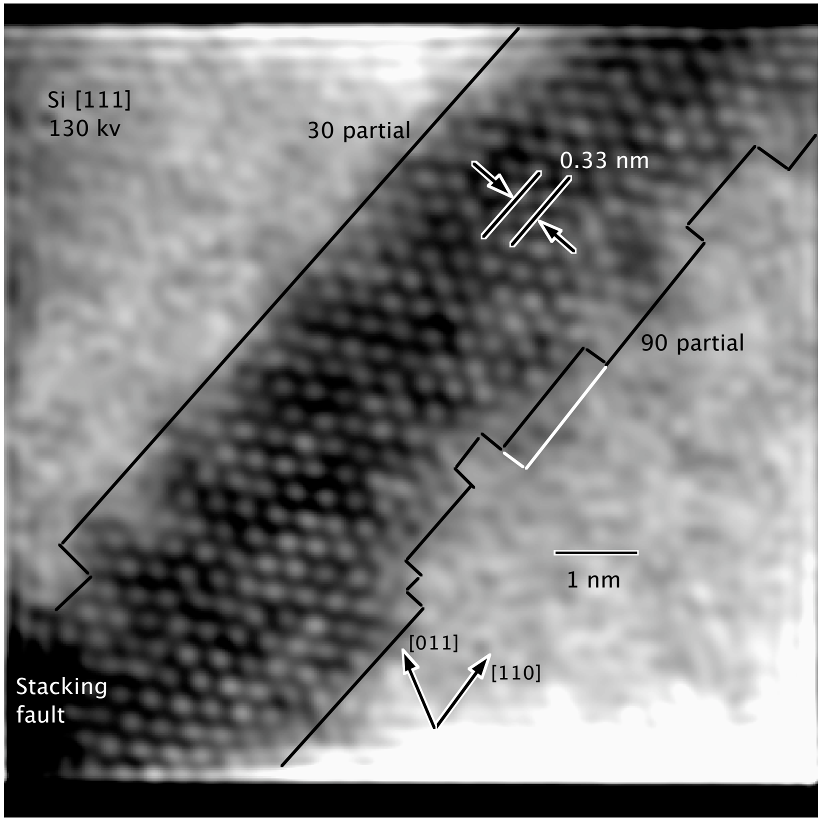
Key Scientific Challenges:

- Predicting the performance of materials in extreme environments and of nuclear waste forms during storage (sometimes for geologic time periods).
- Designing new radiation resistant materials.
  - The radiation resistance of materials is often dramatically affected by interface effects between: precipitates & matrix "nanolayers" etc.

Key Technical Challenges:

- In situ structural and chemical characterisation of materials at pressure and temperature and under irradiation.
- Cross correlation of experimental and modelling efforts especially when seeking to extrapolate from: a) thin films to the properties and performance of bulk materials and b) simulant materials to fully radioactive materials.
- Handling of radioactive materials during electron scattering characterisation and specimen prep.

Grand Challenge:
Dynamics of Deformation in Crystalline Materials



TEM image of dissociated 60° dislocation in silicon after relaxation. Bright diagonal band of regular dots are six-membered rings in the ribbon of SF separating 30° and 90° partial dislocation lines. Black lines run along cores of the two partial dislocations. Kolar, Alexander, JCHS. PRL 1996

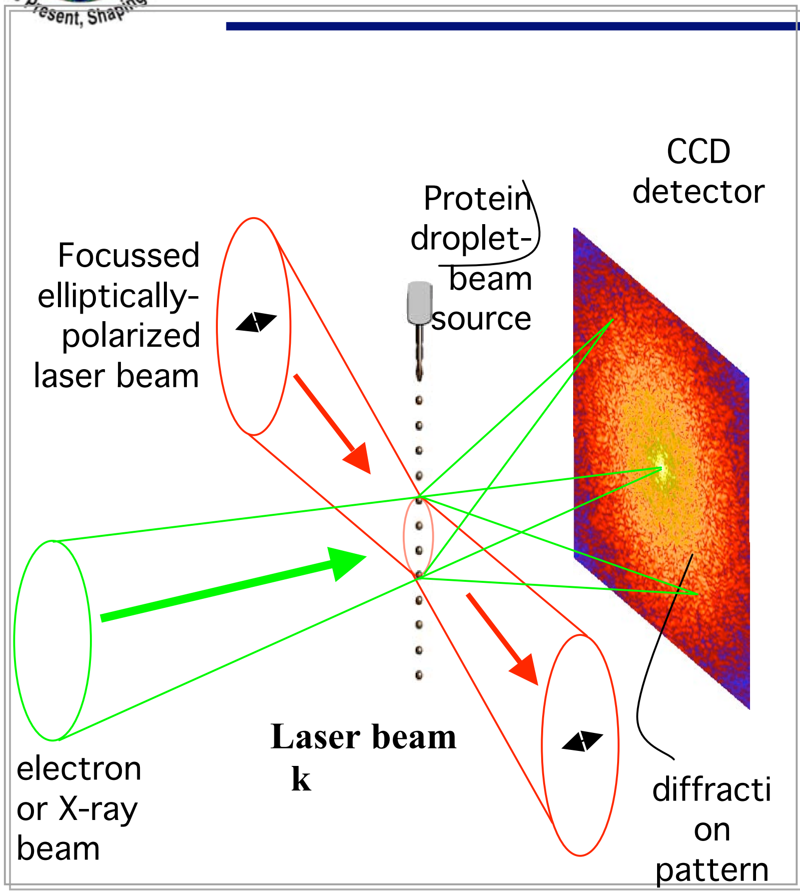
Key Scientific Questions:

- What fundamentally limits crystals strength: kink formation **or** atomic-scale obstacles to kink motion?
- Can we observe dynamics of kink formation and motion at an appropriate (_s) temporal resolution?
- Do kinks collide during deformation?

Key Technical Challenges:

- CCD camera with _s temporal resolution
  - 1k _ 1k detector
  - No blooming
  - Large dynamic range
  - Exposure and readout times in _s range

Grand Challenge: Solving the Structure of Proteins that Cannot be Crystallized



Experimental image of 4micron droplet beam

Key Scientific Questions:

- Can we form images of individual proteins via a combination of real- and reciprocal-space imaging methods?
  - 70% of drug molecules interact with a membrane protein, most of which cannot be crystallized

Key Technical Challenges:

- Robust and reliable diffractive imaging
  - Can diffractive imaging methods be developed to the point where routine automated analysis can be performed?
- Cryo-EM at 0.3 nm resolution
  - Can cryo-EM be developed to the point where individual amino acids can be resolved?

Grand Challenge: Automated Nanocrystallography at Atomic Resolution

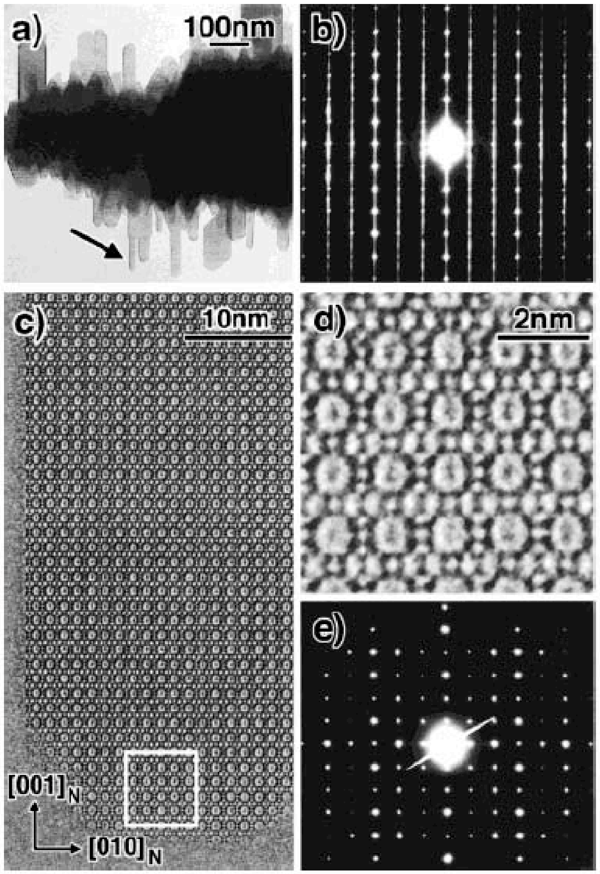


Figure 1. (a) Low-magnification TEM image, (b) electron diffraction pattern (showing very strong diffuse line corresponding to the coexistence of polytypes A and B), (c) HREM image of the overgrown crystal along $[100]_N$, (d) an enlarged image of a part of (c), and (e) ED pattern of the overgrown crystal.

Terasaki et al solve Zeolites by combining HREM with diffraction. Automate this in 3D ?

Key Scientific Questions:

- Can we solve nanocrystal structures by diffraction at the microscope?
  - Coordinates and elemental identities of all atoms comprising a structure
  - Charge density map showing spatial distribution of valence electrons

Key Technical Challenges:

- Combine imaging & 3D diffraction data.
- Understanding the Stobbs factor
  - The discrepancy between calculated and measured intensity distributions in (S)TEM images must be understood
- Fully quantitative diffraction
  - At present only CBED, surface TED, and 2D protein crystal data are quantifiable

Grand Challenge: Paying for Electron Scattering Research

This is an expensive game we play …

Thesis: not all research should be done at national user facilities …

Key Budgetary Concerns:

- Large initial investment
  - Top-tier instruments now $2M to $5M
  - "Upgrades" now possible at $1.25M per corrector
- Large yearly maintenance investment
  - Service contracts are at approx. 10% of initial cost
- Dedicated, qualified staff needed
  - PhD level staff member, and associated salary

Key Technical Challenges:

- Science budgets continue to shrink
- Few avenues to find large initial investment needed
- Hourly rates can increase individual research budgets substantially, in some cases hindering success of proposals

Grand Challenge: Physical and Electronic Structure of Nanomaterials Susceptible to Radiation Damage

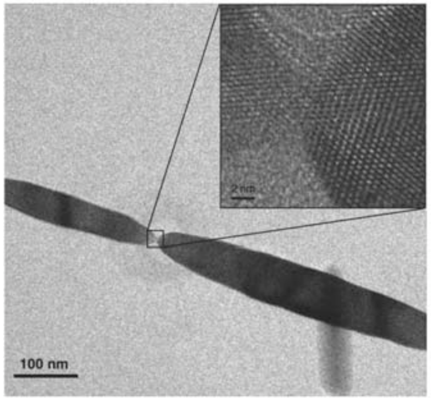
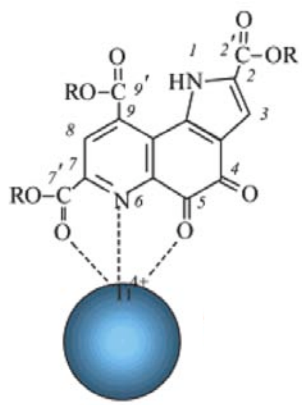


Figure 3. TEM image of anisotropic TiO_2 nanoparticles functionalized with biotin and coupled together through avidin. The inset shows a high-resolution image of the coupled nanorods with enhanced contrast seen in the region between the two tips.

Functionalized TiO_2 nanorods,
from B. Rabatic et al., *Adv. Mater.* **18**, 1033 (2006)



Tridentate complex of $Ti(IV)_{surface}$ on a TiO_2 nanoparticle, with pyrroloquinoline quinone, from N.M. Dimitrijevic et al., J. Phys. Chem. B **100**, 25392 (2006)

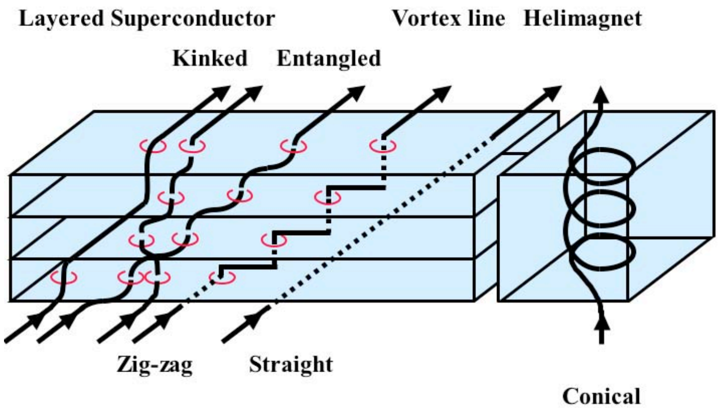
Key Scientific Questions:

- Statics and dynamics of field distributions (electric, magnetic)
- Atomic resolution physical, chemical and electronic structure at hybrid materials interfaces
  - Soft-hard interfaces
  - Interactions of linkers and biomolecules with nanoparticles

Key Technical Challenges:

- Reducing/eliminating damage at all steps: during specimen preparation, imaging and analysis
  - Lower accelerating voltage while still maintaining resolution
- Increased analytical sensitivity
- Achieving smaller probes, without tails, with acceptable beam current
- Space for sample environments & for sample rotation to multiple orientations
- Better contrast for low-Z materials

Grand Challenge:
3D Arrangement of Superconducting Vortices



Observation of 3D Arrangement of Superconducting Vortices

Key Scientific Questions:

- What is the 3D arrangement of magnetic lines of force in superconductors?
  - Flux pinning greatly depends upon the arrangement of vortices

Key Technical Challenges:

- Improvement in resolution, approaching the wavelength limit
- Fast sensitive detectors for gathering electron information about specimens with no electron loss
- Tilting specimen stage on which a specimen can be observed from all angles with sub-Å resolution
- Bright, monochromatic, polarized electron source, which allows interferometric, spectroscopic, and dynamic observations

Grand Challenge:
The Time-Frequency Domain

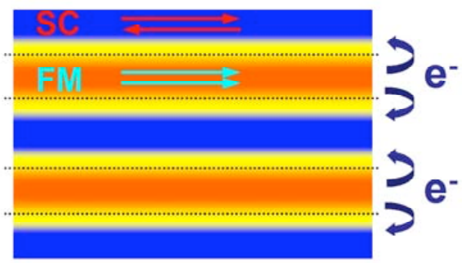
Key Scientific Questions:

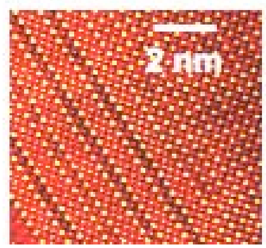
- Develop in-situ microscopy for nanosynthesis, and observation of material response at the nanoscale
  - Watch materials grow at the atomic level
  - Observe the flow of entropy, and its fluctuations, at the nanoscale! (Non-equilibrium thermophysics)

Key Technical Challenges:

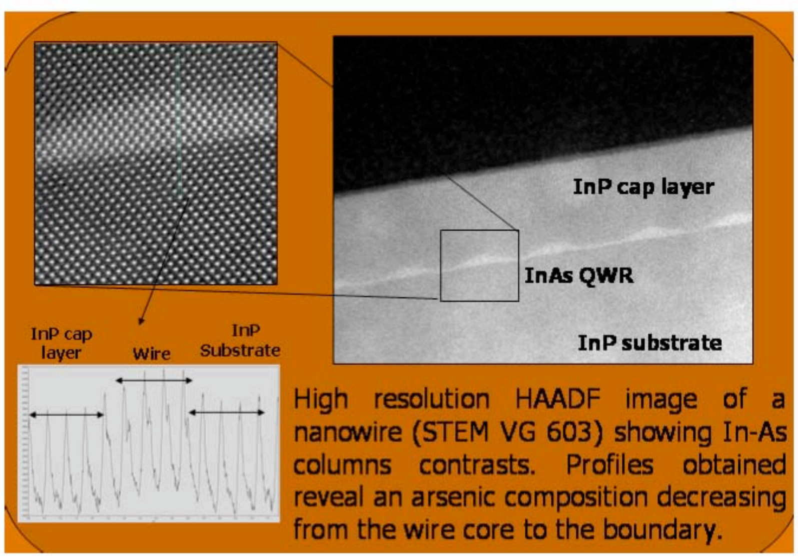
- Need to build fast detectors
  - Time sequences for many atomic processes need fast detectors
- Need to build fast, high-intensity, sources
  - One-shot fast pulses can use slow detectors
- Need to build convenient, "electron transparent", reaction chambers
- Construct an FIB-in-a-microscope, complete with probe station

Grand Challenge:
Towards Functional Low Dimensional Materials





• Ferromagnetic/superconducting interfaces



High resolution HAADF image of a nanowire (STEM VG 603) showing In-As columns contrasts. Profiles obtained reveal an arsenic composition decreasing from the wire core to the boundary.

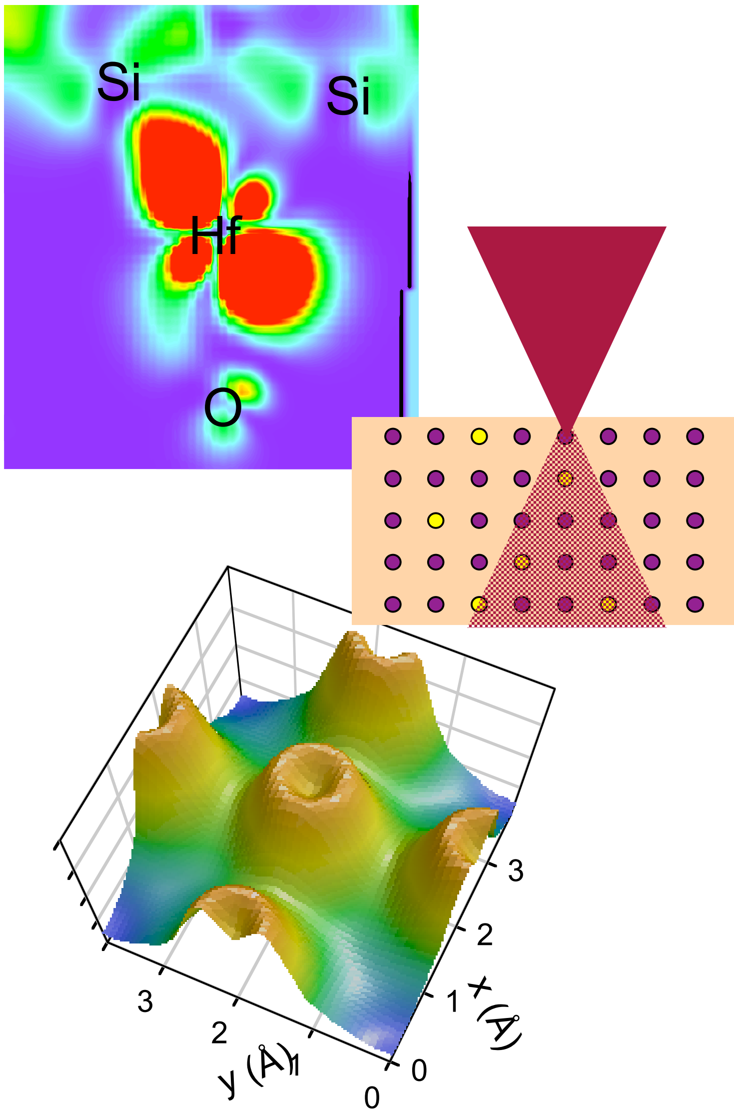
Key Scientific Questions:

- Low D semiconductor nanostructures
- Wide bandgap semiconductors
- Fuel cells/ membranes
- Energy conversion and electronics: Interplay of different phenomena
  - Magnetism
  - Superconductivity
  - Ferroelectricity, etc
- Engineering of epitaxial strain
- Phase separation
- Self organized growth

Key Technical Challenges:

- Specimen preparation
- Beam damage
- Interpretation: new theory

Grand Challenge:
Spectroscopy with Sub-Ångström Beams



Key Scientific Questions:

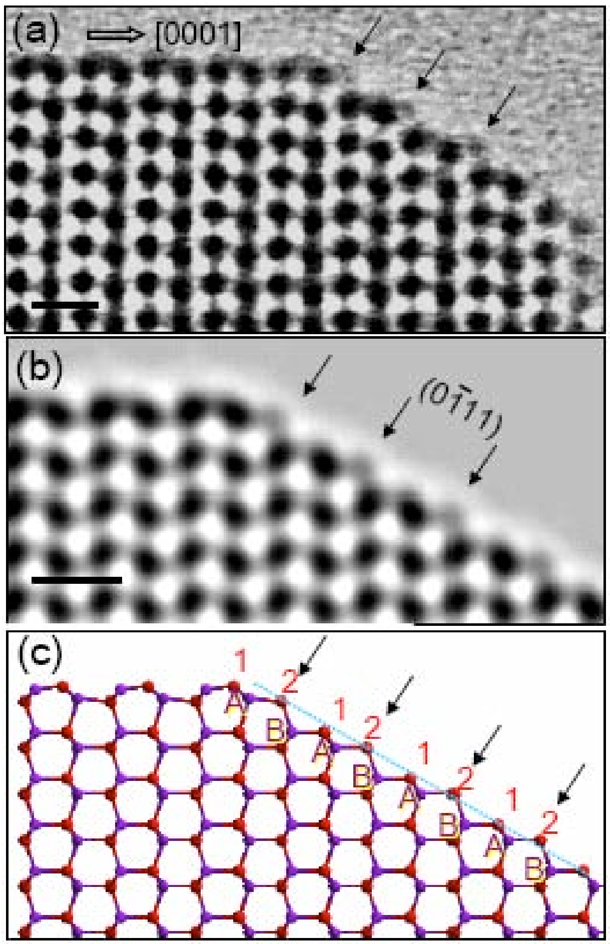
- 3D mapping of wave functions inside materials
  - Low D systems: quantum dots, interfaces, wires…
  - Mapping orbitals?
  - Properties of point defects,
  - Nanophase materials…

Key Technical Challenges:

- **Stability:** new instrumentation
- **Interpretation:** new theory

Grand Challenge: Surface Atomic Structures of Nanoparticles and Nanowires

HRTEM images of (01-11) surfaces of ZnO nanocrystals



Y. Ding and Z.L. Wang, Surface Science, 601 (2007) 425–433

Key Scientific Questions:

- How do the surface atoms reconstruct?
- How to precisely determine the positions and electronic structure of surface atoms?
- How to determine surface vacancies/defects?
- How to imaging doping element?

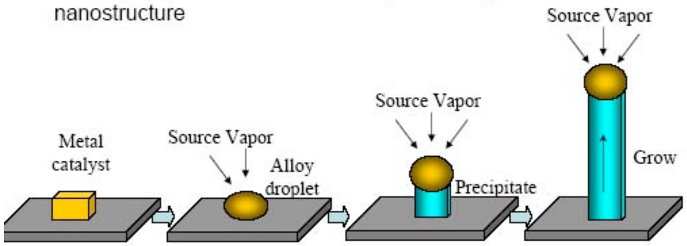
Key Technical Challenges:

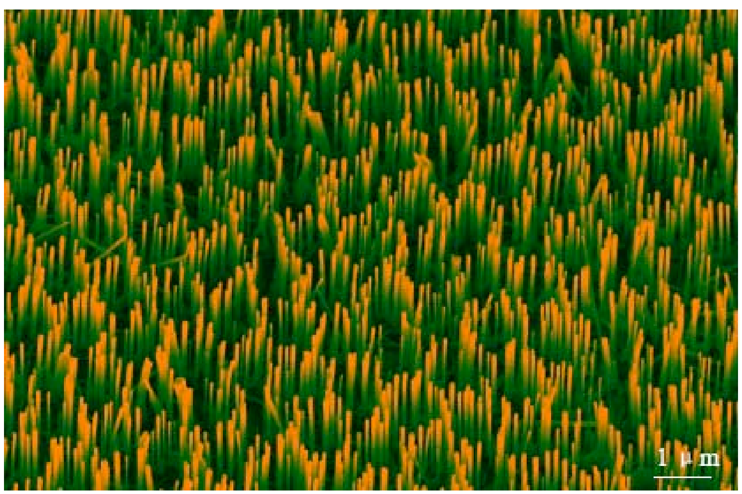
- Quantifying 3D surface atom positions at the absence of diffraction data
- Quantifying EELS data for surface atoms
- Understanding interaction of surface atoms with adsorbed molecules

Grand Challenge: In-situ Nucleation and Growth of Nanostructures: Thermodynamics vs Kinetics

Growth Mechanism
—Vapor-Liquid-Solid (VLS) Process

1. Source material sublimates forming a ***vapor*** phase
2. Upon the coming of source vapor, catalyst melts forming a ***liquid*** alloy droplet
3. The droplet saturates when source vapor keeps coming
4. Solute precipitates out from the droplet forming a ***solid*** 1D nanostructure





Wang et al., Nano Letters, 3 (2004) 423-426.

Key Scientific Questions:

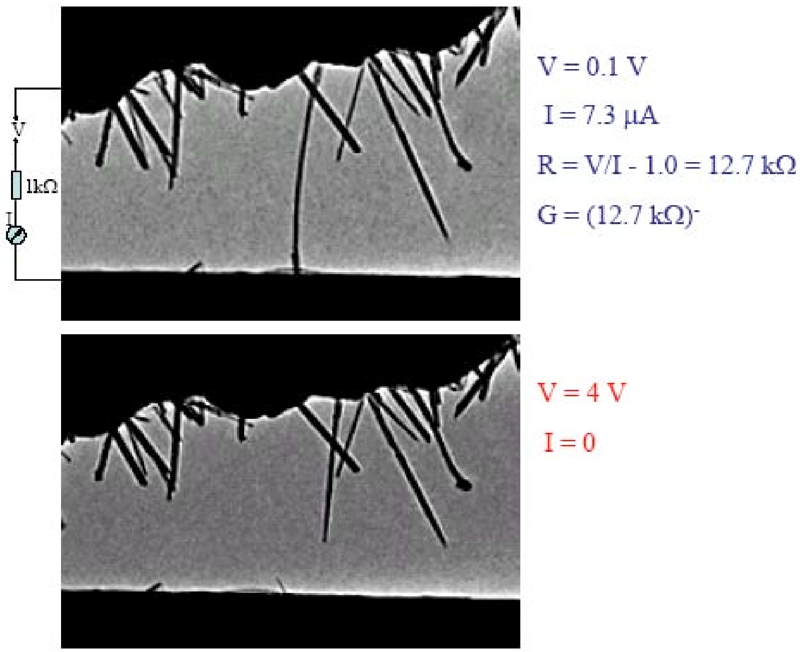
- What determines the chirality of carbon nanotubes?
- What is the mechanism for the nucleation and growth of nanowires?
- What was the role of catalyst in the initial nucleation?

Key Technical Challenges:

- In-situ observation of nanomaterials growth at atomic resolution in E-TEM
- In-situ high-spatial resolution chemical analysis/imaging of the growth species at the early stage
- Fast chemical mapping of both light and heavy elements

Grand Challenge: In-situ Nanomeasurements and Optical Spectroscopy

In-situ observation of quantized conductance of nanotube



Poncharal, J. Phys. Chem., 106 (2002) 12104-12118

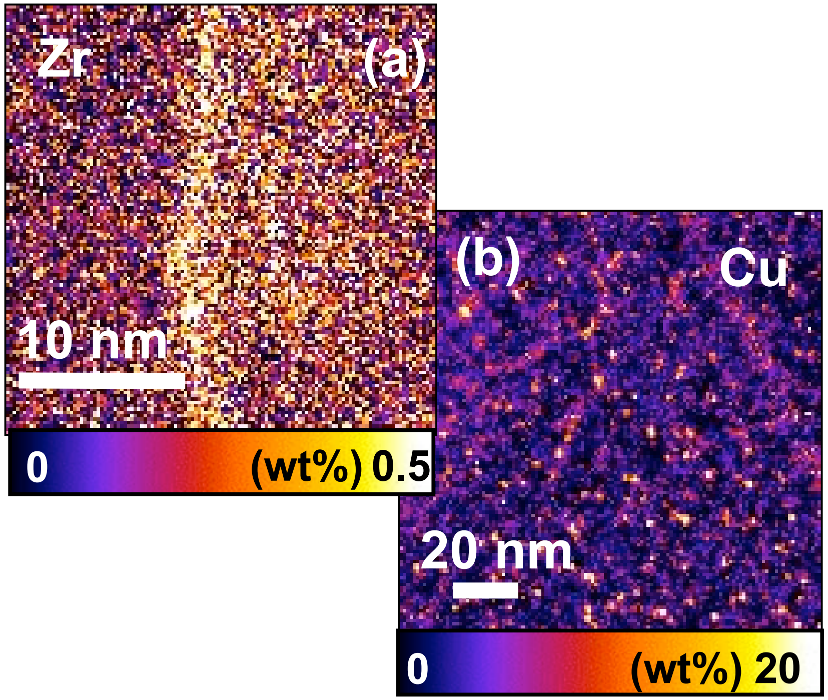
Key Scientific Questions:

- What is the relationship between structure and property (mechanical, electrical, optical)?
- What is the chemical bonding information at nm spatial resolution?
- What is the structure at organic/inorganic interface?

Key Technical Challenges:

- Integration of TEM with AFM/STM
- Integration of TEM with Raman and ultrafast laser spectroscopy
- Precision of the measurements
- Quantum effect?

Grand Challenge: Combined Compositional and Diffraction Imaging in 3D TEM at the Atomic Level



All compositional and any associated structural TEM information, while localized at the sub-nanometer level in 2D is averaged through the specimen thickness in the third dimension. So detection of Zr changes within the plane of the GB in this superalloy specimen (a) is not feasible. Likewise variations in Cu content associated with precipitation on dislocations in this low-alloy steel (b) cannot be discerned as a function of depth or nature of the dislocation.

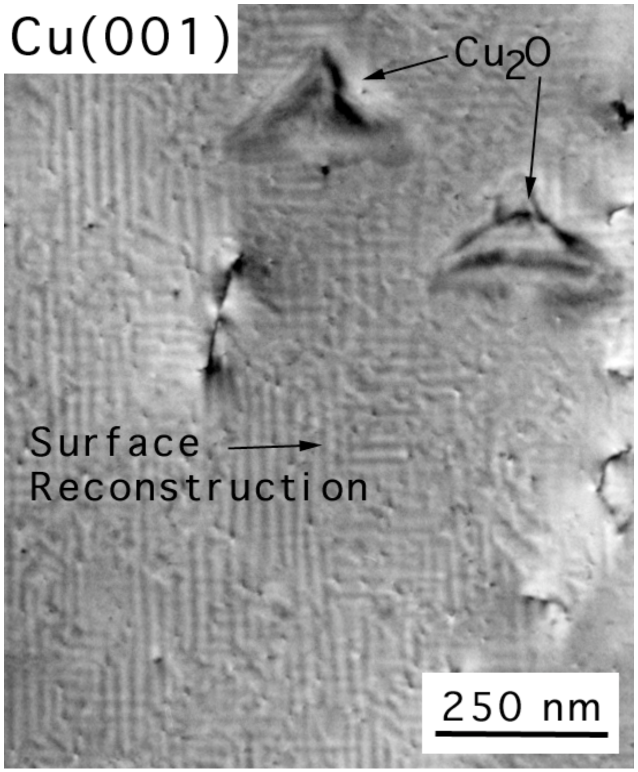
Key Scientific Questions:

- How does local chemistry change within the plane of a crystal boundary?
- How does local chemistry change along a single line defect?
- Can we detect chemistry changes at single point defects?
- Can we discern crystallography changes in the third dimension in a TEM - e.g. ledges on planar interfaces, jogs on dislocations at the same time as measuring the chemistry changes?

Key Technical Challenges:

- Reduce the depth of field of electron probes to the atomic level.
- Maintain sufficient current in the probe to generate detectable compositional signals at specific depths in the specimen.
- Increase the speed of spectrum-image acquisition by an order of magnitude.
- Detect full convergent-beam diffraction information simultaneously with all chemical information.

Grand Challenge: Atomic-scale Mechanisms of Oxidation



Epitaxial Cu_2O islands form on the Cu-O surface reconstruction of Cu(001) during *in situ* oxidation at $P(O_2)$ = 5x10-4 torr, 350°C. These results revealed that oxygen surface diffusion is the primary mechanism of initial transport, nucleation and growth of the oxide.

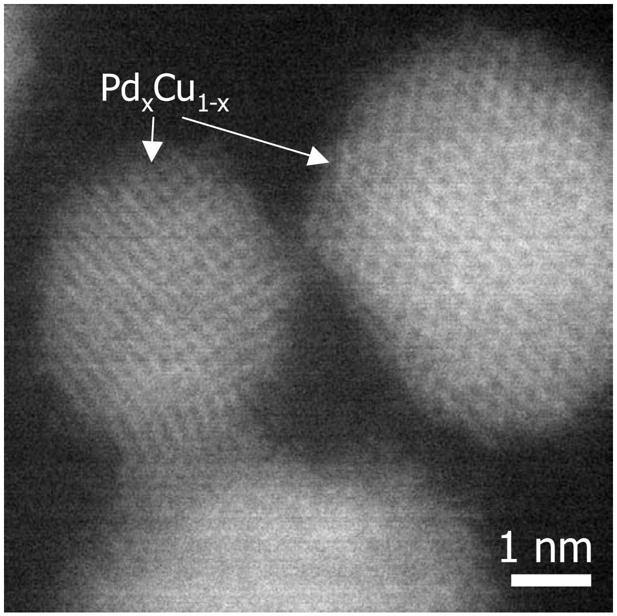
Key Scientific Questions:

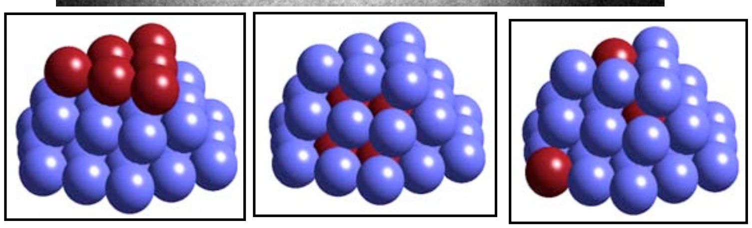
- Oxidation is important to both environmental stability and nano-oxide processing. Classical theories of oxidation assume uniform film growth since previously available experimental tools could not image the nanoscale changes during gas reactions. In situ UHV-TEM can bridge the gap between surface science studies of gas-surface reactions and bulk oxidation studies.

Key Technical Challenges:

- Ultra-high vacuum (clean surface conditions)
- Direct line-of-sight to the sample area.
  - Reactive gasses
  - In situ deposition
- Ability to attach other instruments near the specimen area. (e.g. RGA, sample prep. chamber)
- Simultaneous atomic-scale imaging and spectroscopy with time resolution.
  - Temporal gap between theory (ps) and experiments (sec).

Grand Challenge: Heterogeneous Catalysis





Z-contrast image from an aberration-corrected STEM of ~3 nm Pd-rich Pd-Cu bimetallic catalysts for the removal of nitrates and other contaminates for the purification of our drinking water. What is the distribution of Cu and Pd (surface segregation, core-shell or homogeneous distribution)?

Courtesy of M. Ghass, SuperSTEM, Daresbury, UK

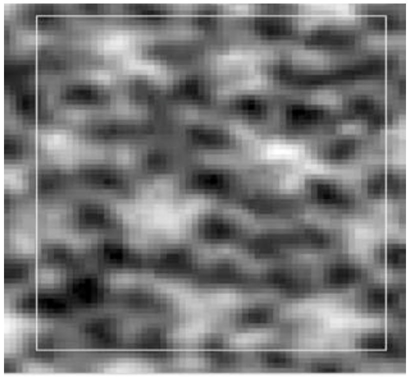
Key Scientific Questions:

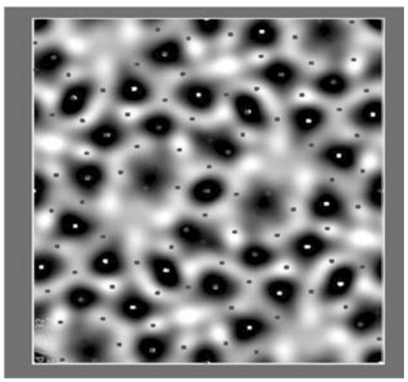
- Heterogeneous catalysis is basically surface chemistry on a supported metallic nanoparticle. Correlations between nanostructure and activity is necessary to determine the fundamental chemistry.

Key Technical Challenges:

- Controlled environments to include atmospheric pressures, wet conditions, and moderate temperatures with precise control of the gasses and/or liquid flow.
  - Reaction, fouling/poisoning, regeneration
- Atomic scale 3-D tomography
- Simultaneous atomic-scale imaging and spectroscopy in real time during reactions.
  - Detect electronic charge transfer (EELS) between the reactant gas and metal nanoparticle or support.
  - Signal-to-Noise (e.g. improved detectors)
  - Time resolution of a chemical reaction.

Grand Challenge: Partial Oxidation Reactions in Heterogeneous Catalysis





HREM Image of $Mo_1V_{0.32}Nb_{0.1}Te_{0.25}O_x$[1]
Simulated Image **of Structure**

Key Scientific Questions:

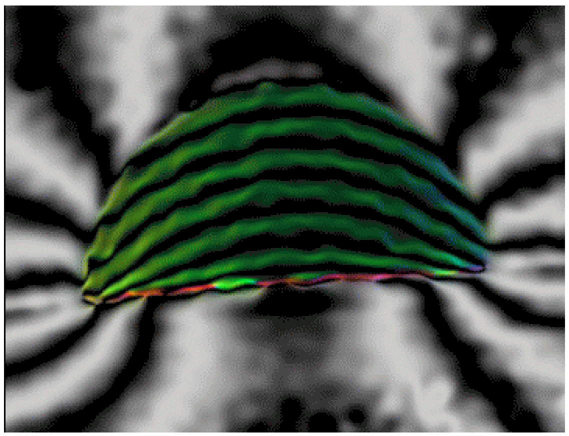
- Verify modified Mars van Krevelen mechanism, Bulk O^{2-} vs. surface dissociated O_2 diffusion
  - Observe partial oxidation of propane reaction utilizing lattice oxygen at T, P_i (i= O_2, C_3H_8) (T ~ 700 °K) ?
- How does point substitutions (W, Ti, Sb) modify oxygen interaction with propane to form propene for complex mixed metal oxides ?

Key Technical Challenges:

- Micro-environmental cell with O_2 , propane at T ~ 700 °K at > 1 Torr for aberration-corrected real time lattice imaging.
- Oxygen vacancy hopping rate ~ 80 cm^{-1} ,τ ~ nsec @ 1000 °K. Need sufficient time resolution.

1) P. DeSanto, D. J. Buttrey, R. K. Grasselli, C. Lugmair and A. F. Volpe Jr, ACS Natl. Mtg. 2002, Boston, MA

Grand Challenge: Conformal 3D Mapping of Magnetic Field Distributions



Magnetic Field lines surrounding an individual lithographically fabricated nanostructure in two dimensions.

Key Scientific Questions:

- How do the Magnetic Fields in fabricated nanostructures interact as a function of
  - size, shape, configuration (i.e. arrays, layers…)
  - What is the 3D configuration of the extended Magnetic Field in a static but externally applied fields
  - What is the 3D configuration of the extended Magnetic Field in a dynamic but externally applied fields

Key Technical Challenges:

- Measure the 3 Dimensional Magnetic Field distribution
  - for individual structures
  - for lithographic arrays (large area 10's of microns)
  - as a function of dynamic applied fields (both in and out of plane)
  - at temporal resolutions from msec->nsec
  - at fields which are greater than a few hundred gauss