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Single-Molecule Techniques for Advanced In-Situ Hybridization

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One of the most significant achievements of modern science was the completion of the human genome sequence. Despite this monumental accomplishment, researchers have only begun to understand the relationships between this three-billion-nucleotide genetic code and the regulation and control of gene and protein expression within each of the millions of different types of highly specialized cells. Several methodologies have been developed for the analysis of gene and protein expression *in situ*, yet despite these advancements, these analyses are extremely tedious and time-consuming. With this project, we are leveraging LLNL's technology and expertise to accelerate and enhance the sensitivity of gene- and protein-expression analyses. Specifically, we are employing single-target-detection techniques and instrumentation for the detection of low levels of expression. These advancements will enable precise localization of gene expression within a cell or for multiple genes or proteins simultaneously.



Synthesis, Strength and Ductility of Bulk Nanocrystalline Metals

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The structural properties of metals and alloys depend upon the size of the crystal grains of which they are comprised. Theoretical analyses suggest that if the grain size is reduced from typical values in the 1 μm - 1 cm range to those in the 10-100 nm range, significant enhancements in strength and ductility can be expected, potentially leading to many new applications for these metals. However, production of bulk nanocrystalline materials is a substantial scientific and engineering challenge, and most techniques result in imperfect materials containing significant levels of porosity or impurities. This talk describes our efforts in MSTD to develop one of the more promising methods to produce bulk nanocrystalline metals of high purity and density, that of pulsed electrodeposition. Additionally, our preliminary data on the hardness and abrasion resistance of electrodeposited nanocrystalline nickel are presented, and issues of fundamental scientific interest are identified.



Thermodynamic Properties of Molecules and Dislocation Migration Mechanisms: Insights Gained by Computer Simulations

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The ability of theory and simulations to provide valuable information about material properties is highlighted by two research projects. First, a framework is developed to predict the relative concentrations of molecules in liquid-vapor equilibria. Specifically, quantum mechanics, thermodynamic perturbation methods and molecular dynamics are used to calculate the relative solvation free energies of two molecules. When calibrated against experimental data, this method predicts key thermodynamic properties of new and complex moieties. Finally, the dependence of mechanical behavior on dislocation mobility has long been known, yet an understanding of the underlying physics is only beginning to emerge. This project focuses on the use of molecular dynamics to investigate dislocation motion mechanisms and dislocation-defect interactions at the atomic level. Results for dislocation mobility in aluminum over a range of strain rates is presented along with comparisons to other FCC systems.



Surface-attached Loops and Interlocking Molecules

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We are working to develop new mechanically interlocking molecules for the formation of multifunctional and tunable self-assembled monolayers. The long-term goal of the project is the creation of sensors with properties that can be controlled at the molecular level. Initial studies are directed toward the synthesis and characterization of model systems that we are calling surface-attached loops. Experimental results from these systems will be presented followed by an outline of how this information will be used in the design and preparation of surface-attached interlocking molecules.



Preparation of Ge Nanocrystals with Novel Surface Termination

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Semiconductor nanocrystals offer the opportunity to tune the optical and electrical properties simply by changing size. The reaction of Mg_2Ge and other Zintl salts with excess GeCl_4 yields Ge nanocrystals from 2-10 nm in diameter, depending on the reaction conditions. Since the particles are so small, most of the atoms are at or near the surface; this makes control of the surface termination vital. As prepared, the nanocrystals have a chloride-terminated surface, which may be changed by reaction with an appropriate Grignard reagent or Li alkyl. The ability to change the surface chemistry of the nanocrystals is unique to this preparation method.



Re-Shock Experiments in LX-17 to Investigate Reacted Equation of State

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Experimental data from measurements of the reacted state of an energetic material are desired to incorporate reacted states in modeling by computer codes. In a case such as LX-17, where the time dependent kinetics of reaction is still not fully understood and the reacted state may evolve over time, this information becomes even more vital. Experiments were performed utilizing a 101 mm gun to measure the reacted state of LX-17 using a re-shock method. This method involves backing the energetic material with thin plates (of a known equation of state) that reflect a shock back into the detonated material. Thus, by measuring the parameters of this reflected wave, information on the reacted state can be obtained. The experiments were driven by a projectile to near the CJ state ensuring a quick transition to detonation near the front of the sample. Embedded manganin piezoresistive gauges were used to measure the pressure profiles at different Lagrange positions during the event. A discussion of this work will include the experimental setup utilized, pressure gauge profiles, data interpretation, and future experiments.



Microbes and Actinides in the Environment

What do they do to each other? What do we know and how can we use them?

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Microorganisms are the most abundant organisms on earth, yet most of them are unknown to us. For instance, microbiologists cautiously assume that only 1 % of extant microorganisms are known; the other 99% may, however, have influence on actinide speciation, fate, and transport. Today actinides are found globally distributed on the earth surface due to fall-out from atmospheric testing and in form of legacy waste from weapons production and power generation.

Microbially mediated processes resulting in bioremediation or retardation of actinides might be of significant interest at contaminated DOE sites throughout the complex. We are exploiting the Nevada Test Site (NTS) as an ideal natural laboratory to study the movement of actinides in geologic formations. Our work is centered on understanding of microbial impact on actinide movement directly in the field rather than selecting one species and studying its interaction with actinides. Currently, we are characterizing the microbial community structures, the geochemical conditions, and the actinide inventory of samples collected at the NTS and adjacent valleys. We would like to determine if a relationships between the actinide inventory in soils and microbial community structure exists. If correlations can be discerned, then the capability of the relevant microorganisms will be investigated further to determine their influence on the fate of the actinides.



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Sites that have been exposed to nuclear surface testing at the NTS were selected for our first investigation, allowing analysis of long-term (50 years) exposure of endogenous bacteria to actinides,

thereby allowing for adaptation of the micro fauna and subsequent transformations and transport. The NTS offers more realistic conditions to extant environmental than we can ever simulate in the laboratory. Geologically equivalent samples from areas with only actinide fallout are studied in parallel. First preliminary results will be presented.

The project is a collaborative effort of the members of the Isotope Tracer and Transport Group, ANCD, the parts of the BBRP group headed by Gary Andersen, and the GET team around Joanne Horn.



Modern Chemistry Techniques Applied to Metal Chelation with Medical and Environmental Applications

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Workers at LLNL and across DOE have suffered beryllium exposure and actinide contamination. At present, there is no cure for beryllium sensitization except removal from site of exposure, while chronic beryllium disease is only controlled with immunosuppression steroids and no cure exists. Current medical treatment for actinide decontamination is administration of DTPA chelator, a technique which hasn't changed since the 1950's. Environmental contamination has been a DOE legacy since the Manhattan Project and remains to be so.

This work proposes to address improved techniques for the development of more effective and selective chelators, leading to the ultimate goal of having a small number of successful chelators for (a) *in vivo* chelation of Be, (b) *in vivo* chelation of U and (c) environmental chelation of U. The work brings together Divisions and Directorates across LLNL, with collaboration between scientists and medical staff. Techniques available at LLNL such as SIMS, EXAFS and CMS analytical capabilities will be used to determine the chemical thermodynamics, structure and efficiency of the metal chelate complex and its effectiveness in removing contamination.

This work is included in Safeguards, Security and Environmental Protection's LDRD proposed portfolio and preliminary research has already been undertaken to assess chelator options. The results of the proposed work may have implications in the environment, industry and medical treatment of metal contamination and poisoning.



First Results of Reaction Propagation Rates in HMX at High Pressure

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We have measured the reaction propagation rate (RPR) in octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) powder in a diamond anvil cell over the pressure range 0.7-35 GPa. In order to have a cross-comparison of our experiments, we conducted RPR experiments on nitromethane (NM) up to 15 GPa. Our results on NM are indistinguishable from previous measurements of Rice and Foltz. In comparison to high-pressure NM, the burn rates in solid HMX are 5-10 times faster at pressures above 10 GPa. Numerical simulations of the burn rate of pressurized HMX were also performed for comparison to the results obtained. The simulated burn rates closely approximate the observed rates at pressures up to 3 GPa. However, further refinement to the computational model is required for the calculated burn rates to approach those observed at higher pressures.



Quantum vibrations in molecules: A new frontier in computational chemistry

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The vibration of a molecule is a quantum mechanical phenomenon. The current treatment of molecular vibrations in quantum chemistry is usually based upon the harmonic oscillator approximation. Wide classes of molecules, however, do not behave as simple harmonic oscillators. Examples include molecules with torsional degrees of freedom, floppy molecules with multiple thermally accessible configurations, or molecular clusters. In these important problems, the interplay between electronic effects and anharmonic quantum vibrations can be very strong. We are developing methods to allow the combining of a quantum treatment of the electrons via *ab initio* methods with a quantum treatment of the nuclei via path integral Monte Carlo (PIMC). A new energy estimator is presented along with preliminary chemical results.



Application of dendritic methodology to the preparation of new sol-gel precursors

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Nanostructured materials can be prepared using sol-gel chemistry, a process that involves the condensation of reactive monomers into nanometer-sized “clusters” that polymerize into a gel in one synthetic step. While this technique allows for the preparation of new material compositions, sol-gel chemistry is limited by the inability to separate the process of cluster formation from gelation. This limitation leads to structural deficiencies in the gel state that ultimately impact the physical properties of the xerogel, aerogel, or nanocomposite. We are using dendrimer chemistry to separate the cluster formation step from the traditional gelation process so that new nanostructured materials with unique topologies and compositions can be produced. The dendrimers will be used as *pre-formed* clusters of known size, shape and surface functionality that can be cross-linked in a controlled fashion to form the gel network. Toward this goal, we are synthesizing new dendritic compounds as sol-gel precursors that will allow for greater control over the bulk properties of the resultant sol-gel materials. In particular a range of alkyne dendritic compounds will be reported.



Towards bio-inorganic smart membranes

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A large variety of filtration membranes can be found on the market: pore diameters range from tens of nanometers to tens of microns, and various materials are available (ex: polycarbonate, polytetrafluoroethylene, cellulose esters). These products mainly act as passive devices, selecting molecules according to their size and some coarse chemical properties (ex: separation of hydrophilic and hydrophobic molecules).

The goal of our project is to assemble three types of materials: semiconductor (silicon), metal (gold) and organics (self-assembled monolayers, SAMs) to build a bio-inorganic membrane which will be highly selective and 'smart'. The main idea is to etch pores in a silicon wafer to obtain a membrane, coat the pore walls with gold and anchor functionalized SAMs designed to harvest target molecules. These membranes will be versatile since both pore size and SAM functionality can be adjusted according to the target. Our ultimate goal is to convert these passive membranes into 'smart' membranes, able to determine the concentration of target in situ and in real time. A way of doing this is to build a regular array of pores and to use the membrane as a photonic waveguide.

It will be shown that we are now able to prepare regular arrays of pores in a silicon substrate with diameters ranging from hundreds of nanometers to microns. We will also discuss some work in progress like the gold plating of the pore walls.



Cellular Imaging and Dose Estimation of Isotopically-labeled Molecular Targeting Agents

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Focus and Scope: To develop an integrated imaging/simulations system for characterizing intercellular and subcellular distributions of isotopically enhanced molecular targeting agents and estimating resulting radiation dose distributions at the microscopic level.

Rationale: The goal in radiation therapy is to maximize tumor cell kill (efficacy) while minimizing adverse effects on normal cells (toxicity). Targeted radiotherapy attempts to do this by directing radiopharmaceuticals to tumor cells via tumor-specific targets found only on the surface of tumor cells. The distribution of radiotargeted pharmaceuticals within the tumor mass and within individual tumor cells is unknown but can determine a drug's efficacy and toxicity. Determination of the distribution pattern, combined with accurate radiation simulations will allow design of therapeutics whose radiation emissions maximize efficacy while minimizing toxicity.

Methods: We propose using secondary ion mass spectrometry (SIMS) to localize drug distribution. Although SIMS is widely applied in materials science and geoscience, there are currently only a few groups applying this technique to analyze biological samples. We will extend LLNL's SIMS capability to analyze the distribution of radiotargeted drugs currently undergoing clinical trials by our collaborators at UC Davis Medical Center. These data will be used as input into an image fusion software and single-scatter electron transport code developed at LLNL. Finally, the resulting calculated energy deposition profile will be compared to clinical data to determine how these new data contribute to a better understanding of the mechanisms underlying drug function and how they can be used to improve drug design.



Biological and Materials Science Applications of Single Molecule Spectroscopy

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Single molecule optical spectroscopy is a powerful tool for investigating a variety of systems free from the ensemble averaging present in bulk spectroscopic measurements. Research using single molecule optical spectroscopy over the past decade has revealed unique photophysical phenomena and has enhanced our understanding of molecular interactions. Our research group uses single molecule detection and spectroscopy to study and characterize systems that have applications in biological and materials sciences. In the biological sciences, we use surface enhanced Raman spectroscopy (SERS) to better understand the biophysical properties and interactions of biomolecules such as DNA and proteins. We are also developing instrumentation and experimental schemes aimed at ultra-sensitive pathogen detection using single molecule fluorescence co-localization. Once completed, this system will allow for the detection of femtomolar quantities of a specific target molecule. Our research into materials is focused on polymer materials and nanocrystals (quantum dots). The unique properties of MEH-PPV polymers allow them to emit light and may have applications in ultra-thin LED displays. The fluorescent/electroluminescent properties of these polymers are dictated by the electron delocalization within the polymer. Our results indicate a solvent dependent effect on the shape and, therefore, the electron delocalization found in these polymers. Finally, we are working in collaboration with other research groups to better understand the luminescent properties of CdSe and Si nanocrystals. Using the single molecule techniques accessible to our group, we are characterizing the photophysical properties of these nanocrystals as well as their potential use as markers in biological applications.