Development of Ceramic Nanophosphors

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Goals:
- Synthesize a library of novel metal and mixed metal alkoxides for use as single source precursors
- Utilize commercially available reagents, as well as developed single source precursors, for the production of ZnWO₄ (ZWO) and HfGeO₄ (HGO) ceramic oxide nanophosphors that will emit light upon external stimulation that does not involve heat

Approach:
- Synthesize tungsten (W) metal alkoxide single source precursors
  - W(OEt)₅ + 5ArOH → W(OAr)₅ + 5EtOH (Ar = aryl)
- Synthesize mixed metal alkoxides for the Zn/W and Hf/Ge systems
  - M(OR)₄ + M'(OR)₄ → M₂M'(OR)₄
- Develop solution routes, specifically focusing on the solvothermal method, to produce ceramic nanophosphors
- Analyze luminescent properties of resultant nanomaterials

Results:
- Synthesized two novel single source tungsten alkoxide precursors, WO(DMP)₅ and WO(DIP)₅
- Produced ZnWO₄ and HfGeO₄ nanomaterials from commercially available reagents utilizing the solvothermal method

Impact:
- Nanophosphors, specifically ZnWO₄, can be incorporated into scintillator materials to detect radiation. Nanophosphors may even be able to distinguish between harmful radiation, such as nuclear weapons, and naturally occurring radioactivity that can be found in many foods.
- HfGeO₄ ceramic nanophosphors can replace nationally critical materials such as lanthanides in solid state lighting. Because hafnium is a great X-ray absorber, HGO is also of interest for bioimaging and biological tagging.
Synthesis of Monodisperse Noble-Metallic Nanoparticles and Their Self-Assembly

Jessica Pu, Hongyou Fan, Binsong Li, Edward Lu

Purpose
- Superlattices of nanoparticles can be converted into 1-3D nanostructures using high pressure sintering.
- Applications in catalysis, bioimaging, and nanoelectronic and optic devices
- An ordered array of nanoparticles is needed for high pressure sintering. This requires stable, readily soluble, monodisperse nanoparticles with various ligands as building blocks.

Results
- Au nanoparticles reduced by morpholine-borane with different capping ligands
- Ag nanoparticles with different capping ligands and precursors (prec)

Approach
- Optimize synthesis and improve solubility and stability by testing different combinations of precursor, ligand, reducing agent, etc.
  - Precursors: AupPPh₃Cl, Ag decanoate, Ag myristate, Ag stearate, Ag[PPh₃]₂Cl, Ag[PPh₃]₂NO₃
  - Ligands: decanoic acid, myristic acid, decanoic acid, dodecanethiol, dodecanethiol, hexadecanethiol, oleylamine
  - Reducing Agents: tert-butylamine borane, morpholine-borane, triethylamine, trioctylamine, oleylamine

Conclusion
- Synthesized nanoparticles with various sizes and ligands with good monodispersity
- Further research is needed to improve solubility and stability of oleylamine-capped Ag nanoparticles

*All scale bars are 20nm
Molecular Dynamics Simulations of OPE and Membrane Interactions

Kelly Stratton - University of Connecticut, 2013; Mentor - Eric Hill; PI - Debi Evans

Background
- There is an increasing need for methods to fight antibiotic-resistant bacteria in hospitals.
- OPEs (Oligo-p-Phenylene-Ethylenes) have shown antimicrobial properties experimentally.
- OPEs target the lipid bilayer of cell membranes, however the mechanism of penetration is not yet known.

Goals
1) Study the interactions of OPEs with model lipid bilayers.
2) Analyze results of all-atom molecular dynamics simulations to determine how OPEs damage lipid bilayers.

Procedure
- Molecular dynamics simulations of different OPE configurations are run using NAMD.
- Visualization and analysis done with VMD.

Results
Membrane Deformation
- The presence of the OPE forces the negatively charged phosphate head groups to move closer toward the middle of the membrane.

Lipid Flip-Flop
- Lipids around the OPEs are distorted.
- One DOPG crossed from the bottom to top leaflet over a period of 50ns.

Pore Formation
- A water pore is formed between two of the S-OPE-3s. By 120 ns in the simulation, over 350 water molecules have passed through the membrane.
- The blue water molecule (to the right) first associates with the yellow charged group, then red, then grey or pink, climbing down the cationic groups of the OPEs like a “ladder”.

Conclusions
- OPEs anchor themselves via the charged groups interacting with the negatively charged membrane.
- S-OPEs cause damage to the membrane.
- Aggregates of OPEs result in the formation of pores which allows the passage of water.
- The mechanism for water permeation involves a “ladder” created by the OPE cationic groups.

The initial configurations of 3 S-OPE-3 and 3 S-OPE-2 simulations in a bacterial membrane model with a 4:1 DOPE:DOPG ratio.
Measuring Diffusion In 3D Alginate Gel Cell Scaffold

**Goal**
- Gradients created by diffusion and cell consumption in extracellular space
- Characterization of diffusion in the alginate gel cell scaffold is necessary to model drug and nutrient transport for 3D cell culture model
- 3D cell culture model used to determine drug and nutrient transport in avascular cancerous tumors which is more analogous to *in vivo* experiments

**Procedure**
1. 5% Alginate pregel with 1.5E+04 M fluorescein was dropped into 2% CaCl₂ solution to create fluorescent calcium alginate spheres. As the fluorescein diffused out of the gel, the spheres were observed and recorded using an epifluorescence microscope. The intensity of the area within the gel was then graphed per time after being corrected by subtracting the intensity of the background noise.

**Results**
Corrected Total Fluorescence Decrease in Alginate Sphere Over Time

![Fluorescence intensity vs. time graph]
- Half life = 8.469 min
- Rate constant K = 0.08184 min⁻¹
- Plateau = 7.658e+006
- R square = 0.99

**Future Directions**
- Repeat experiment using confocal microscope to increase image resolution.
- Decrease signal to noise ratio in order to clearly distinguish spheres from background noise.
- Optimize experiment protocol for reproducibility.
- Finish mathematical analysis to determine diffusion coefficient from data collected.
Effect of Curcumin on Lipid-membrane Induced Aggregation of Amyloid-β Peptide
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Department of Chemical & Nuclear Engineering and Center for Biomedical Engineering,
The University of New Mexico

Background:
- Alzheimer's Disease (AD)
  - Most common for form of dementia
  - More than 5 million Americans are living with AD
- Misfolding, fibrillar aggregation, and deposition of amyloid-β (Aβ) protein is linked to neuronal death in AD

Hypothesis:
- Curcumin inhibits Aβ-lipid membrane interactions
  - By inhibiting the formation of Aβ oligomers and fibrils

Results:
- DLS Assay
- THT Assay
- HPLC Assay

Approach:
- Cell Membrane Model
- Lipid vesicle
  - POPC + POPG
  - 50 µM AB + 100 µM PC/PG
- Assays
  - DLS
  - THT
  - HPLC

Conclusion:
- Inconclusive data
  - Presence of vesicles did not affect dramatically the formation of Aβ fibrils
  - Presence of curcumin did not make a difference in preventing formation of oligomers
  - Control sample of Aβ without lipid vesicle showed decrease in percent of Aβ monomers

Future Work:
- Incubate at 25°C
- Obtain TEM images
- Perform incubations of Aβ alone
  - Compare with publish data
  - Perform incubation of remaining samples
Synthesis of Nanoscale and Bulk-scale Materials for Scintillators
C. Douglas Hardy, Bernadette A. Hernandez-Sanchez, Timothy J. Boyle, Lesly Vega, Sarah Hoppe

Problem
Scintillators are materials that luminesce when struck by radiation. These materials are useful in the detection and identification of radioactive materials in national security purposes. Scintillators that can more accurately identify and distinguish different types of radiation are critical to national security.

Approach
- Synthesize bulk scale scintillator bismuth germanium oxide (BGO) via solid state reaction, dope it with lanthanides to improve light output. Look to synthesize phase pure BGO.
- Synthesize tungsten chalcogenide nanomaterials using novel solution-precipitation and solvothermal routes.
- Characterize the materials using x-ray diffractometry, transmission electron microscopy, energy-dispersive x-ray spectroscopy, thermal gravimetric analysis, differential temperature analysis.

Results
- Synthesized BGO doped with BGO:Ce and BGO:Eu, two phases formed (Bi₂Ge₃O₁₂ and Bi₁₂Ge₂O₂₀). Materials luminesced.
- Synthesized various tungsten chalcogenide nanomaterials from different precursors, focusing on tungsten disulfide (WS₂)
- TEM showed nanorod structures of WS₂ with diameters of <1 nm
- XRD of WS₂ had similar patterns to literature reports of nanorod WS₂ but not matching crystal structure in XRD database
- Annealing the WS₂ in an argon atmosphere at 850°C changed the XRD pattern significantly; all peaks of the annealed sample matched with the peaks of WS₂ on the database, TEM showed nanorods forming layered structure
- No tungsten chalcogenide nanomaterials luminesced, black color of the powder inhibited luminescence

Conclusions and next steps
- Developed new solution routes to tungsten chalcogenide nanomaterials
- Lack of luminescence means tungsten chalcogenide nanomaterials alone will not be effective scintillators
- Want to incorporate the tungsten disulfides into a mixed metal sulfide material, to try and get materials with a non-quenching color.

References
**Templated Graphene Nano-Materials**

**Goals**
- Research ways to make graphene (thin stacks of graphite) with the use of montmorillonite (clay)
- Develop own procedure for production
- Analyze characteristics and benefits toward application

**Approach**
1. Precursors intercalate platelets
2. Cationic species exchange with Ca$^{2+}$ or Na$^+$
3. Adsorb to the silica surface
4. H$_2$O/solvent evacuates as clay dries
5. Precursors remain adsorbed
6. Pyrolyzation decomposes precursors
7. Clay etched away

**Results**
- 2:1 Sucrose Ca-Clay
- 2:1 PNA Ca-Clay
- 2:1 Sucrose Precursor has best mass yield
- 2:1 PNA (N-Phenyl-1-naphthylamine) Precursor has best surface area

**Conclusion**
- Procedure for making graphene is successful
- Graphene acts as an anode in lithium-ion batteries
- Higher surface area graphene is more beneficial to transfer electrons within battery

**Future Work**
- Analyze purity of material
- How effective it is in battery
- Find easier way to make larger amounts of product
Bias gated pixel isolation for infrared InAs/GaSb superlattice detector arrays
Emily Tansey, Stephen Myers, Sanjay Krishna

Motivation
A major limitation of superlattice IR detectors is surface leakage current (SLC). SLC produces noise in the device & consequently decreases signal to noise ratio. SLC arises due to malfunctions in sidewalls, which are formed by physically etching away material to mechanically isolate pixels. To circumvent this, we propose a novel way of isolating pixels without etching individual mesas. Instead, an array of pixels are patterned on one level mesa. The pixels are then electrically isolated by application of a gate bias.

Method
By applying a gate bias ($V_g$) across pixels, the properties of a metal-oxide-semiconductor field effect transistor are employed to deplete inter-pixel regions of charge carriers. Experiments include
- simulations of electron density using Synopsys Sentaurus to model device
- resistance across pixels as a function of gate bias
- current voltage plots at different gate biases

Results
IV curves taken across bottom contacts of variable spacing show desired ohmic resistance, indicating good contact at metal-oxide interface.

Conclusion & Further Work
- Carrier depletion region beneath top contact shows heavy dependency on semiconductor doping level in simulations:
- Further research on extent to which this affects electrical isolation of pixels
- Lower doping in the top absorption region should be explored
- Further exploration of metal-oxide-semiconductor bandgap alignment to better understand how Schottky barriers affect charge flow at interfaces
Size and Morphology Control of Mesoporous Silica Nanoparticles

**Goal**
- To control the size and the morphology of the mesoporous silica nanoparticles

**Significance**
- Knowledge of this research will help better understand the bio distribution of nanoparticles for future drug delivery systems

**Approach**
- Use different concentrations of ammonium hydroxide when synthesizing the particles
  - 0.128M, 0.256M, 0.512M, and 1.024M
- Hydrothermal treat the particles in various temperature settings
  - 60°C, 90°C, 120°C, and 150°C

**Results**

<table>
<thead>
<tr>
<th>Size (TEM)</th>
<th>Doughnut Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>39nm*</td>
<td>TEM</td>
</tr>
<tr>
<td>65nm*</td>
<td>SEM</td>
</tr>
<tr>
<td>183nm*</td>
<td></td>
</tr>
<tr>
<td>263nm*</td>
<td></td>
</tr>
</tbody>
</table>

**Conclusion**
- Easy to control the size and the shape of the particle
- Can control the thinning of the center to make it a red blood cell shape (biconcave)

**Future Exploration**
- Conduct in vivo testing to see the size and shape effects on the bio distribution
- Study the shape formation mechanism
Synthesis of Palladium Nanoparticles
Via Direct Alcohol Reduction

Research Goals:
★ Size control of nanoparticles
★ Control the synthesis in order to control the size of the nanoparticles while depositing on various supports

Procedure:
EXPERIMENTS VARIABLES
SUPPORT
- CARBON
- SILICA
- TITANIA
ACETONE
- RINSE
- NO RINSE
TIME PROGRESSION
- 0 HRS
- 1 HR
- LONGER THAN 1 HR (3.45 HRS & 8 HRS)

Results & Conclusion:
The following data shows conversion vs. selectivity for the hydrogenation of acetylene. The plot is of two batches; one was made at time zero in the nanoparticle formation reaction and the other was made 8 hours into the reaction. Both had a carbon support but half of the each batch was rinsed with acetone.

![Graph showing selectivity of ethylene over time with and without acetone rinse.]

- Acetone rinsing a sample resulted in negative selectivity. This happens due to washing off palladium that is more selective. EDS was used to determine Pd wt% and is presented in the table above.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>t=0</td>
<td>0.94</td>
</tr>
<tr>
<td>t=0 acetone rinse</td>
<td>0.22</td>
</tr>
<tr>
<td>t=8hrs</td>
<td>0.96</td>
</tr>
<tr>
<td>t=8hrs acetone rinse</td>
<td>0.35</td>
</tr>
</tbody>
</table>
Goal:
To form a two dimensionally ordered array of Germanium quantum dots by utilizing stress transfer technique. This process may be highly manufacturable over large scale wafers.

Procedure:
- Fabricate Silicon nanopillars to use as indenters.
- Press Silicon template onto a SiGe substrate using Mo press.
- During annealing process, Ge atoms will diffuse out of stressed regions.
- Grow thin layers of Ge onto SiGe using MBE.

Results:
- Fabrication of Silicon nanopillars has been processed.
- Concentration of Ge in SiGe substrate is found to be 20%.

Future Actions:
- Purchase SiGe wafers.
- Follow proposed procedure.
- Use of EDX to check compositional variation of SiGe.
- Grow thin layers of Ge on SiGe substrate.