SAND2012-9089P

Nanomaterials Research at AML

The Advanced Materials Laboratory, a part of Sandia National Labs since August, 1992

Developing materials science and engineering technology in the National Interest

Sandia National Laboratories

Advanced Materials Laboratory

Department 1815

Bill Hammetter, Manager

AML

Advanced Materials Laboratory

" . . . provide exceptional service in the National interest."

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Many established and novel nanomaterials are currently being developed in 1815 for a wide variety of applications

Boyle
- Nanosolder
- Scintillators
- Bio-imaging
- Laser detection
- Power sources (Batteries)
- Nanofillers for Flywheels
- Responsive Nanocomposites
- Nitrogen Phosphorous Detectors

Brinker
- Nanoparticles for nanotoxicity studies
- "Nature's NPs" (non-infectious virus-like particles, VLPs) for targeted delivery of therapeutics and vaccines
- Mesoporous silica NP-supported lipid bilayers ('protocells') for delivery of diverse cargo

Fan Develop new synthesis methods to fabricate multifunctional nanomaterials, understand structure and properties:
- Nanoparticle synthesis, functionalization, and integration
- Large areas of nanoparticle films and optical coating.
- High pressure synthesis and characterizations
- Porous materials and composites

Hernandez-Sanchez
- Protective Nanocoatings (Water & Wind Power)
- Scintillators (Radiation Detection)
- Uv-Infrared Materials (Solar/Photonics)
- Anode Materials
- Magnetic Assisted Polishing
- Chalcogenide Based Particles

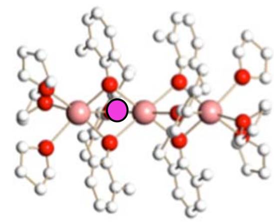
Zavadil
- Energy storage materials & architectures
- Precision nanoscale electrochemical instrumentation & methods
- Electrochemical dynamics – material performance and reliability.

Kaehr Lithographic methods for nanomaterial synthesis and patterning
- 3D patterning of metals, metal oxides, and alloys.
- Nanocomposites and functional biomaterials.

BOYLE: Use novel precursors to tailor the properties of complex nanomaterials

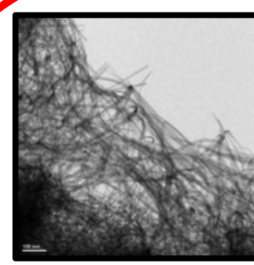
Solution Precipitation Route

Specialty Precursors



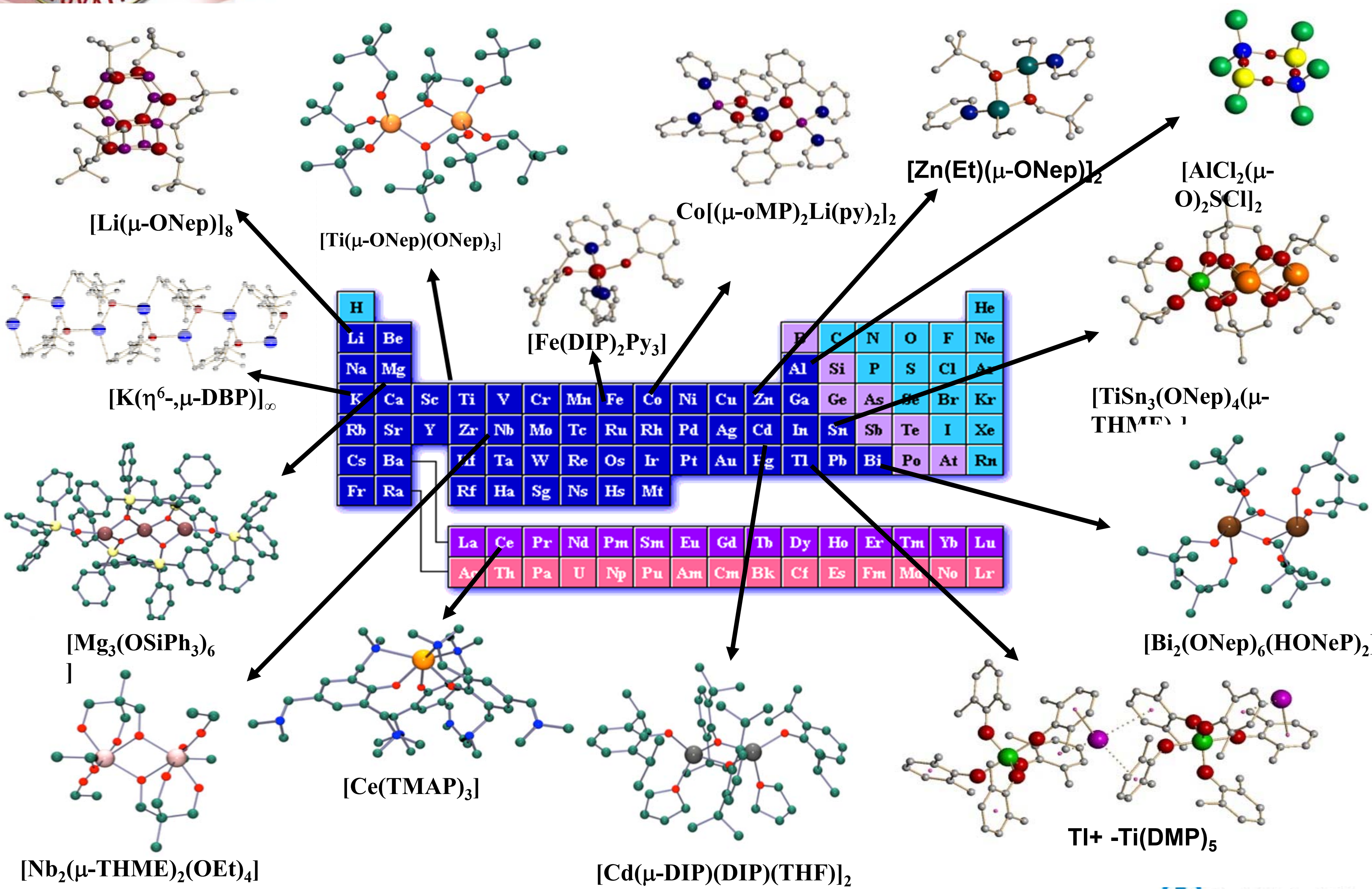
Solvothermal Route

Tailored Nanomaterials



Following solution routes that employ novel precursors, nanomaterials with tailored properties (i.e., size, shape, composition) have been developed

The Periodic Table of Elements is our playground, which lets us . . .



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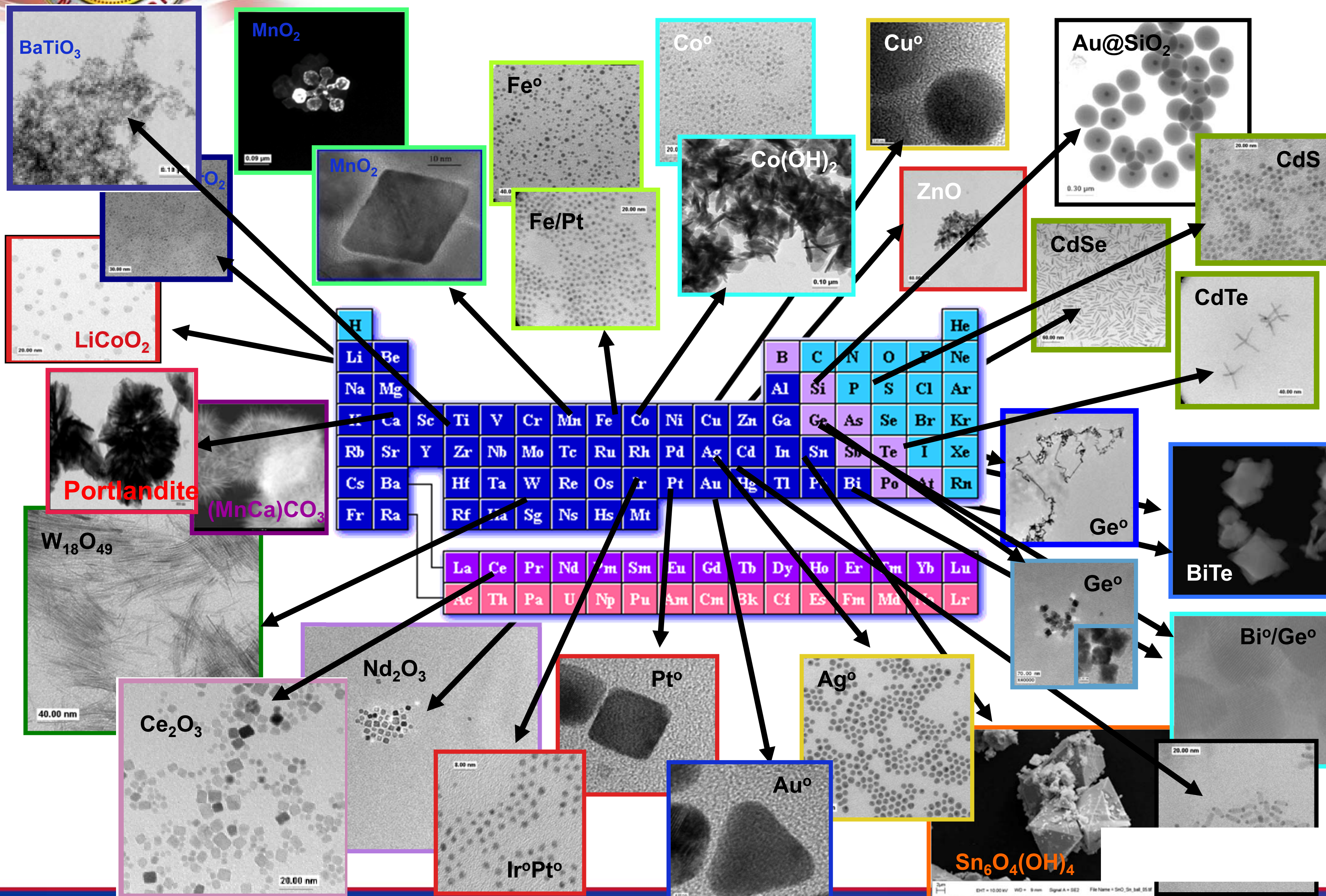
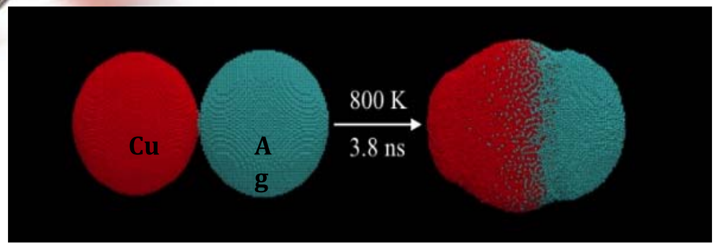
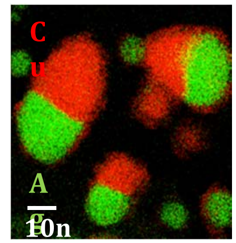
. . . Generate the Periodic Table of Nanomaterials

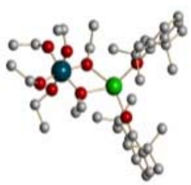


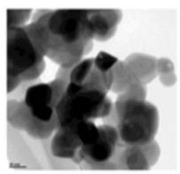
Some examples of their uses are shown below

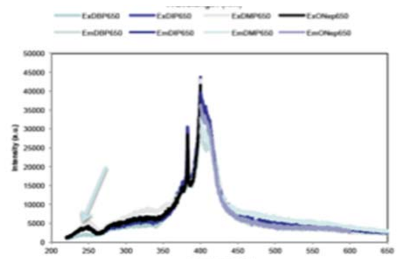




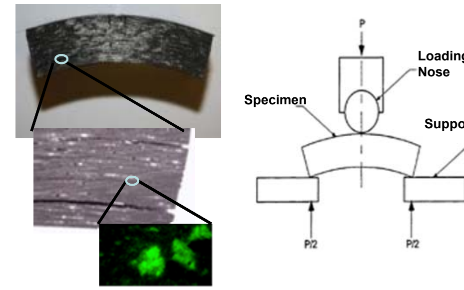
Nansolder: high purity metals for developing understanding of how to exploit lower temperature of nanosolders

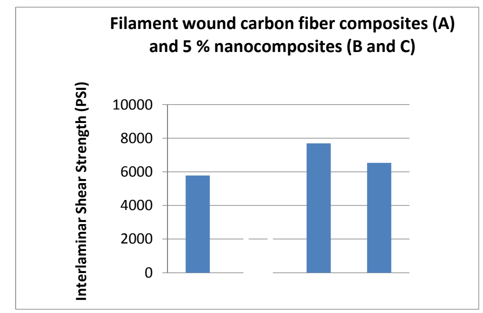






Nanoscintillators: properties of nanoscintillators and composites





Flywheels: Regulating the AC grid with improved Flywheel materials using ceramic nanofillers.

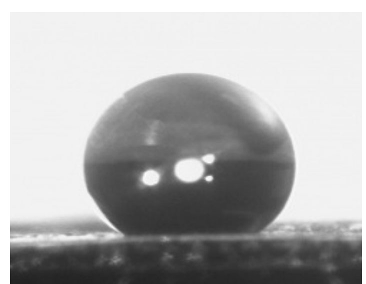
$Zn(CH_2CH_3)_2$ + $Fe(C_6H_2(CH_3)_3\text{-}2,4,6)_2$ → "(Zn,Fe)S"

prior to excitation

excitation with hand-held UV lamp (~365 nm)

Mast Cell with functionalized QDs.

Bio-imaging: using non-toxic naturally occurring fluorescent materials (NOFs) generated biomarkers.



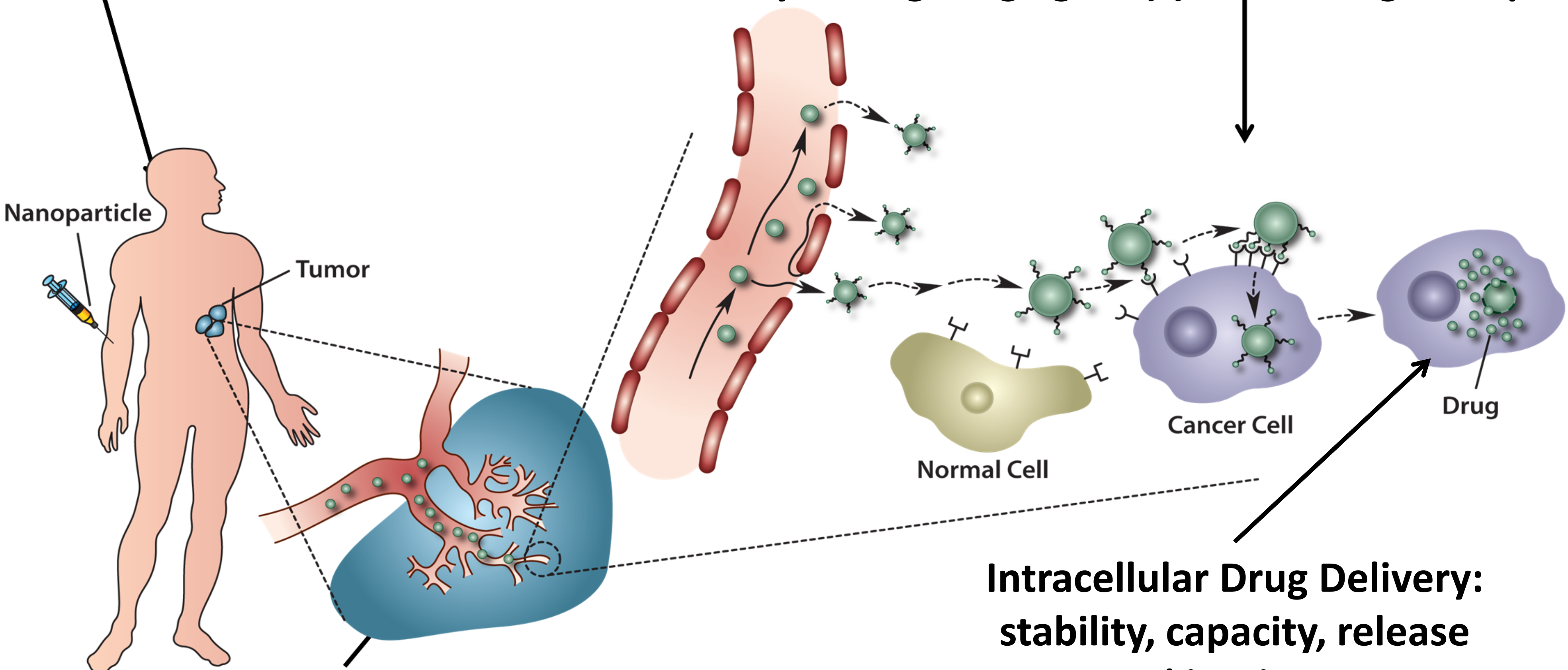
3 sec
60 °C

Responsive Nanocomposites: Rapid superhydrophobic/hydrophilic electrospun nanofibers

BRINKER group: Engineered Nanoparticles for Targeted Delivery of Diverse Cargo

Time in Circulation: size, charge, surface modification(s), shape

Selective Binding & Internalization: type & density of targeting ligand(s), size, charge, shape



Intracellular Drug Delivery: stability, capacity, release kinetics

Penetration into Tumor(s): size, charge, surface modification(s), shape

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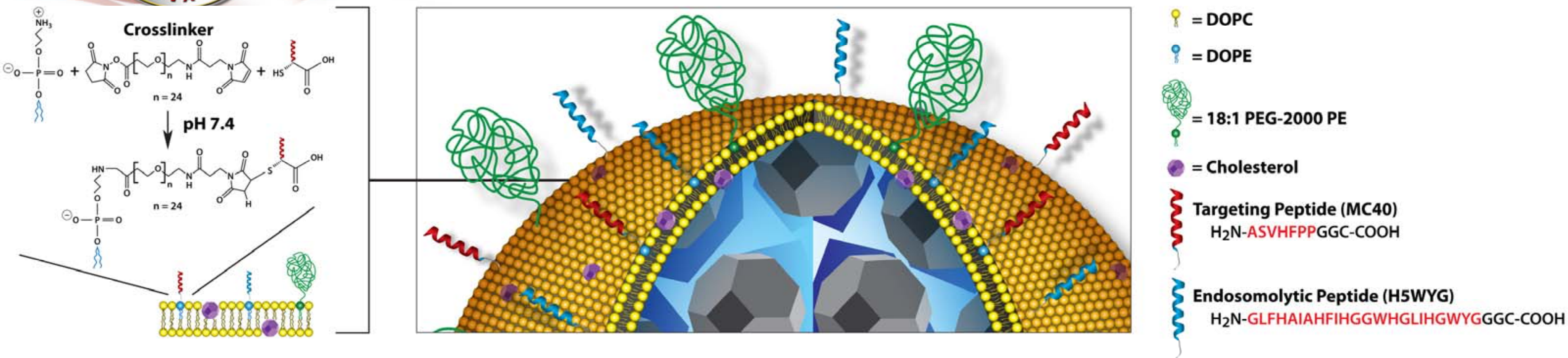
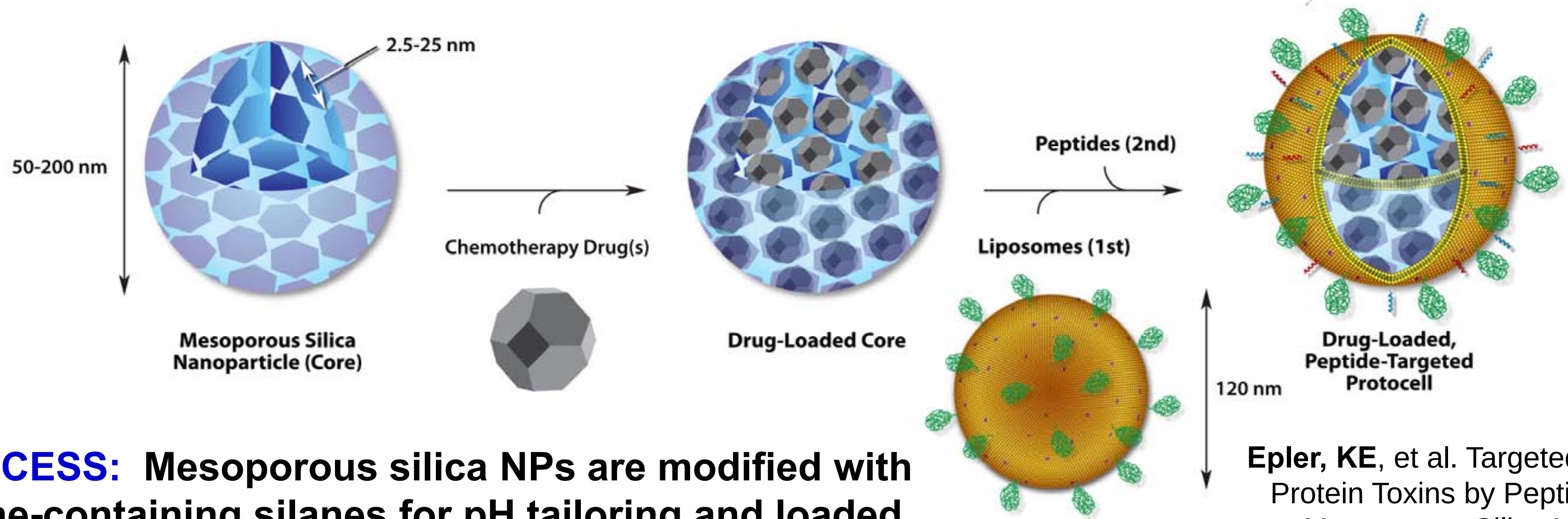
Synthesis of Mesoporous Silica Nanoparticle-Supported Lipid Bilayers (‘Protocells’)

Schematics courtesy of Mona Aragon, 6810





PROCESS: Mesoporous silica NPs are modified with amine-containing silanes for pH tailoring and loaded with desired cargo. Liposome layer is fused to the loaded core and targeting peptides are conjugated to primary amines using a crosslinker.

Epler, KE, et al. Targeted Delivery of Protein Toxins by Peptide-Targeted Mesoporous Silica Nanoparticle-Supported Lipid Bilayers. ***Advanced Healthcare Materials*** **2012, 1, 238 (COVER).**

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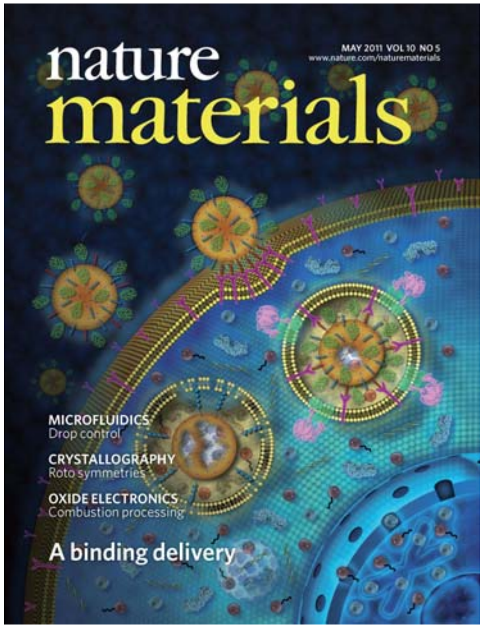
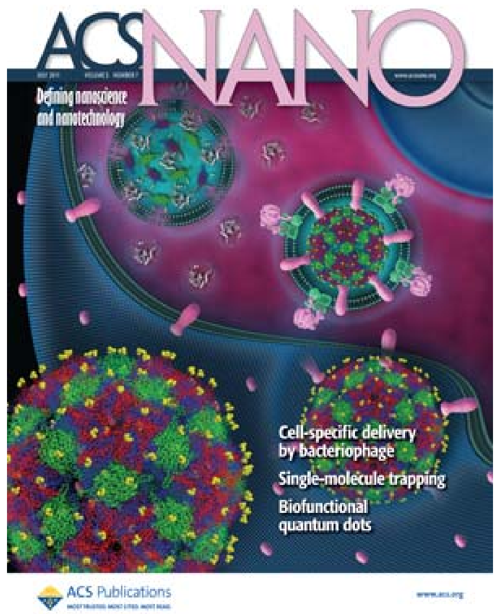
Materials for Nanomedicine – a novel approach to therapeutics for cancer and emerging pathogens

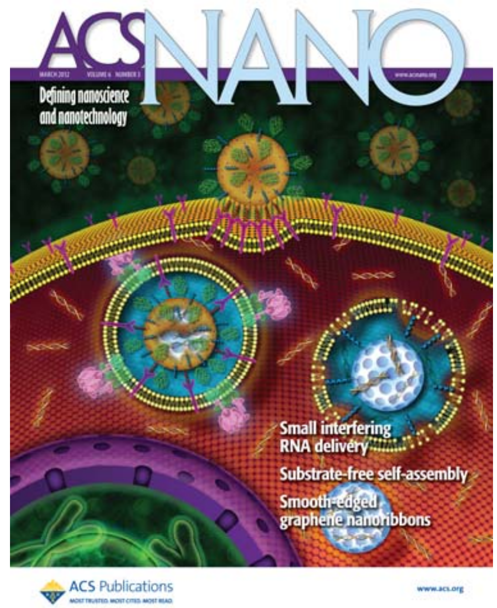
Engineered nanoparticles with fused lipid bilayers (“protocells”)



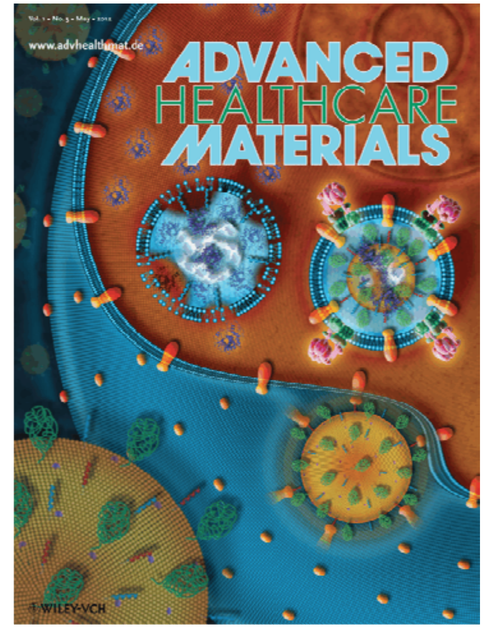
May 2011



July 2011



Mar 2012



May 2012

“The properties engineered into this system elegantly synergize to approach the goal of an ideal targeted-delivery system.”

Darrell Irvine, MIT
Nature Materials
News & Views, May 2011

- **Combines properties of liposomes and nanoporous NPs**
- **High surface area nanoporous core gives high cargo capacity**
- **Surface modification with targeting ligands and trafficking ligands**
- **Core tailored to disassemble at intracellular pH to release cargo**
- **Demonstrated cargo: therapeutic agents (drugs, small interfering RNA, toxins), diagnostic agents (quantum dots)**
- **Overcomes challenges of specificity, cargo capacity, stability**

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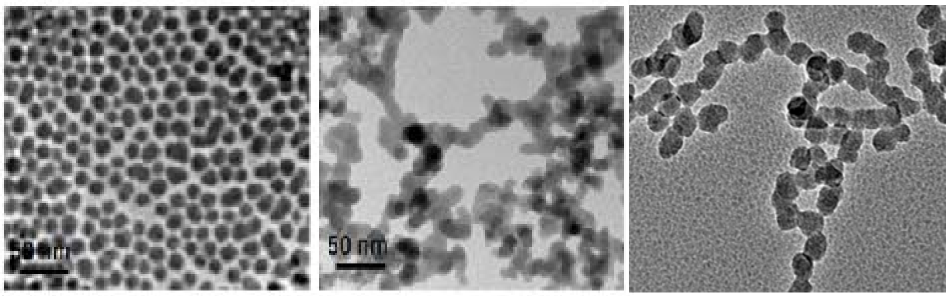
Physicochemical characterization of amorphous silica nanoparticles for toxicity studies (SNL-UNM-UCLA)

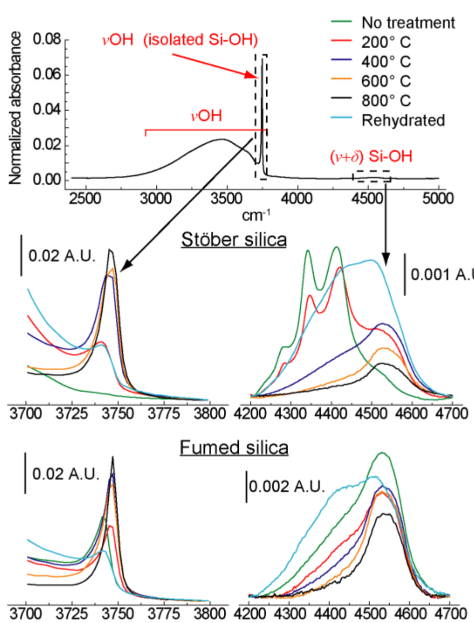
Stöber silica **Fumed silica** **Aggregated Stöber silica**

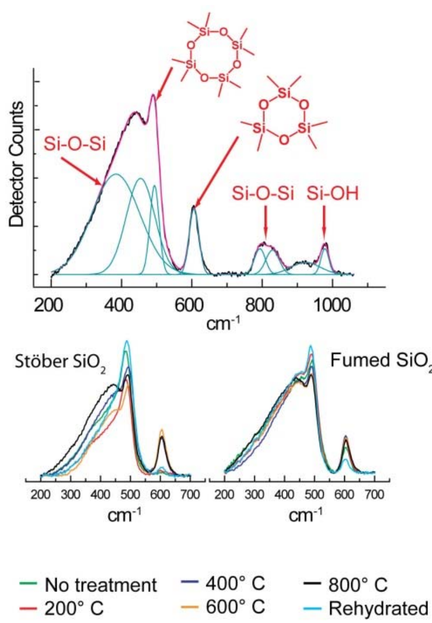


Goal: Compare the physical and chemical structure of SiO_2 particles synthesized at low (Stöber silica) or high (fumed silica) temperature for correlation with toxicological data

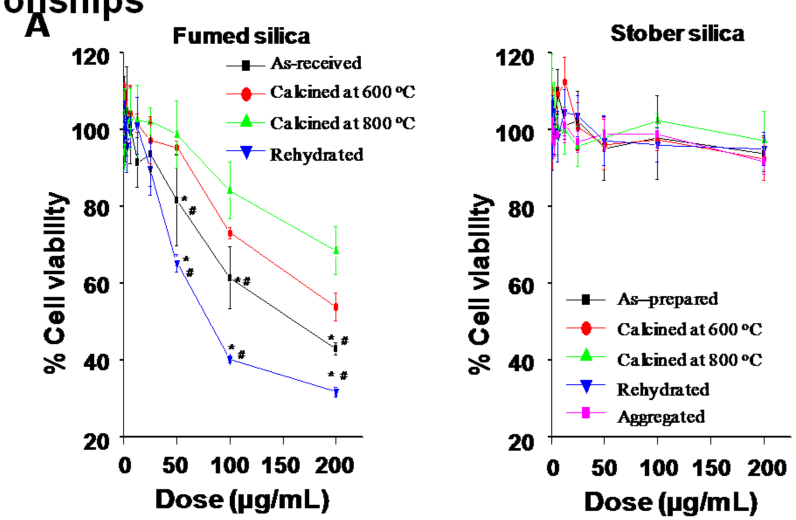
Processing Pathway Dependence of Amorphous Silica Nanoparticle Toxicity: Colloidal vs Pyrolytic. Zhang, H.; Dunphy, D. R.; Jiang, X.; Meng, H.; Sun, B.; Tarn, D.; Xue, M.; Wang, X.; Lin, S.; Ji, Z.; Li, R.; Garcia, F. L.; Yang, J.; Kirk, M. L.; Xia, T.; Zink, J. I.; Nel, A.; Brinker, C. J. *Journal of the American Chemical Society* Sept 2012, *134*, 15790-15804.

Spectroscopic data shows chemical structure of particles (IR on left yields concentration of Si-OH groups, Raman data on right measures silica ring structures)

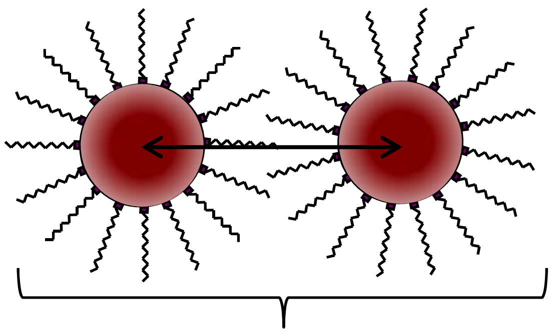




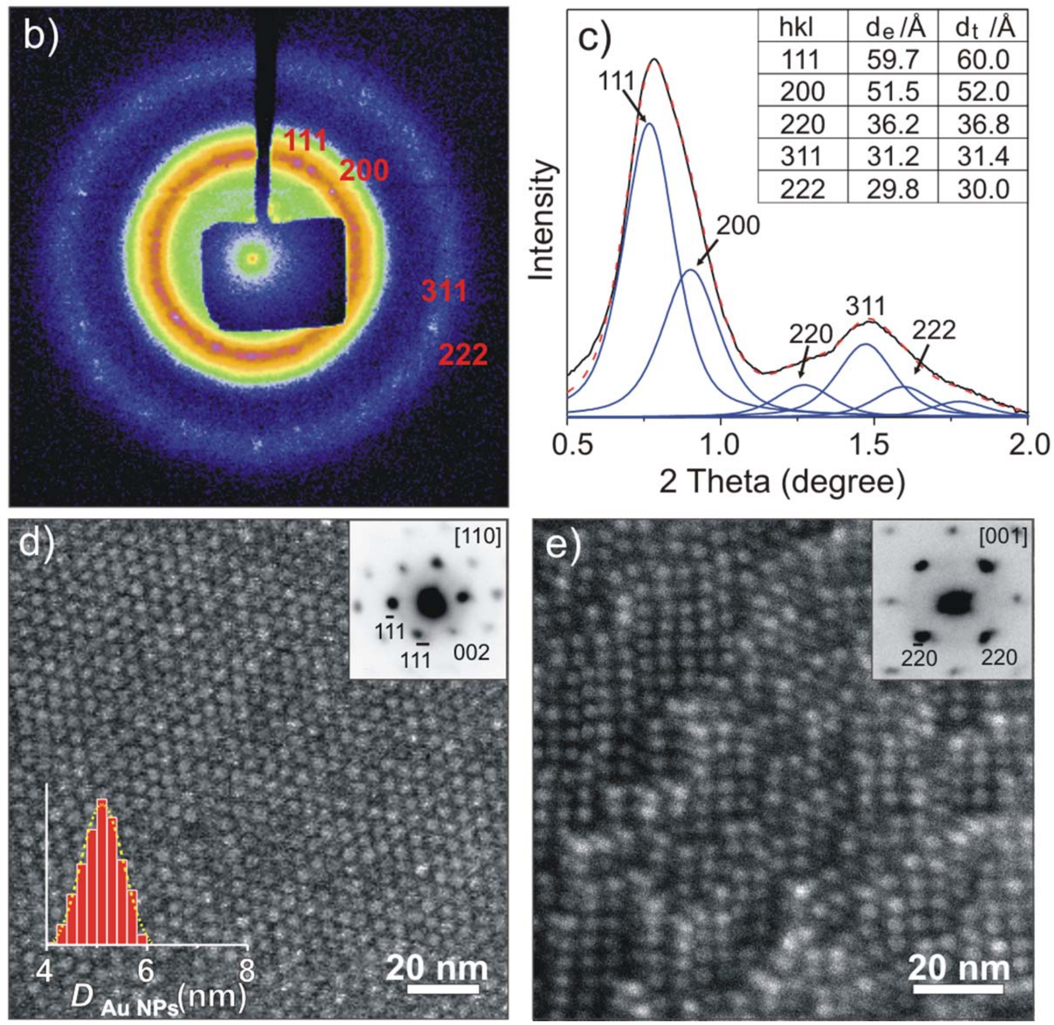
Data iscorrelated with cellular assays (UCLA) to create models of nanoparticle structure/toxicity relationships



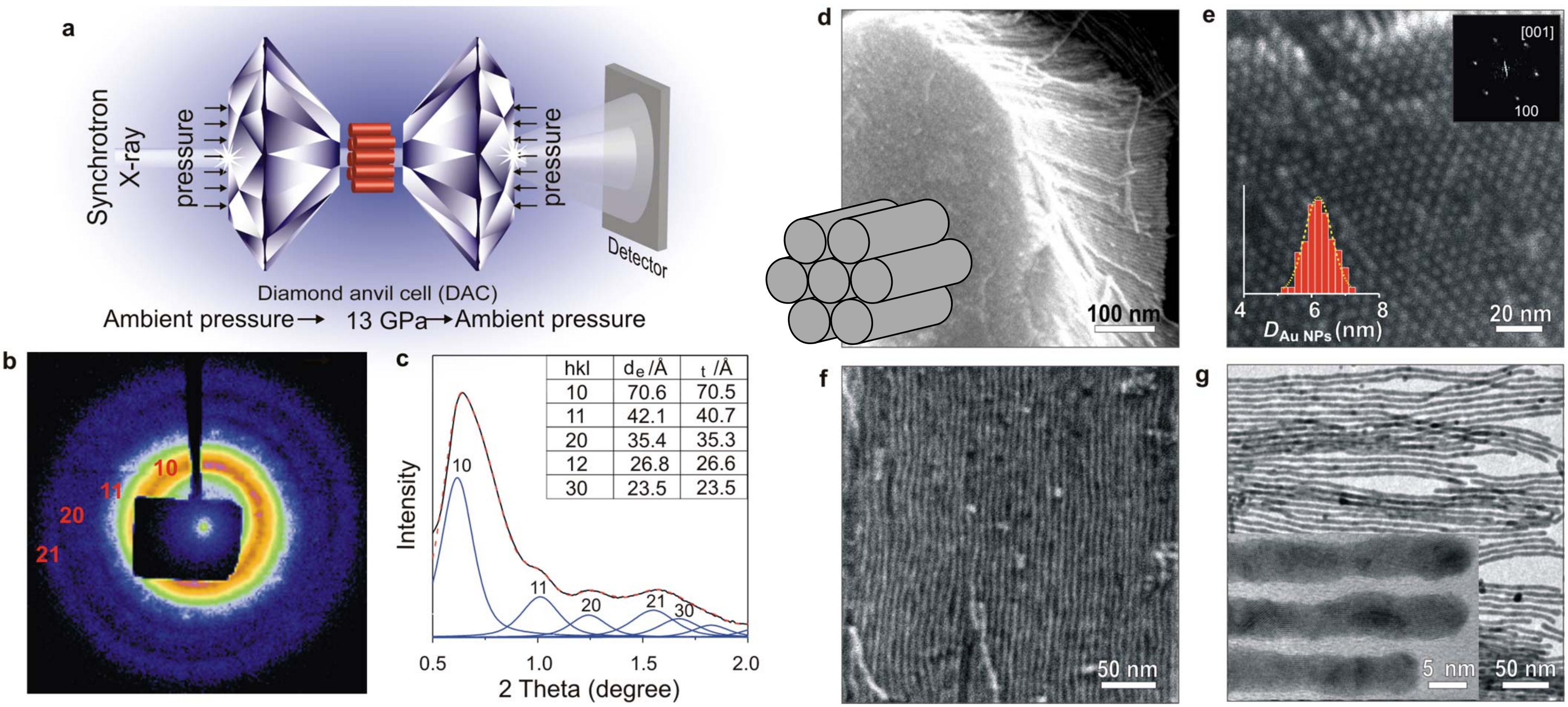
FAN: Develop new synthesis methods to fabricate multi-functional nanomaterials and to understand structure and properties



Balanced interparticle interactions



High pressure induces formation of nanowires



Wu H.*et al*. *Angew. Chem. Int. Ed.*, 49, 8431-8434, 2010.

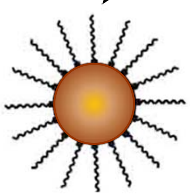
Self-assembled large area of nanoparticle coatings (R&D 100 Award + FLC Technology Transfer Award)

Self-assembled nanoparticle coatings as a manufacturing processes for scale up coating with good uniformity, no cracking/defects, thermal stability, and compatible with current fabrication processes.

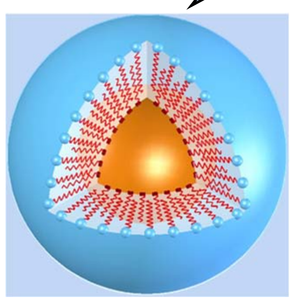
Metal nanoparticles
e.g., Gold, silver, etc.
Semiconductor nanoparticles
e.g., PbSe, Ge, CdSe etc.
Metal oxide nanoparticles
e.g., TiO_2, SiO_2, ZrO_2 etc.
Magnetic nanoparticles
e.g., FePt, $FeMnO_4$, etc.

Water-Soluble nanoparticles

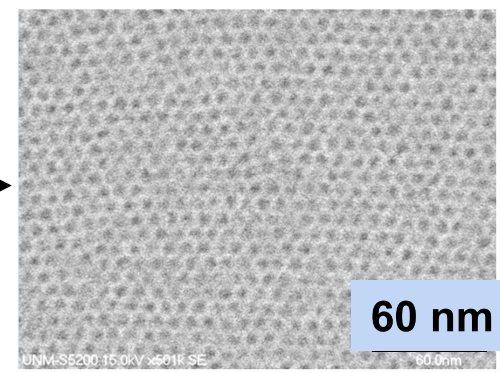
Tunable coating properties:
- Optical property (n, etc)
- Electrical property (σ, etc)
- External field activated property alteration
- Hydrophobic



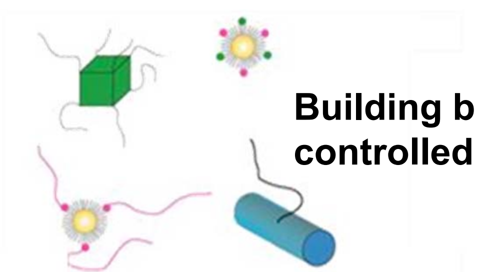
1, surfactant
2, lipid,
3, block copolymer



Engineering Process
- Self-assembly
- Directed-assembly
- Interfacial-assembly
- Rheological control
- more



Large area of robust, self-assembled nanoparticle films



Building blocks with controlled size and shape

Fan, et al. *Science* 2004

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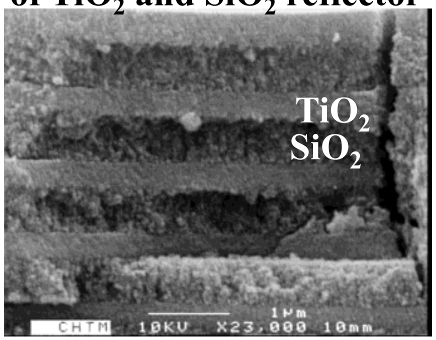
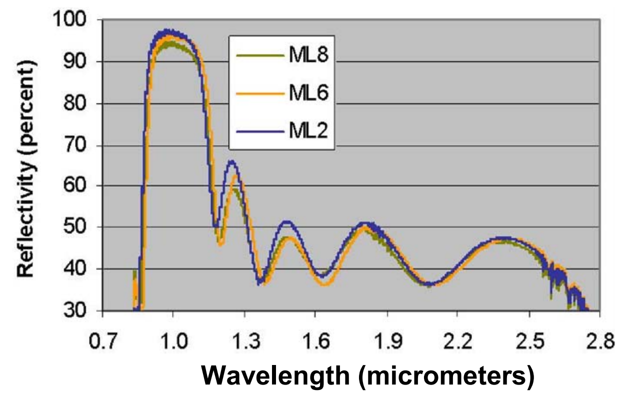
Nanoparticle Coatings to Near Infrared Reflectors (2007 R&D 100 Award)

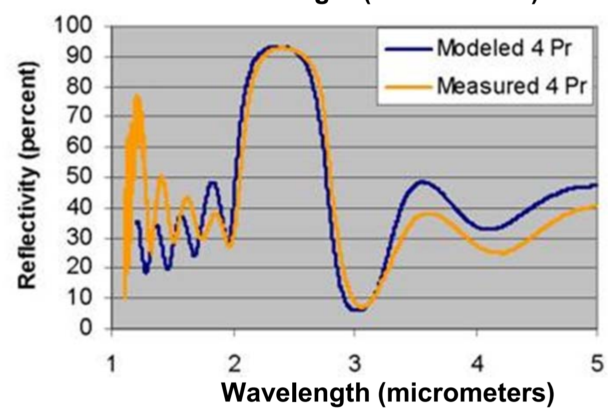
Quarter wave stacking of self-assembled nanoparticle films for near infrared reflectors, overcomes the harsh conditions from conventional processing (CVD, sputtering, etc) with improved functionality.

SEM image of quarter wave stacking of TiO_2 and SiO_2 reflector

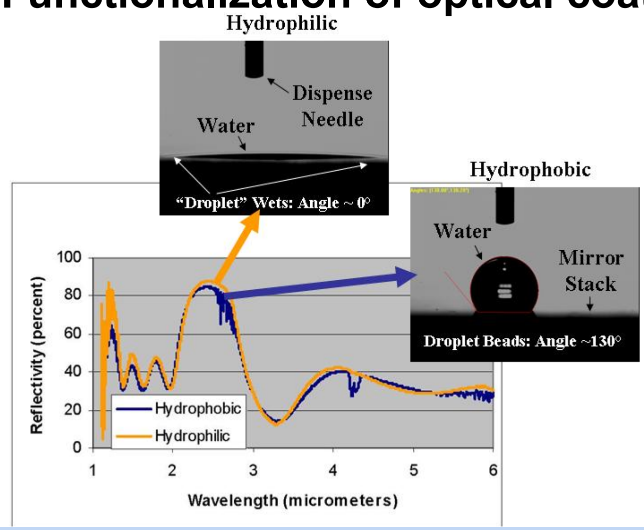


Reflectivity studies show high and reproducible reflectivity over controlled wavelength windows (1-2µm, 2-3µm, 8-12µm, etc)





Functionalization of optical coatings



Model design shows 99.9% reflectivity and address key manufacturing issue.

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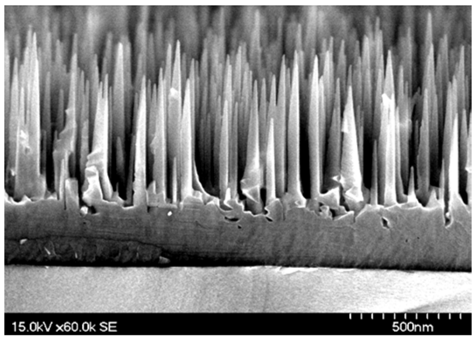
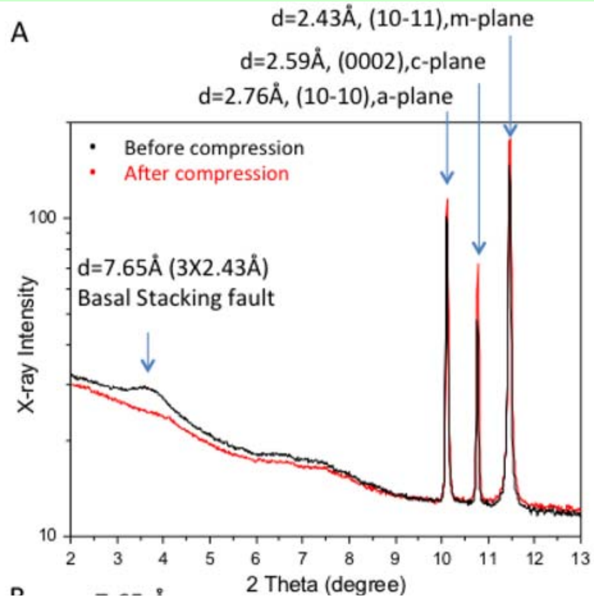
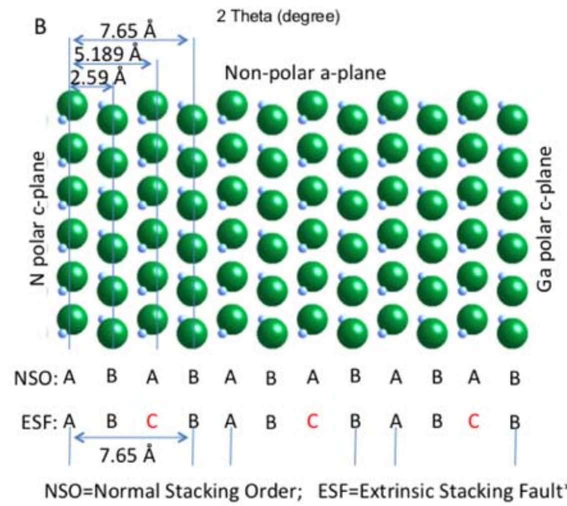
Pressure – induced defect reduction

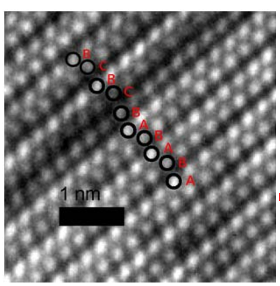
The results of high-pressure synchrotron x-ray scattering studies show that as low as 0.6 GPa compressive stress can dramatically reduce stacking faults and point defects in GaN nanowires, further based on an observed 60% reduction in defect-related yellow luminescence.

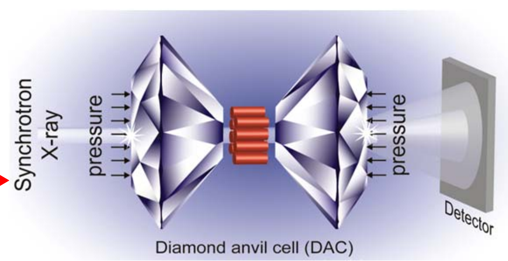


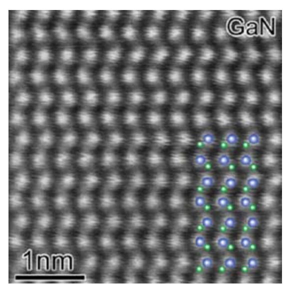
- **MOCVD: Emcore D125**
- **Substrates: 2” r-sapphire**
- **Precursors: TMGa/NH3/TMAl/TMIn**
- **NW Growth: Ni-catalyzed**
- **Growth temperature: 780°C**





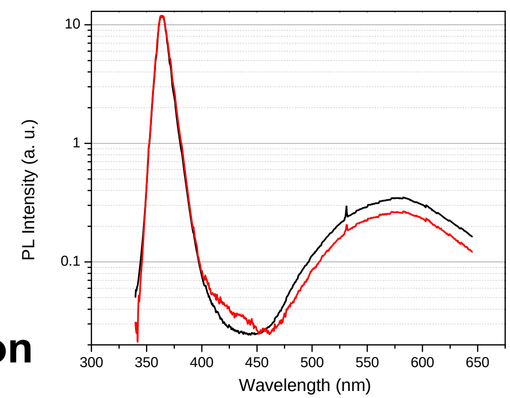






GaN with stacking faults Before compression

After compression



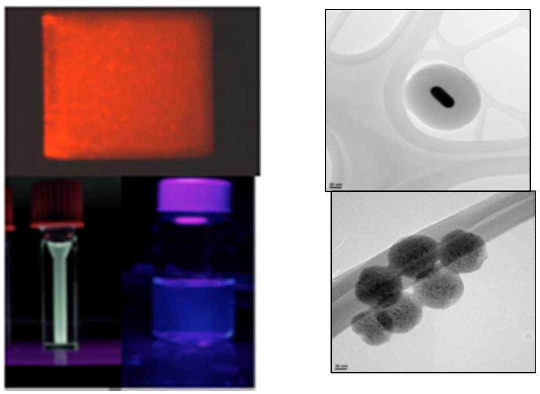
- **Defect related yellow luminescence**
- **Significant 60% reduction**

HERNANDEZ-SANCHEZ: Nanoparticles for Energy, Detection, & Interactions

SCIENCE • ENGINEERING • INNOVATION

Scintillators & Photonics

Understanding nanoscale radiation mechanisms & Uv-vis light interactions.

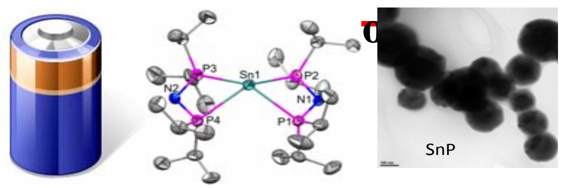


Chalcogenides

Infrared Imaging or Solar

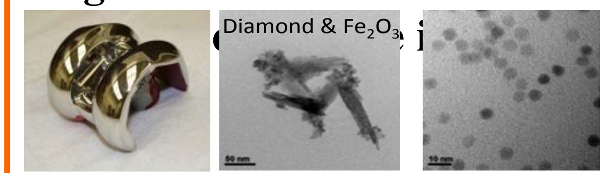
Phosphides

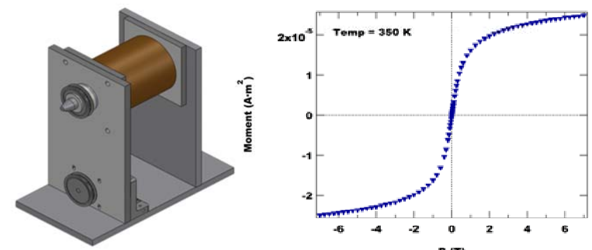
Anodes, Magnets,



Magnetic Assisted Polishing

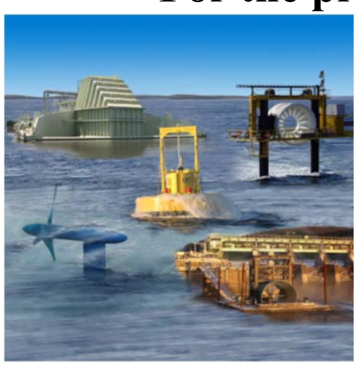
Magnetic & Abrasive Particles

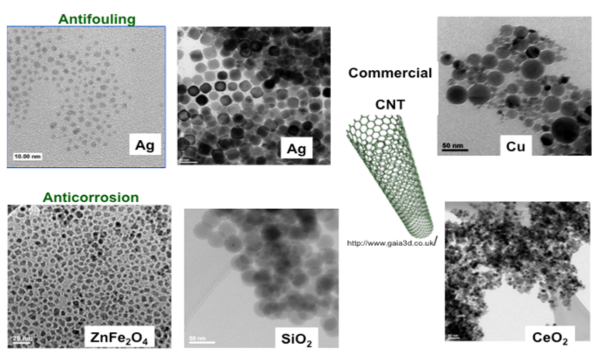


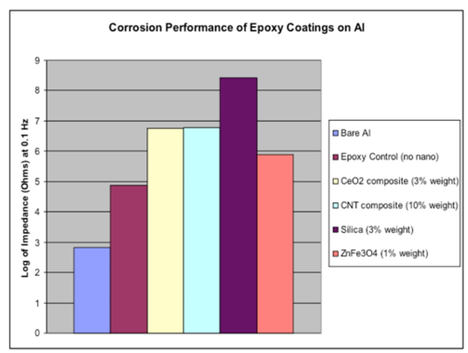


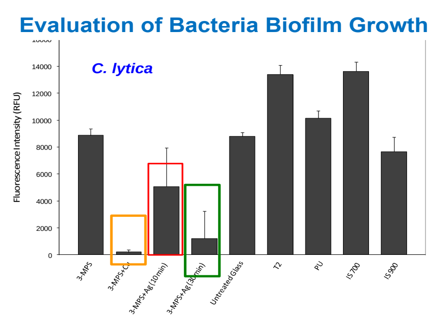
Protective Nanocoatings for Marine & Hydrokinetic Technology

For the prevention of corrosion, biofouling, sediment erosion, and mineral fouling



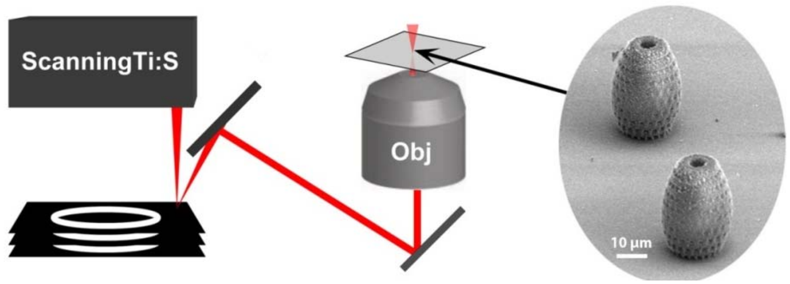






KAEHR: Laser-based lithographic methods for nanomaterial synthesis and patterning

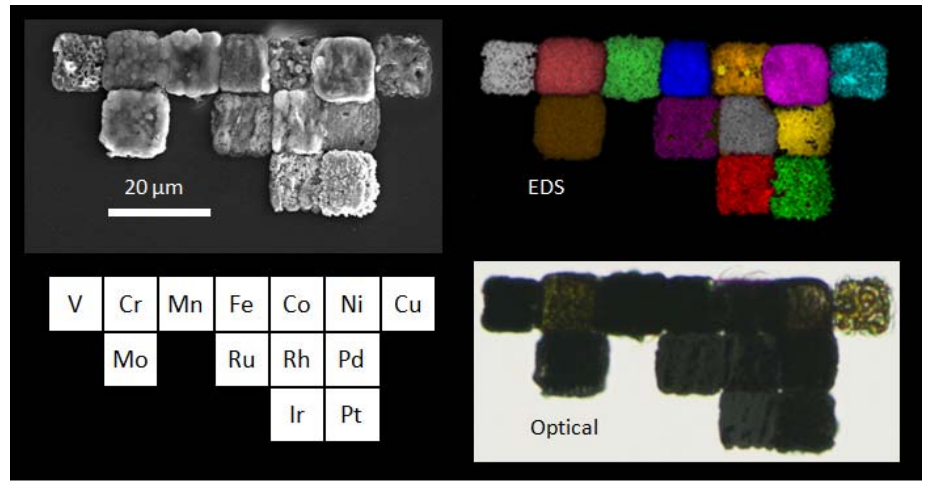
Mask-Directed Multiphoton Lithography (MPL)



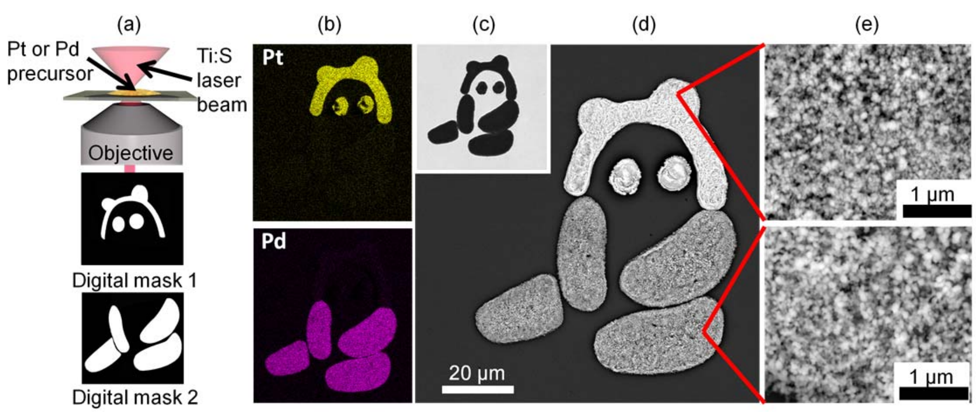
mask sequence **3D microstructure**

Kaehr and Shear, *JACS* 2007 129 (7),1904-1905.
Nielson, Kaehr and Shear, *Small*, 2009, 5, 120-125

For arbitrary patterning of nanostructured transition metals, metal oxides, and alloys

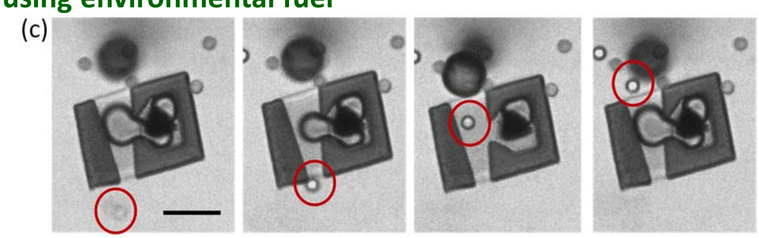


Example: Patterning of nanocrystalline Pt/Pd for…



…autonomous micro-devices driven by environmental cues.

Below: Nanocrystalline Pt confined in a asymmetric 3D hydrogel chamber directionally pumps micro-particles using environmental fuel



Zarzar, L. D.; Kaehr, B et al *JACS* 2012, 134, 4007-4070.

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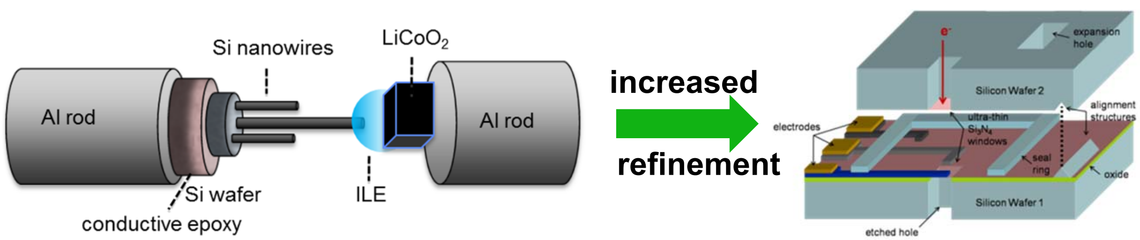
ZAVADIL: Precision Nanoscale Electrochemistry

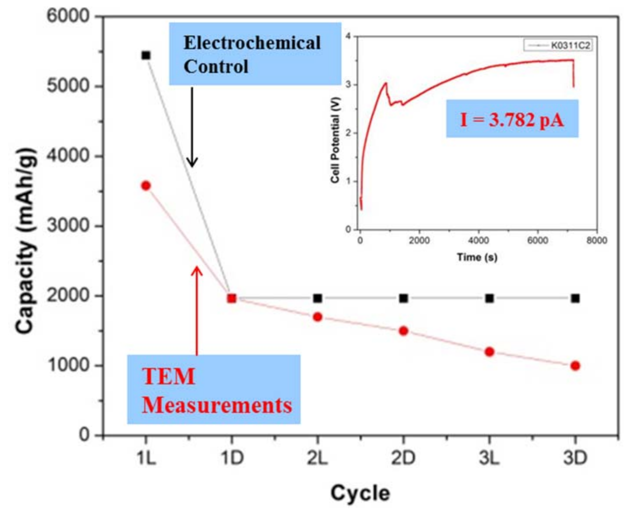
Nanoscale materials promise improvements in battery performance

- **capacity and energy density through nanoscale alloy formation (Li –Si)**
- **power density through decreased charge transport distances**

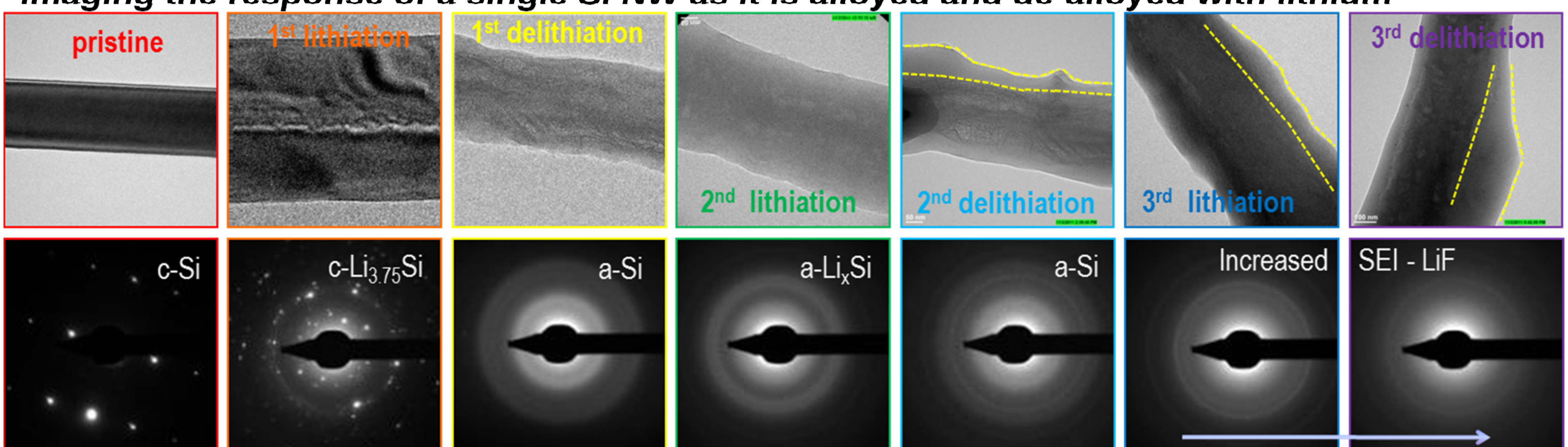
New understanding is required of how size impacts material performance and reliability

Goal: develop nanoscale diagnostics to explore in operando material response➡*quantitative electrochemical tools + TEM*



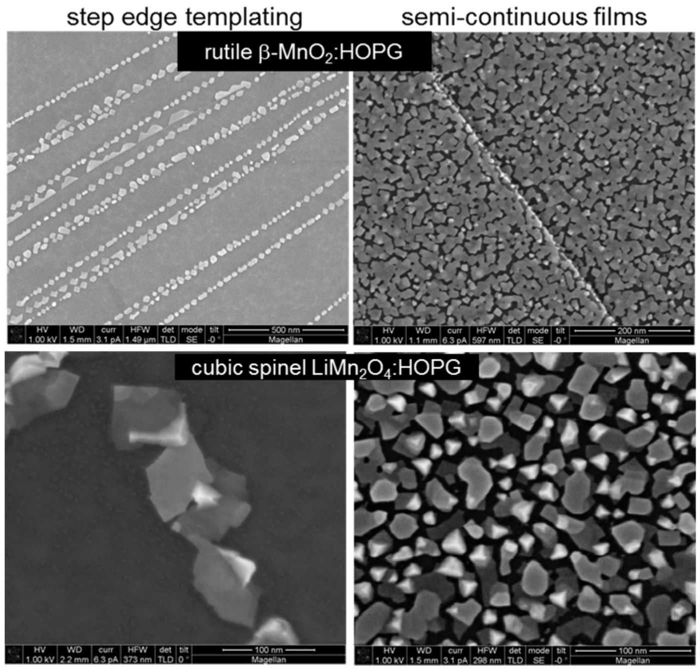


imaging the response of a single Si NW as it is alloyed and de-alloyed with lithium

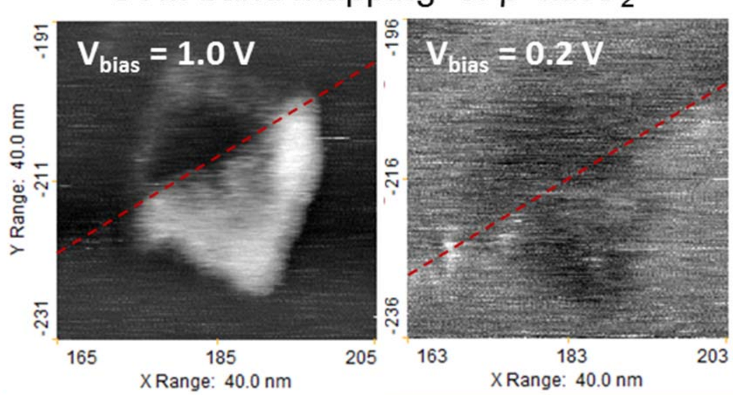


Electrochemical Dynamics using Model Oxides & Scanning Probe Microscopy

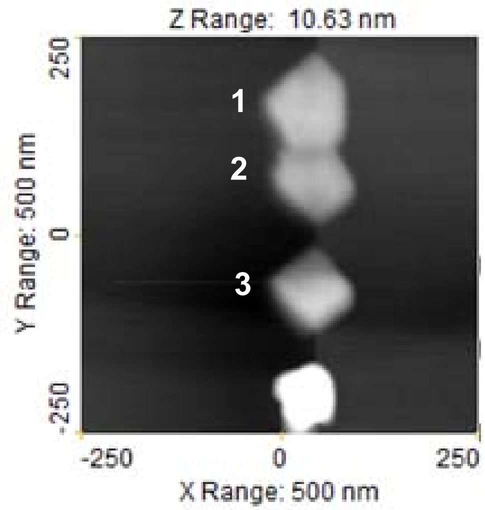
Creating populations of energy storage particles on carbon surfaces

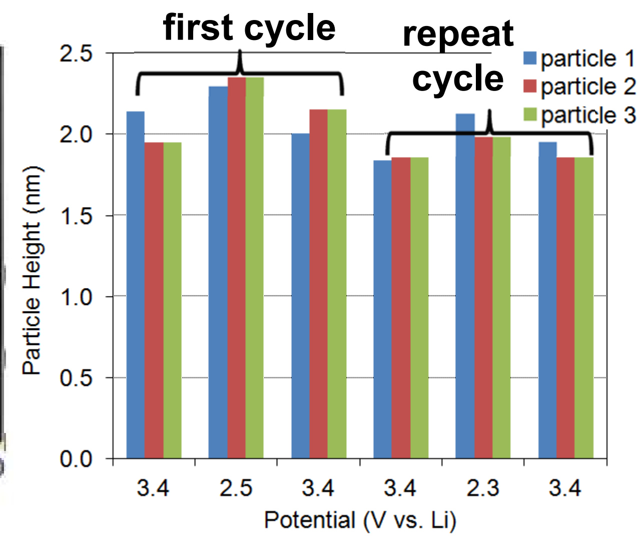


STM band mapping of β–MnO$_2$



Monitoring particle response toward Li$^+$ in an electrolyte





Observing 10% a,b axis expansion in real time using electrochemical AFM

What we learn:

- **factors influencing charge storage kinetics**
- **degradation mechanisms**
- **signatures of compromised reliability**

We develop the knowledge required for improved energy storage system reliability

Questions?

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