LA-UR-12-23400
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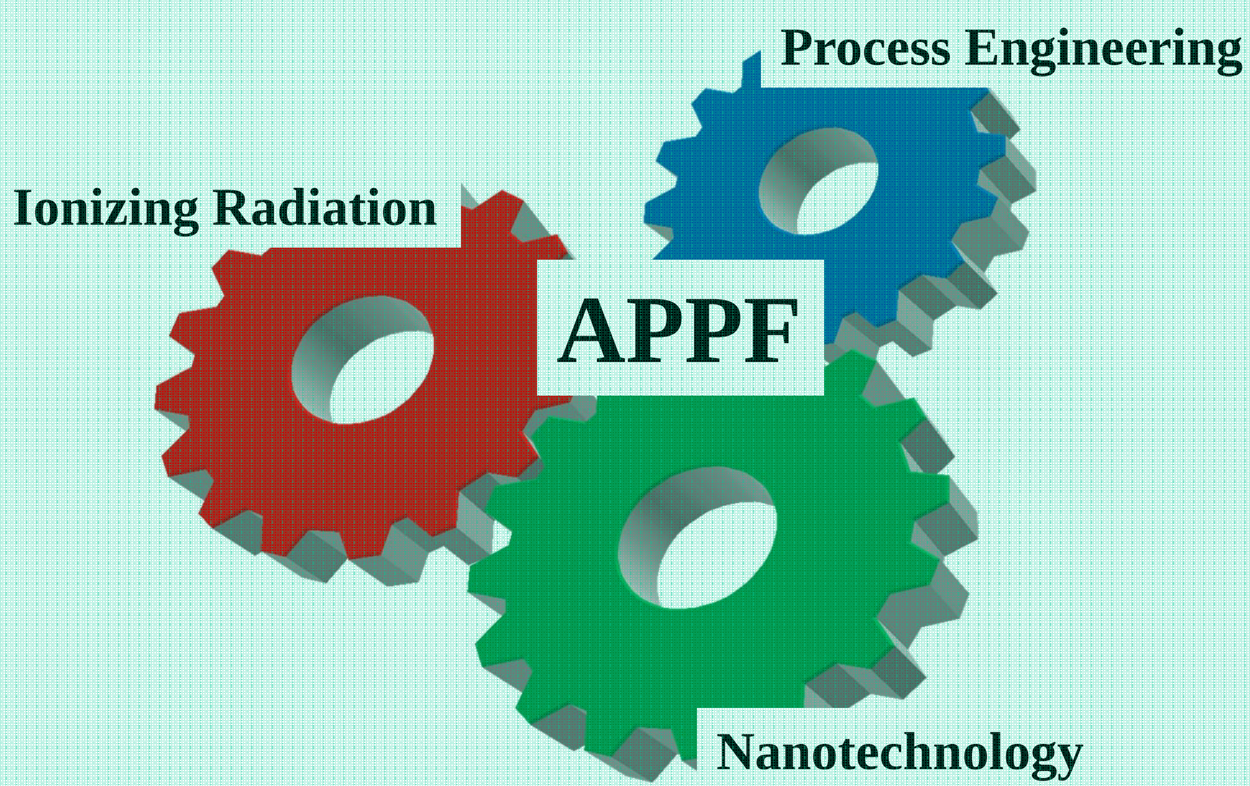
Title: Advanced Polymer Processing Facility

Author(s): Muenchausen, Ross E.

Intended for: Advanced Manufacturing Workshop, 2012-07-25 (los Alamos, New Mexico, United States)

Advanced Polymer Processing Facility (APPF)



Ross E. Muenchausen, MST-7

Advanced Manufacturing Workshop, Los Alamos, NM, July 25-26

Los Alamos
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MDI
Materials Design Institute
Los Alamos National Laboratory
University of California, Davis

Advanced Polymer Processing Facility (APPF)

Outline

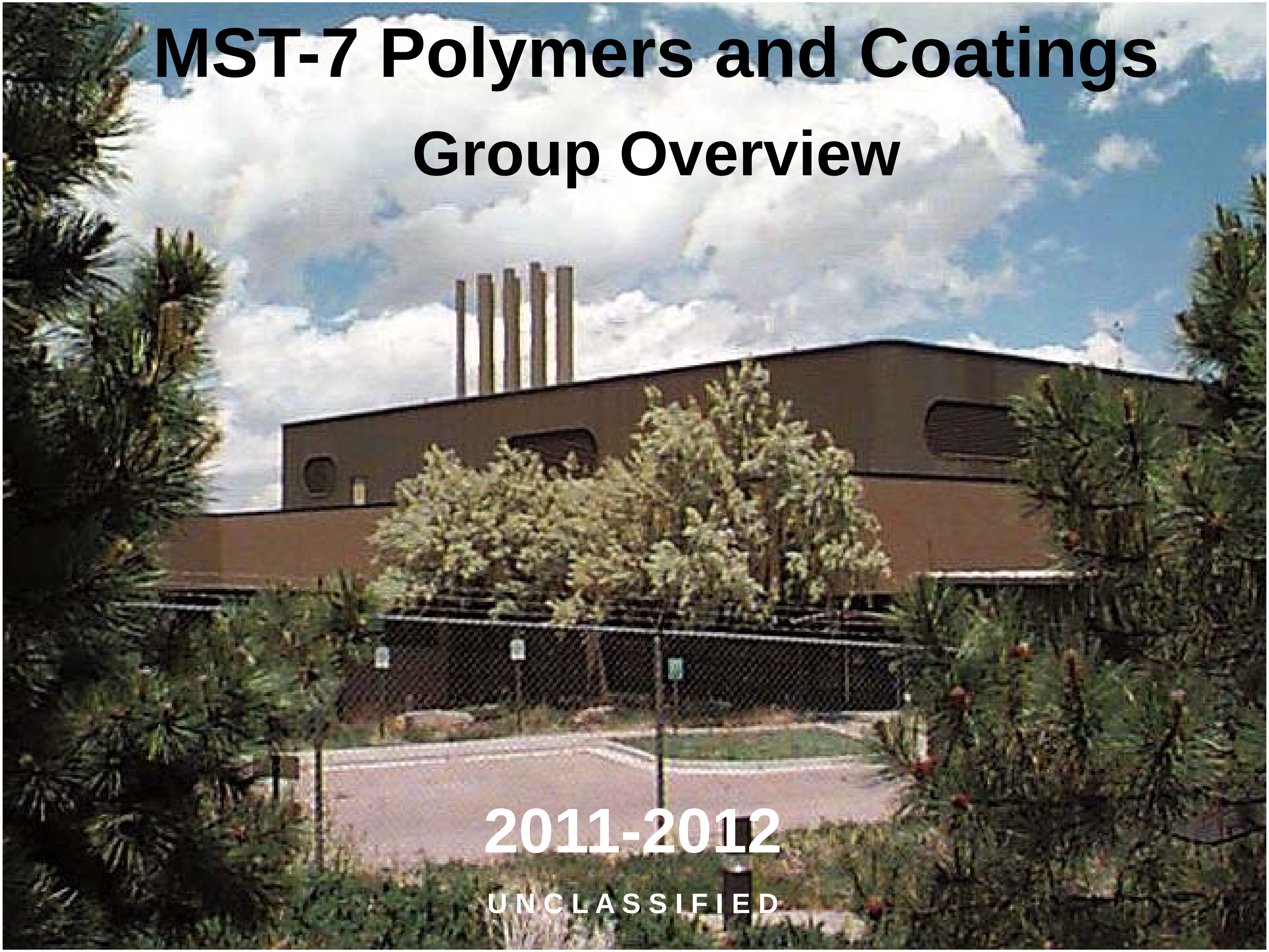
MST-7 Group overview
Laboratory Materials Pillars/ MaRIE overview
APPF concept description
Summary

MST-7 Contributors

Mike Blair, Rob Gilbertson, Chris Hamilton, Markus Hehlen, Andrea Labouriau, Andy Nelson, Kim Obrey, Brian Patterson, Dom Peterson, Derek Schmidt, Igor Usov, Cindy Welch

MST-7 Polymers and Coatings

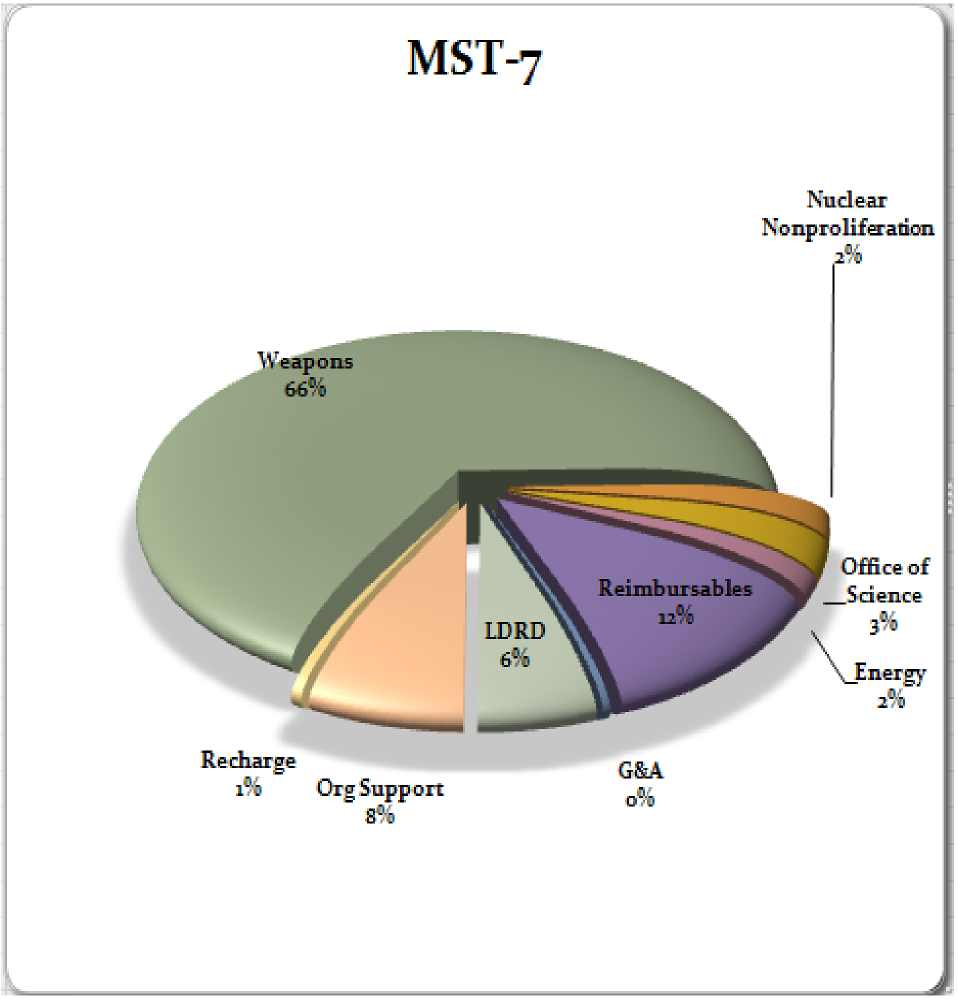
Group Overview



2011-2012

UNCLASSIFIED

MST-7 FY12 Operating Budget: $18.1 M



FUNDING BREAKDOWN:

33 % stockpile and surveillance (NW)
33% science campaigns (ICF, HEDP)
15% WFO (GS, TT)
10% basic research (LDRD, BES)
9% indirect

STAFFING BREAKDOWN:
53 employees

22 Sci. & Eng.
16 Professional
15 Postdoc & Students

About equal split between Science & Engineering focus areas.

Immolative Polymers

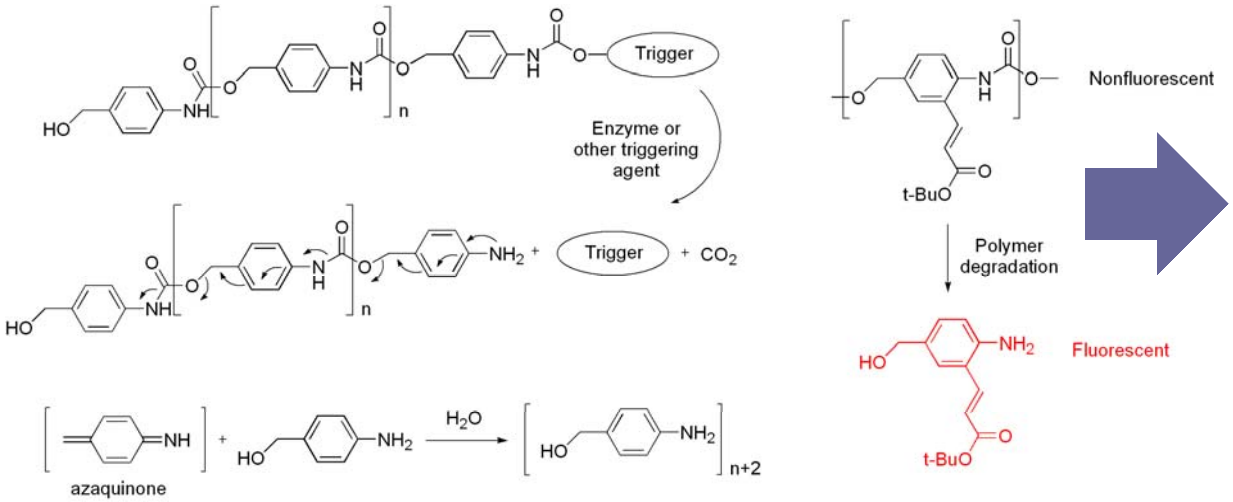


Figure 1: Self-immolative polymer degradation.

Can be triggered in multiple ways

Enzyme, Ionizing radiation, light, chemical reaction

Many other possible triggers

May include immolative branches

Potential in sensing, drug delivery, foams, etc.

Current proposal out include ER, nanoporus foams, latent fingerprint visualization

Ongoing LANL ER proposal

Triggered by ionizing radiation

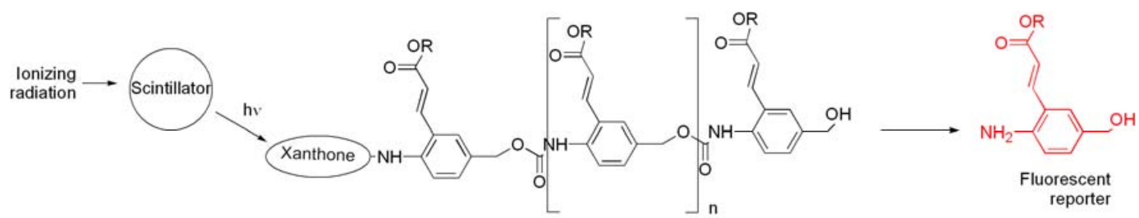
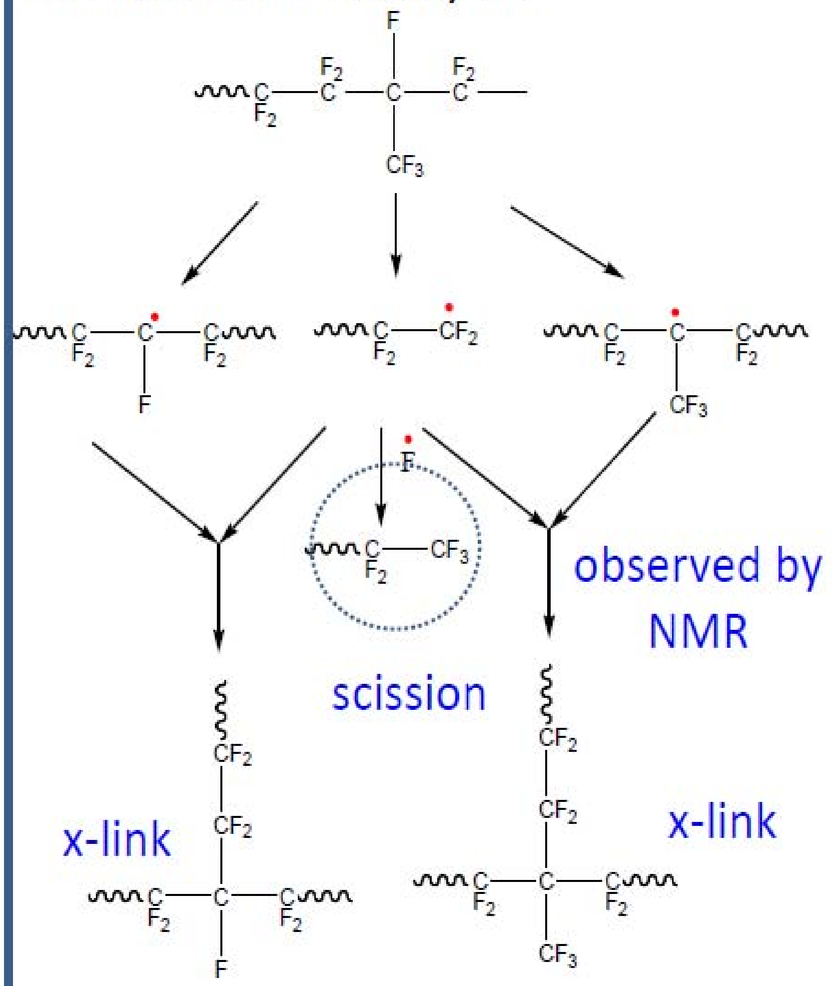


Figure 2. Proposed self-immolative polymer system for dosimetry.

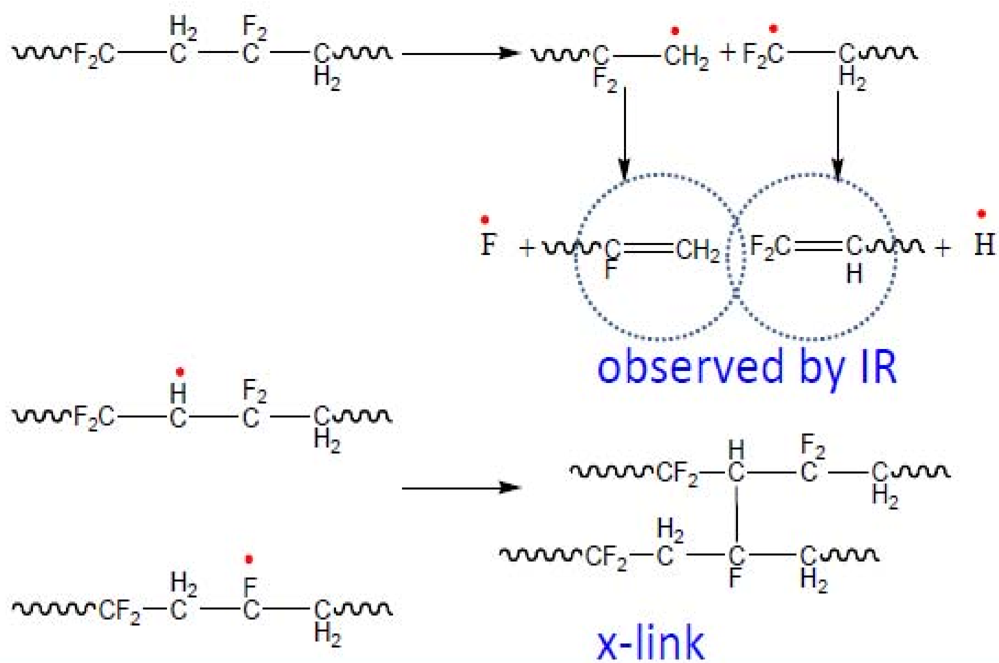
R. Gilbertson (MST-7), J. Boncella (MPA)

Mechanisms & Gamma Tolerance

Possible **PHFP** radiolysis:



Possible **PVDF** radiolysis:



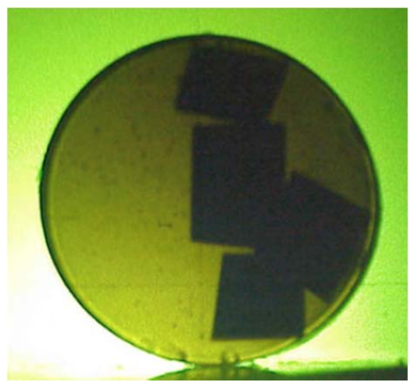
Gamma Tolerance:

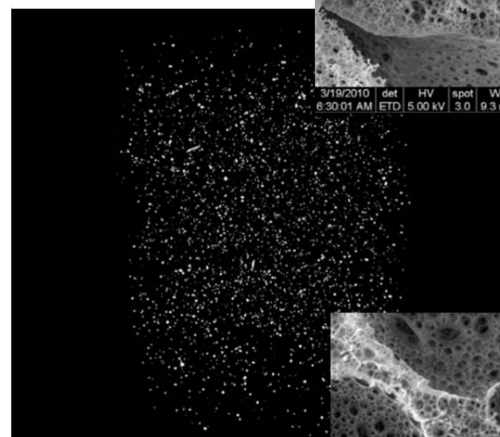
KelF-800 (PCTFE, PVDF) > **Viton A** (PVDF, PHFP) > **THV 220G** (PVDF, PHFP, PTFE)

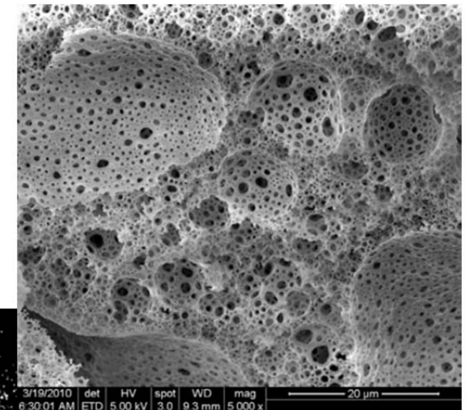
PCTFE > PVDF > PHFP >PTFE

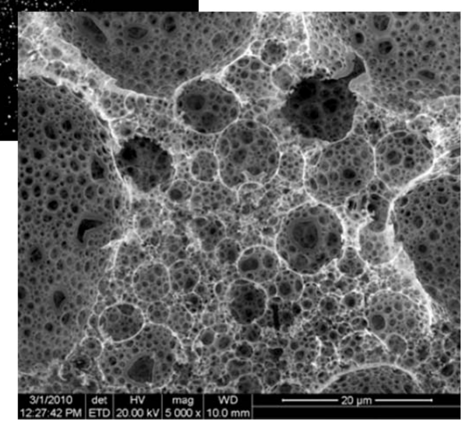
Doped Foams and Aerogels for ICF Targets

- **Synthesis of small targets needed for ICF applications**
- **Metal particles/ foils dispersed in silica aerogels are needed to affect radiation flow in target materials**
- **Halogen doped PS-DVB polymer foams**









L to R: foils in SiO2, 3D µxCT reconstruction of particles in SiO2,, SEMs: polystyrene and Cl doped PS foams.

C. Hamilton, B. M. Patterson, D. W. Schmidt, K. A. DeFriend Obrey (MST-7)

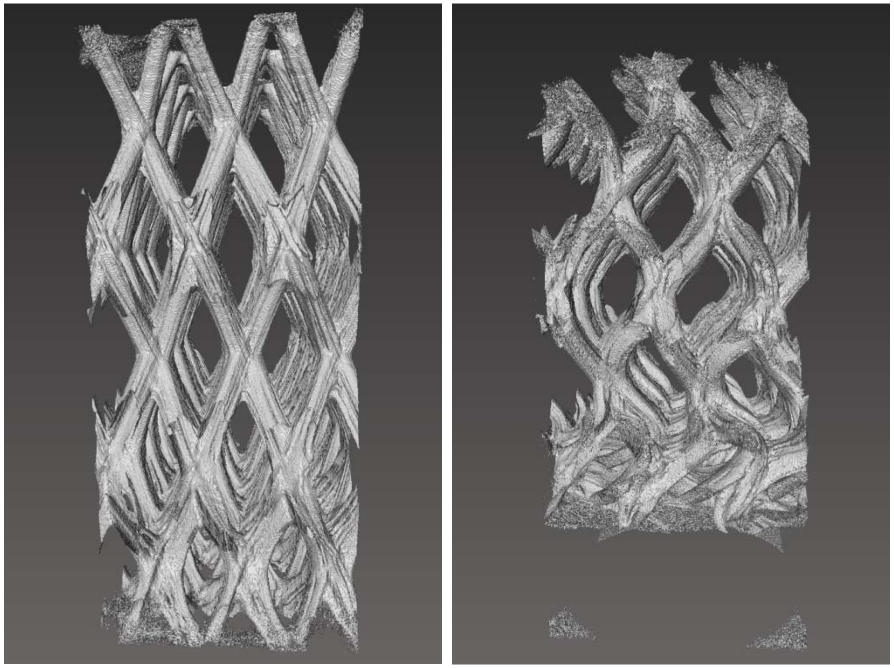
50 nm resolution nano-CT instrument capability

Purchased end of FY 11, fully operational Q1 FY12

New data collected using current micro-CT instrument shows 3D behavior of polymer lattice response to compression

Uncompressed

Compressed 3 mm



Lattice imaged uncompressed (1-cm thick) and re imaged after compressing in 0.5 mm steps up to 5 mm total compression.
Material cells bend and rotate without any brittle fracture

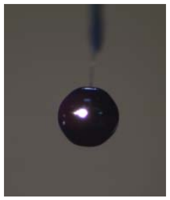
B. M. Patterson, K.C. Henderson, D. Capelli (MST-7)

A few examples of FY11-FY12 Omega experiments

ABEX: Asymmetric experiment

Purpose: To test the affect of asymmetric drive on late time hydrodynamic and burn behavior in the capsule. P8 modulations were machined on the capsules: amplitudes of either 2.5 um, 5 um and 10 um.

First ever machined modulated capsule.



Completed target with 5um modulations

DP-EOS: Dense Plasma EOS

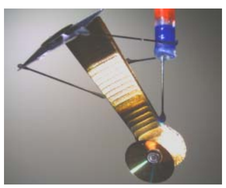
Use shock and release technique for measuring EOS of dense aluminum plasma.

First ever aerogel machined to this thickness.

Shear

Develop & conduct laser driven experiments examining the effect of shear and deformation on complex hydro.

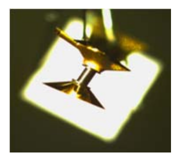
Targets are similar in complexity to Off-Hugoniot/Agex-EOS



Colliding Shock

Develop and conduct laser driven experiments examining the effect of strong shock on mix

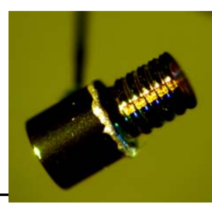
Be spools with machined features and foam inserted into spool.



NIF-5

Improve understanding of radiation transport in radiatively-driven experiments

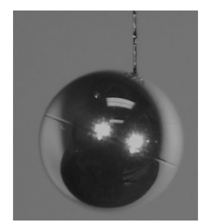
Omega platform for Pleiades NIF experiments



DIME: Defect Implosion Experiments

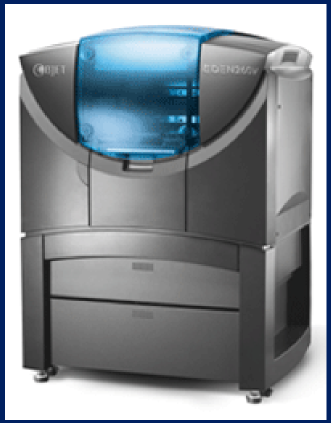
Interface velocity under polar direct drive (PDD) conditions is the first step toward examining ICF feature-dependent hydrodynamics and burn

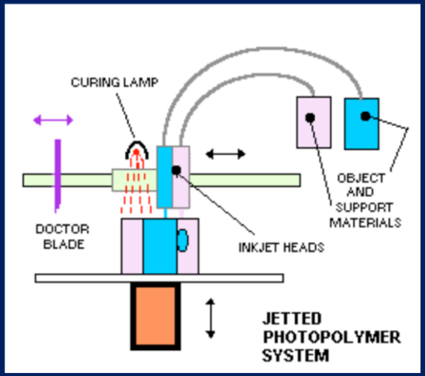
Platform development for A of I NIF experiments



D. W. Schmidt, K. A. DeFriend Obrey (MST-7)

Rapid Prototyping





3-D Polyjet Prototyping Printer

Process

- The jetting heads deposit a single super-thin layer of photopolymer onto the build tray
- After building each layer, UV bulbs immediately cure each layer
- The internal tray moves down with extreme precision and the jet heads continue building until the model is completed

Technical Specifications

- STL or SLC input file format
- X-Y resolution 42 µm
- Z resolution 16 or 30 µ m
- Minimum wall thickness 0.6 mm (24 mils)
- Build envelope is 10 in x 10 in x 7.9 in
- Materials: family of rigid or flexible resins
- Allows for unattended builds up to 72 hr

Costs (2012)

- Object material: $0.3 – 0.5/cc
- Support material: $0.15/cc
- Machine Time: $3-5/hr
- Pre-processing: 5-15 FTE-min
- Post-processing: 15-60 FTE-min

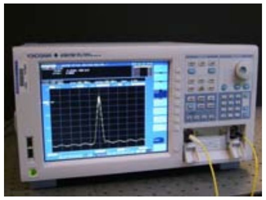
MST-7

Optical Sensors / Forensics

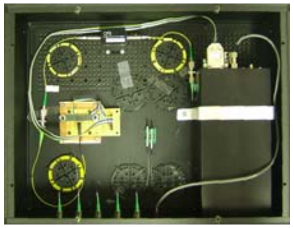
Fiber Optic Sensors

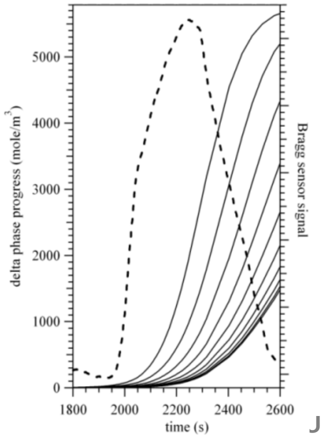
Combining fiber-optic and opto-electronic components with custom dielectric filters to enable new sensors for weapons research and Homeland security applications

Fiber-Optic Laboratory



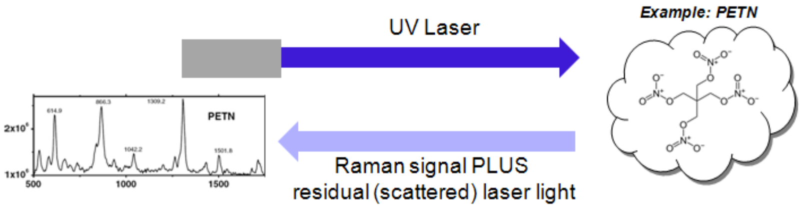
OPTIS: A Fiber-Optic Pressure & Temperature Sensor for the Joint Munitions Program

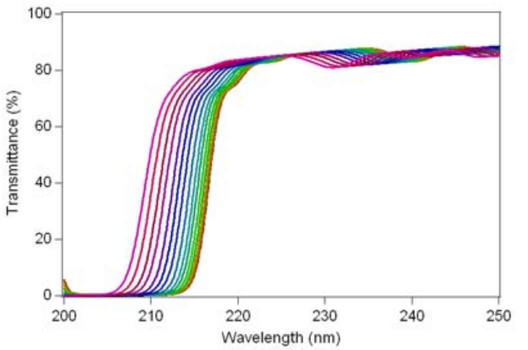




Standoff UV Raman Spectroscopy

Pushing the state-of-the-art standoff Raman spectroscopy by working in the ultraviolet and fusing the optical hardware with Multivariate Analysis (MVA) algorithms





Custom UV low-pass filter optimized for standoff detection of explosives

M. Hehlen, K. Hubbard (MST-7)

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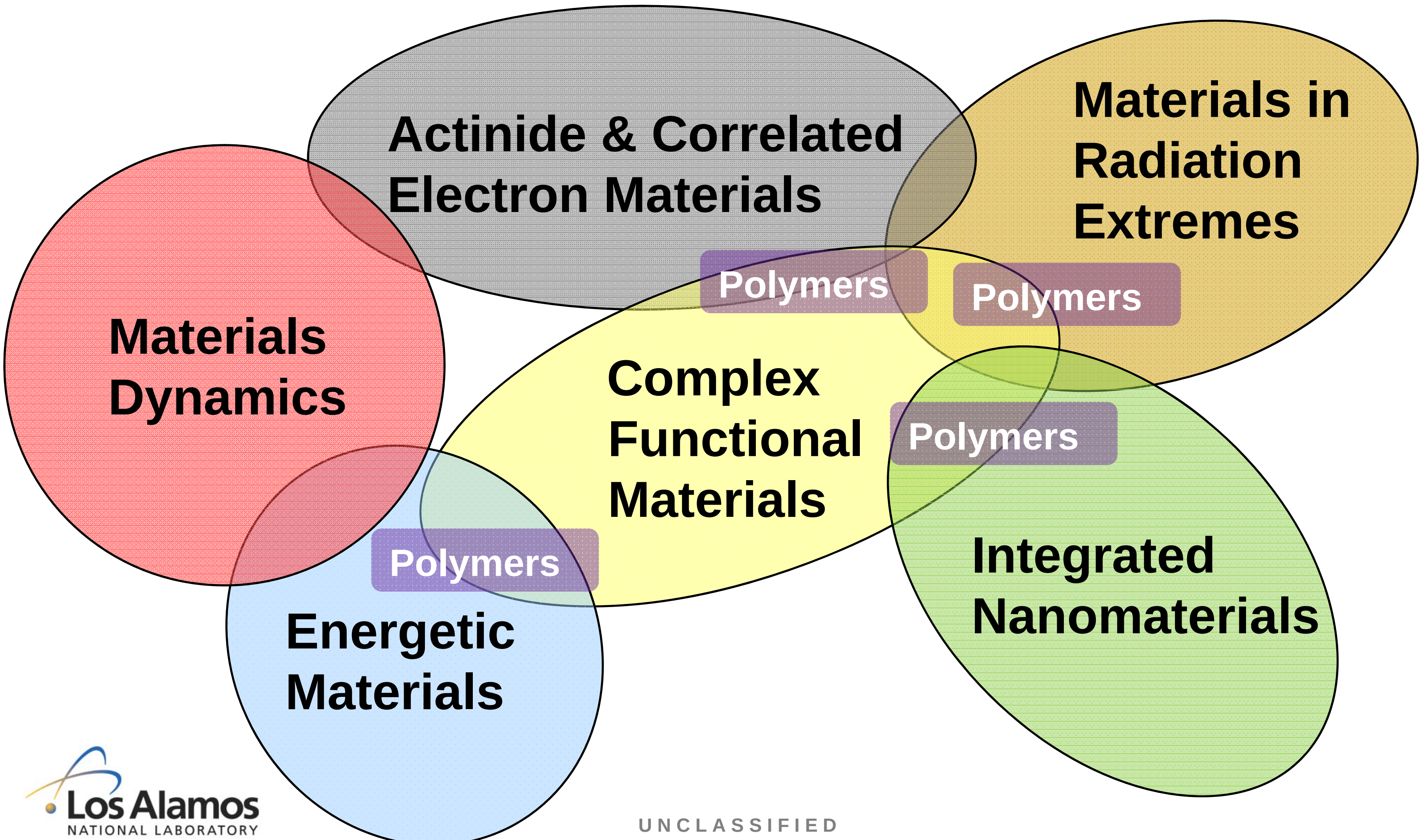
Development of Fuels Research Laboratory at LANL

- Development of Fuels Research Laboratory (35-455) driven by needs of DOE-NE Fuel Cycle Research and Development program
- Capabilities include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), laser flash analysis (LFA), and dilatometry from cryogenic temperatures to 2600 K
- Focus is development of ceramic nuclear fuels (UO_2 + derivatives, ThO_2, UN, etc)
- Numerous advanced techniques are being pioneered at LANL with applications to fuels and beyond
- Structural nuclear materials, engineering applications, and basic science investigations are also of interest
- Non-DU operations underway, U and Th operations started January 2012

A.T. Nelson, J. T. Dunwoody (MST-7), K. McClellan (MST-8)

Six ‘Areas of Leadership’ span the Materials Pillar



Grand Challenges for Engineering

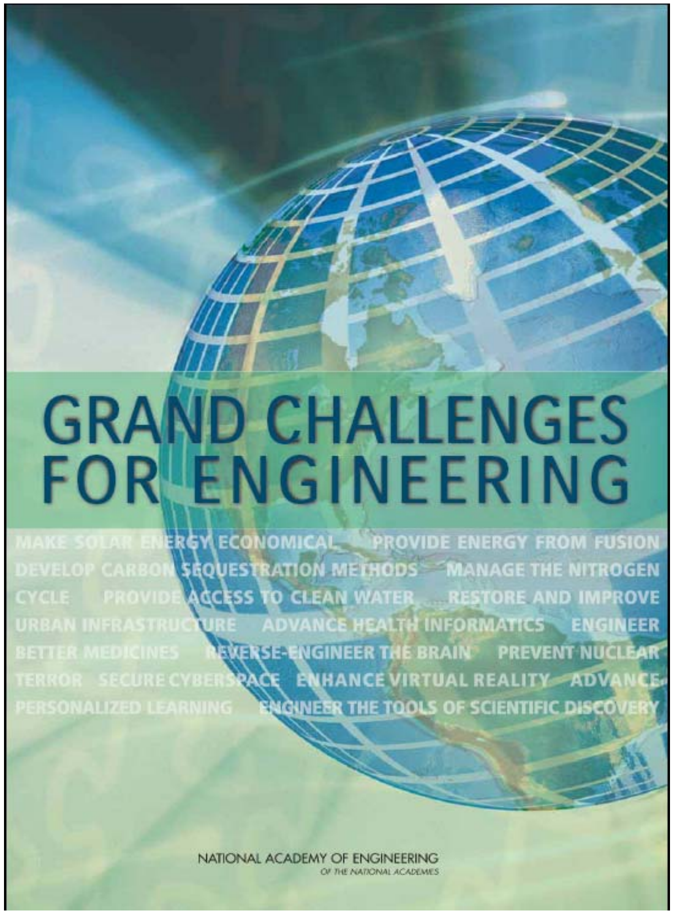
National Academy of Sciences List:

1. Make solar energy economical

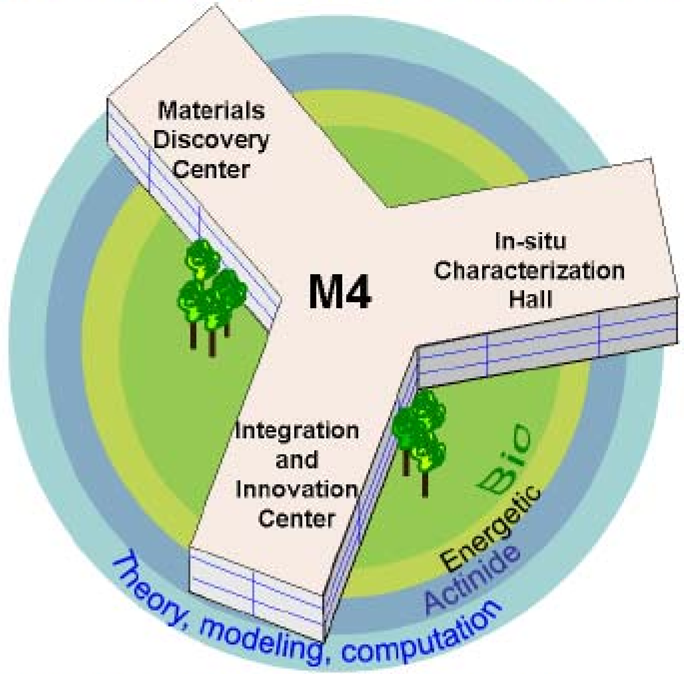
2. Provide energy from fusion

3. Provide access to clean water

…



Materials Discovery: The MaRIE-M4 Facility



T Mark McCleskey (focus lead)
David Teter (Chairman of the Board)

BOD: John Bingert, Sherri Bingert, Dana Dattelbaum, Deanne Idar, Ed Kober, Ken McCellan, Edward McKigney, Kevin Ott, Jeanne Robinson, Rich Schaller, Darryl Smith, Toni Taylor

Contributors: Frank Alexander, Sasha Balatsky, Eric Bauer, Rico DelSesto, Bob Field, Alp Findikoglu, Michael Fitzsimmons, Bob Hackenberg, Pat Hochanadel, Dan Hooks, Mike Hundley, Quanxi Jia, Tom Lienert, Turab Lookman, Amit Misra, Mike Nastasi, Thomas Picraux, Roland Schulze

M4: Fundamental effects of radiation on nanostructures: One example:

- A current driver for radiolytic production of nanoparticles (NPs) is to achieve narrow (± 5%) size distributions.
- Size-dependent morphology and thermodynamic stability must be characterized for functionalized NPs, e.g. core-shell structures.
- Requires close integration with advanced spectroscopies and computational methodologies (M4) to translate function→structure relations to advanced manufacturing pathway.

Singlet Oxygen Water Treatment

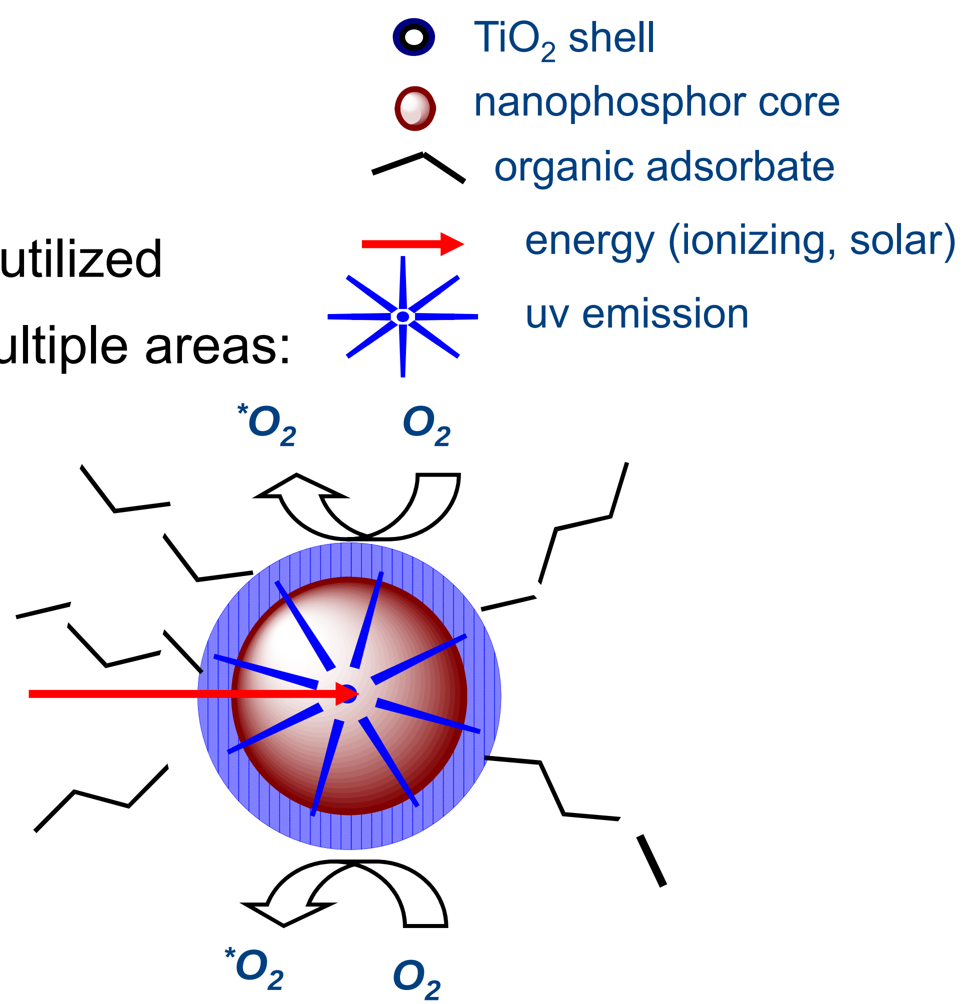
Advantages of Core-shell Approach:

- All inorganic (no photobleaching)

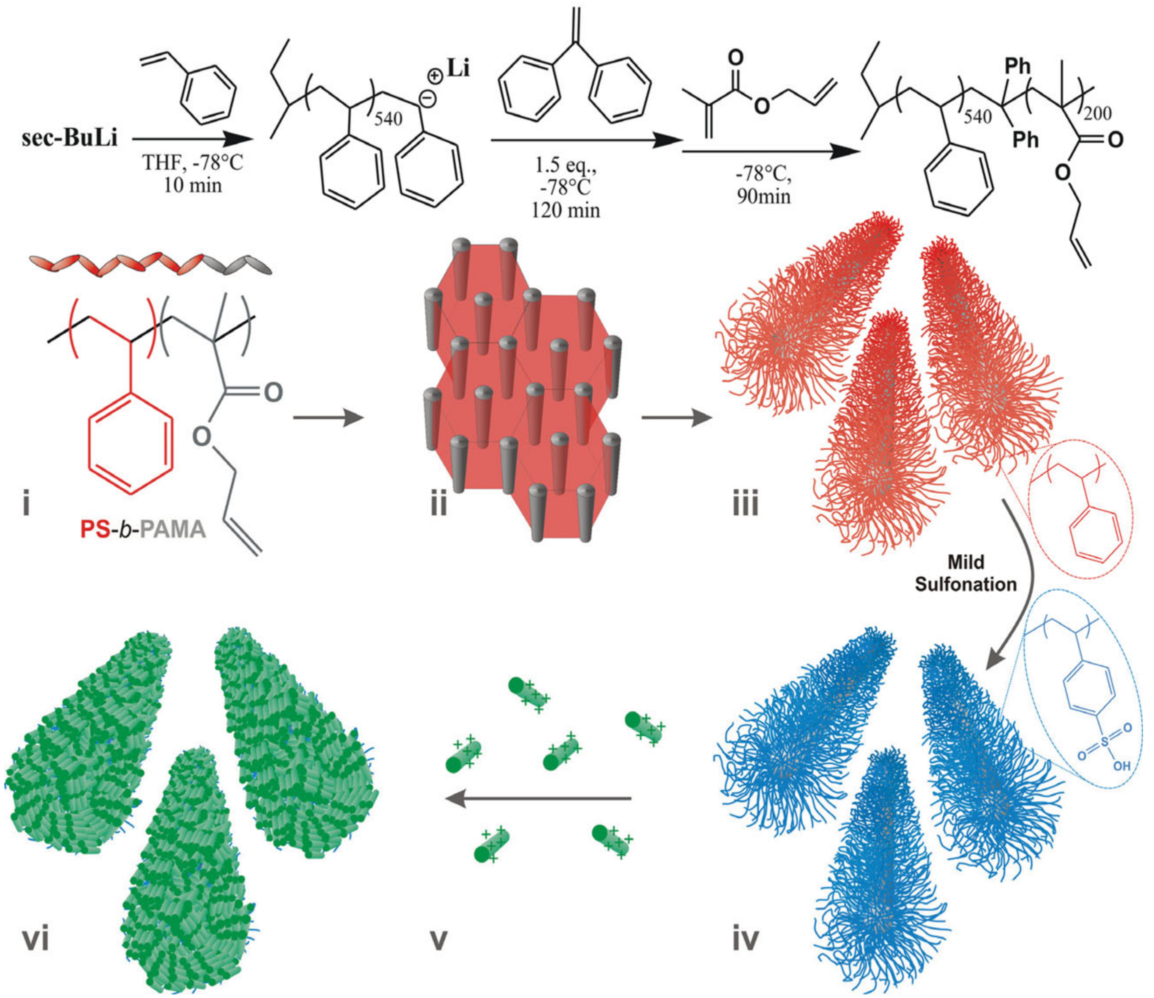
- Broad range of input energies can be utilized

- Basic technology can be applied to multiple areas:

  - wastewater treatment
  - manned space missions
  - chem/bio decontamination
  - cancer therapy
  - fine chemical synthesis

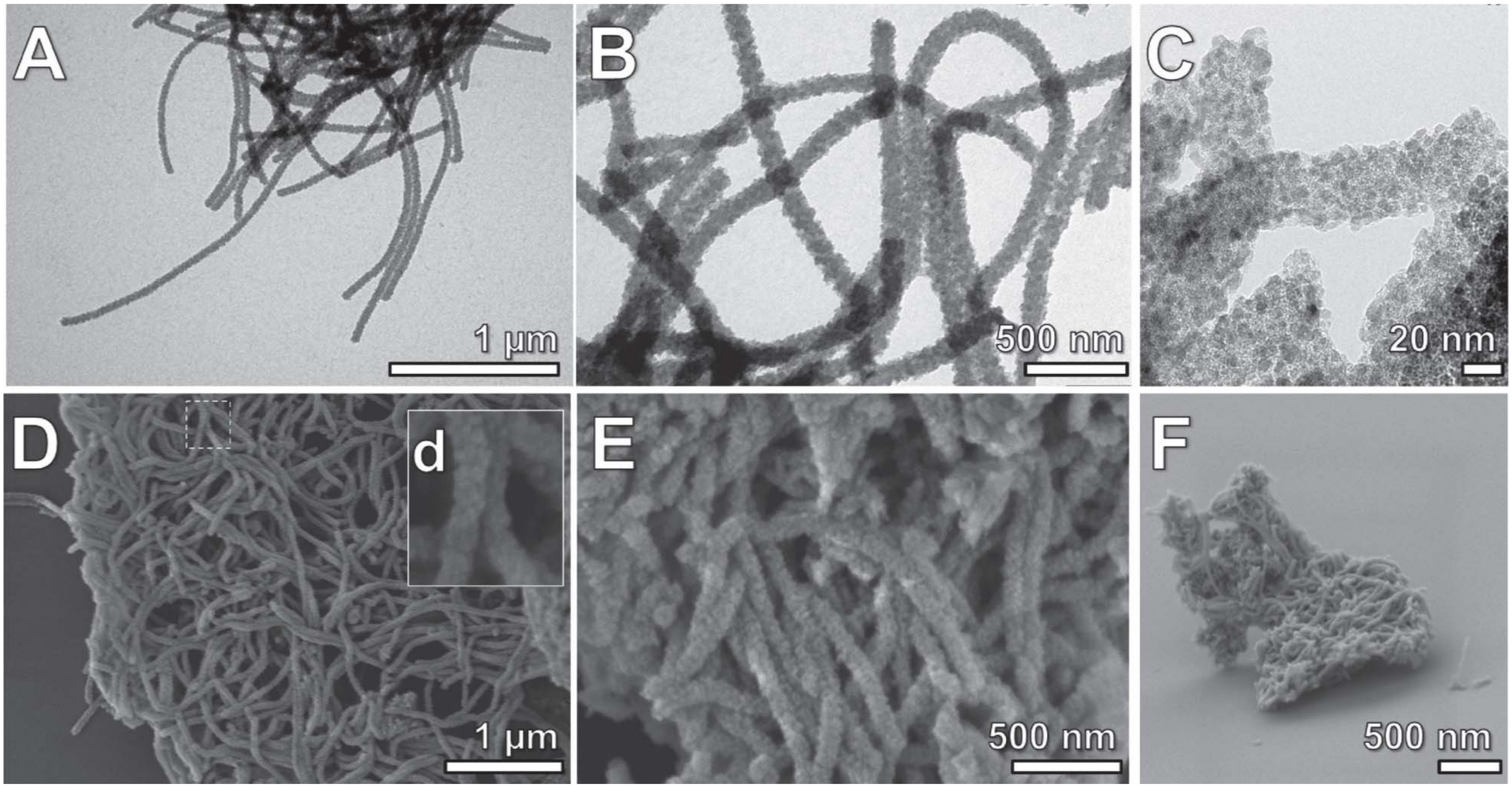


TiO2 Nanomaterials from Polymer Templates



(Müllner, M.; Lunkenbein, T.; Miyajima, N.; Breu, J.; Müller, A. H. E. *Small, In Press.)*

TiO2 Nanomaterials from Polymer Templates

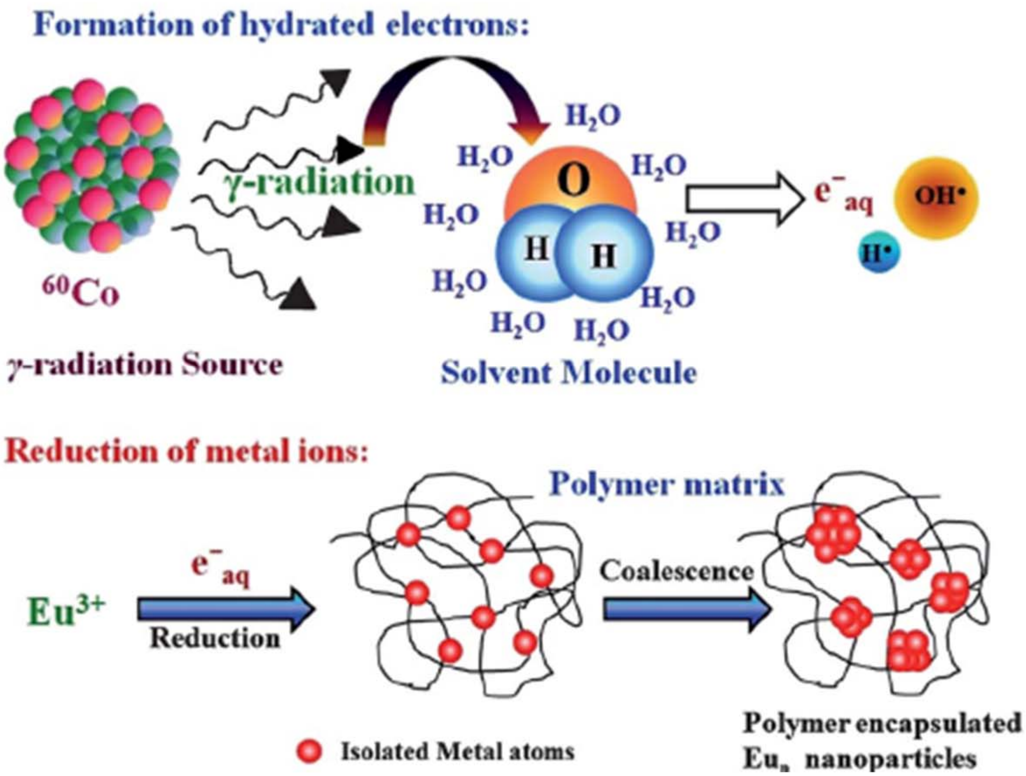


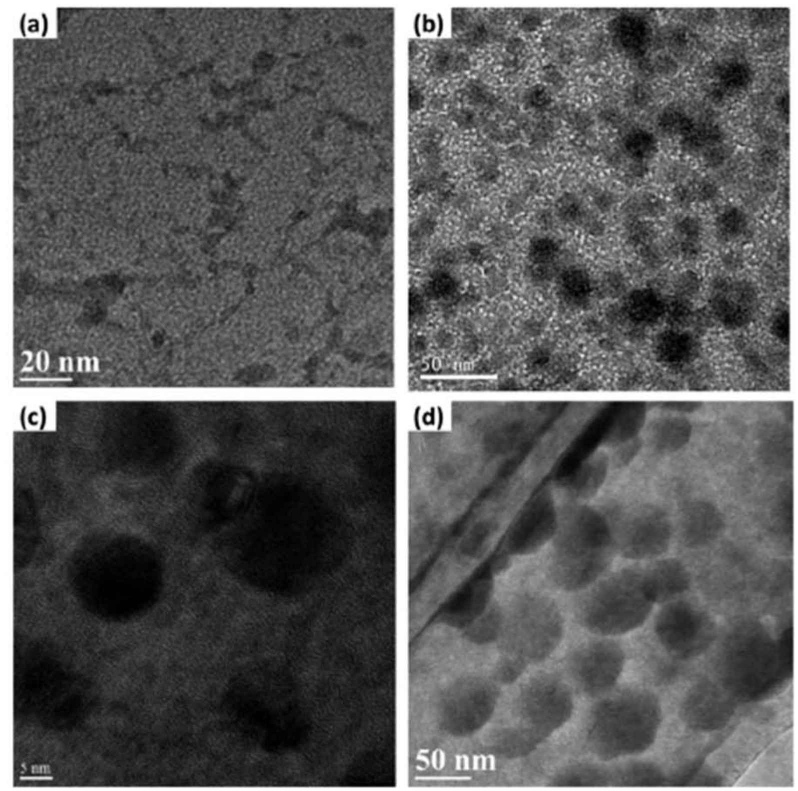
A–C) TEM images of as-synthesized anisotropic rutile nanostructures, D) SEM images of as-synthesized rutile nanowires, and E,F) calcined rutile nanowires on a tilted sample stage (75 ° viewing angle). (Müllner, M.; Lunkenbein, T.; Miyajima, N.; Breu, J.; Müller, A. H. E. *Small, In Press.)*

M4: Fundamental effects of radiation on nanostructures

- Radiolytic processes in bulk heterogeneous systems are poorly understood; system complexity increases with nano-dimension component(s).
- Need control of radiation driven free radical chemistry at the nanoscale.
- Emergent behavior observed for energy and charge exchange between nano-component phases as compared to pure components.
- Fuel cell efficiency, solar energy conversion, LED and OLED efficiency are all related to charge carrier transport and collection efficiency from the NPs to the electrodes.

Synthesis of rare earth metal nanoparticles in polymer matricies





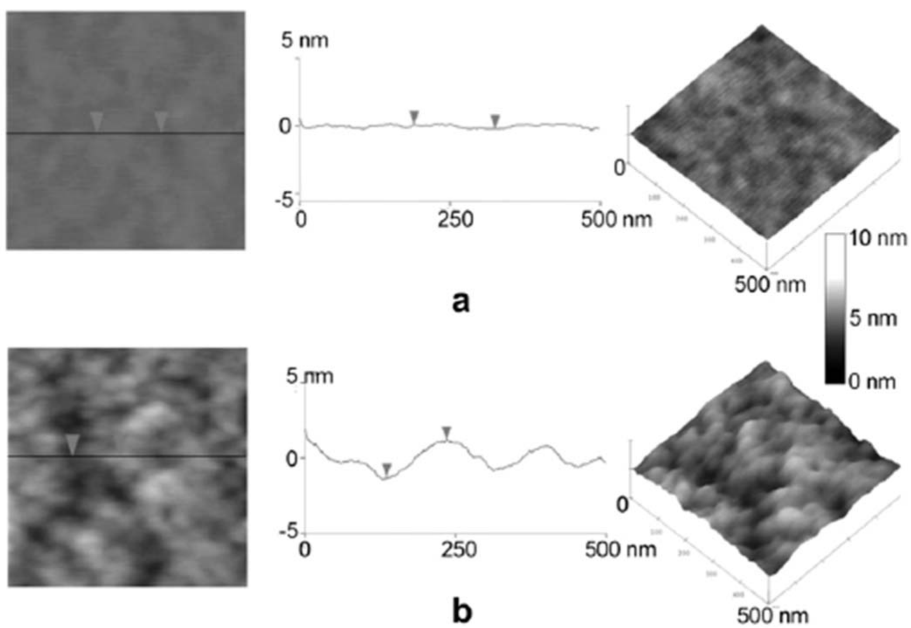
Chall et al, J. Mater. Chem, 22, 2012, 12538-12546

APPF: Technological applications-DOE missions

- Advanced lithography (< 10 nm) using electron-beam, focussed ion beams, and x-ray’s
  - Next generation semiconductor devices
  - Membranes for ultrafiltration
  - Hybrid devices for chemical and bioagent detection
- Radiolysis of nano-catalytic sytems
  - Water/soil remediation
  - Water radiolysis (nuclear to hydrogen energy conversion

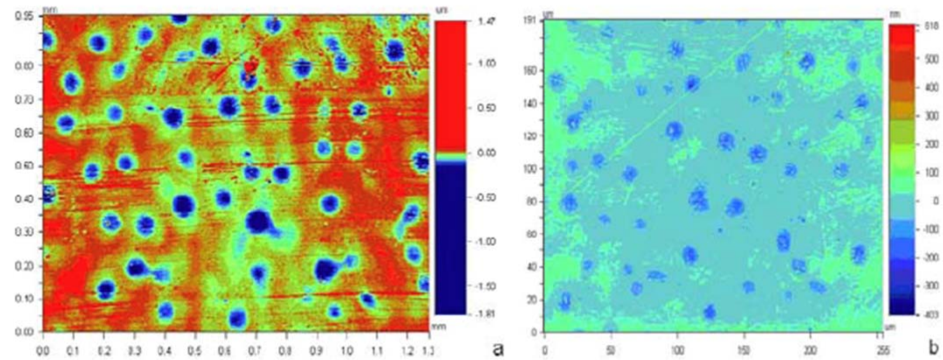
Control of film properties using radiation cure techniques

AFM of PVP films; a- unirradiated, b-e-beam iradated (5 kGy)



Weaver, et al, Polymer, 52, 2011, 5746-5755

Modification of epoxy resin/SiO2 composite caused by gamma radiation. a-nonirradiated; b-20 kGy.



Craciun et al, USB Sci Bull., Series B, 73, 75-86, 2011.

APPF: Technological applications-DOE missions

- Advanced polymer, polymer blend and polymer nanocomposites: radiation-assisted synthesis
  - Radiation driven polymerization would eliminate initiators, crosslinkers, etc. potentially having superior aging characteristics
  - Nano-silica/acrylate abrasion resistant nanocomposites
  - Nano-clay/polymer composites with improved physical, mechanical, thermal stability and reduced flammability
  - Renewable polymeric materials (cellulose, chitin, alginate, etc.)
- Structural nanocomposites
  - stiffness and strength approaching metals, corrosion resistant
  - Lightweight, extrudable, moldable
  - Amenable to rapid prototyping process

Advanced manufacturing of structural materials by CVD/CVI processes (I.Usov, MST-7)

Features of structural materials fabricated by CVD/CVI:

- Large portion of the periodic table is accessible (alloys, composites, oxides, carbides, nitrides, borides)
- Tailored shape, structure and composition (grain refinement, chemically graded composition)
- Well established industrial applications (primarily semiconductor materials and protective coatings, and recently CNT manufacturing)

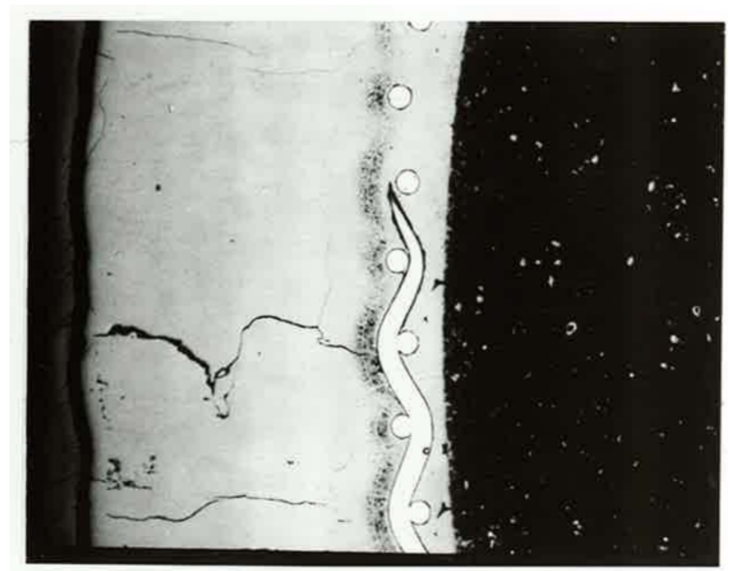
Areas of impact:

- Protective Coatings
- Alloys and composites with tailored structure and composition
- Complex shape parts without machining
- Joining

Gaps:

- Applications of the CVD/CVI field to structural materials has declined since 80’s
- Currently, there is no substantial effort at academia, national laboratories and industry
- Very few equipment manufacturers

Example of Mo-SiC structural composite fabricated by CVD/CVI:



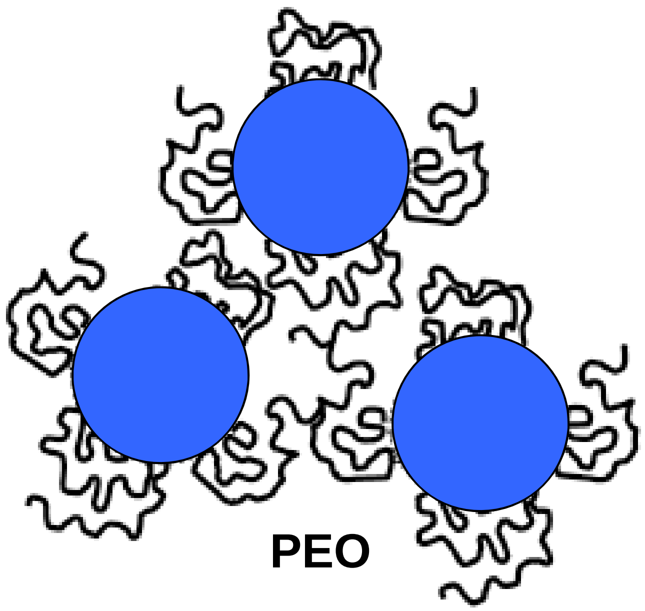
Metallographic section of Mo screen embedded into SiC showing stopping of crack propagation

Key partners:

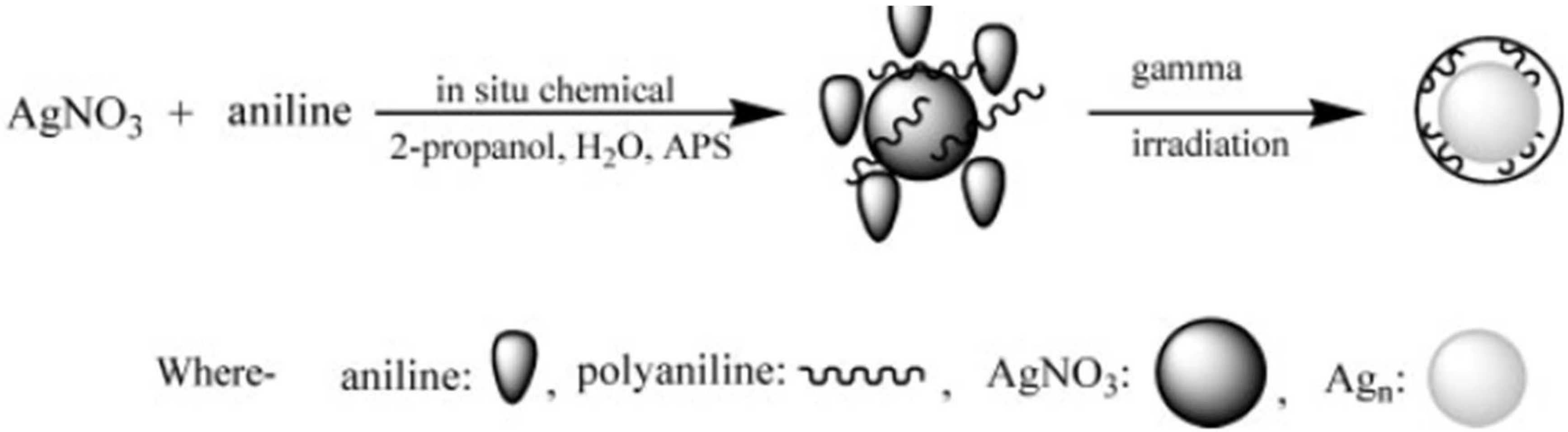
- Electric Power Research Institute
- General Electric
- Plansee
- UC Berkeley

Polymer Stabilization: Nanoparticle Dispersion in Polymer Matrix

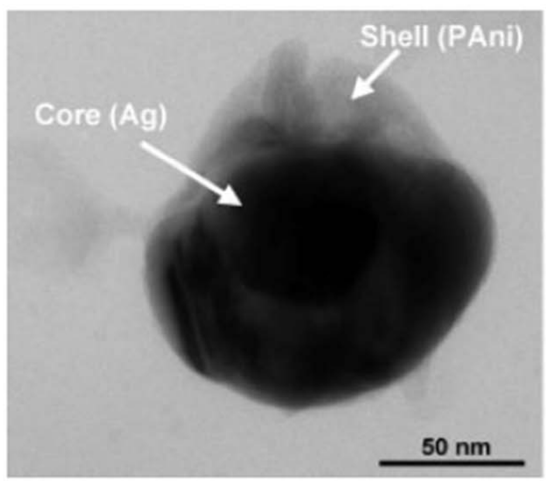
- Polymer (steric) stabilization will be required for dispersion
- IL $\varepsilon \sim 1000$, implies small Debye length-bad for ES
- Nanophosphors dispersed in *polymer* solution
- Film casting technique used to remove solvent
  - Spin-coating
  - Dip-coating
- Need favorable particle-polymer interactions to avoid aggregation during film formation
  - Polyethylene oxide forms complexes with metal halides

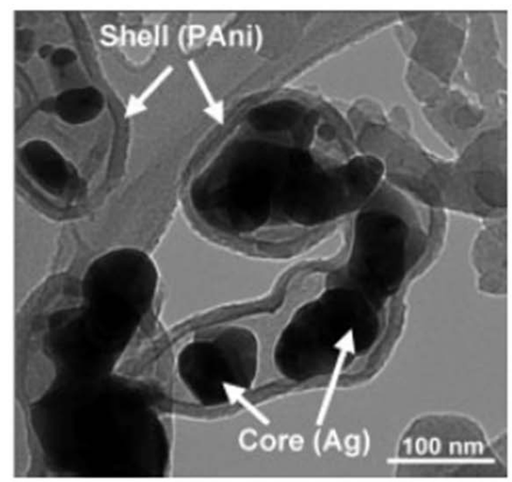


In Situ synthesis of core-shell silver-polyaniline nanocomposites using gamma irradiation



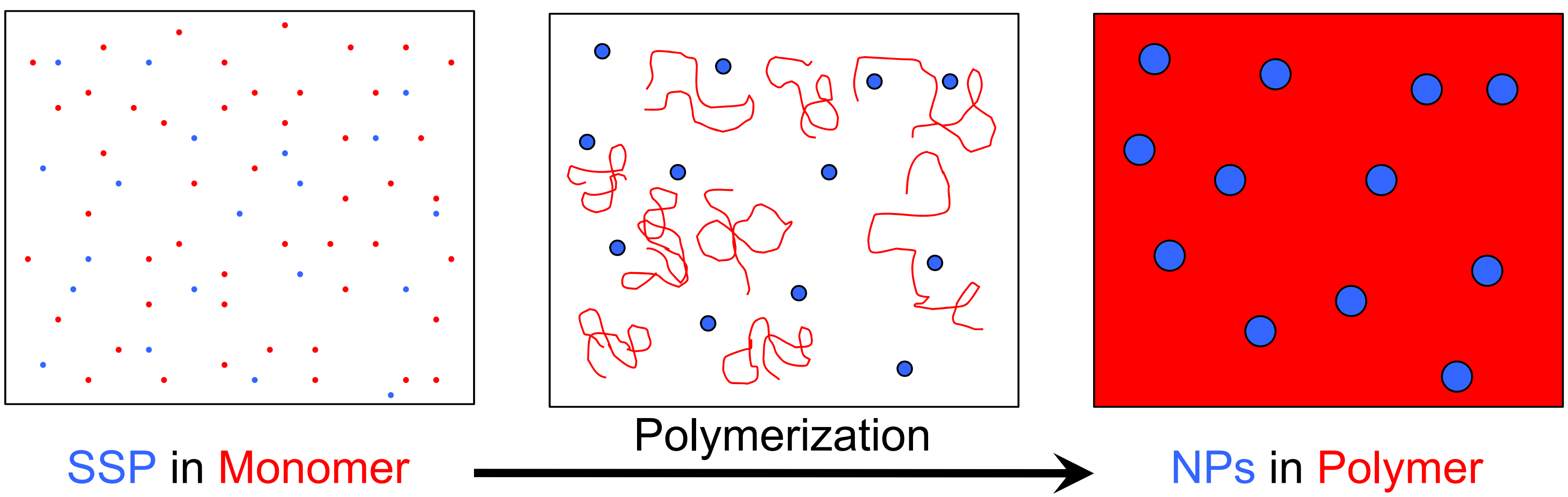
Karim et al, J. Polymer Sci. A, 45, 2007, 5741-5747





Polymer Stabilization: Polymerization Around Nanoparticles

- Nanophoshors dispersed in *monomer* solution
- Subsequent polymerization locks in dispersed state to prevent aggregation
- Combine with “bottom-up” nanoparticle synthesis approach to control size of nanoparticle
  - Dissolve SSP in monomer
  - Remove ligand & initiate polymerization
  - Anticipate decrease in metal halide solubility that will result in nanocrystal formation
  - Size of nanocrystal determined by polymerization kinetics / temperature



Los Alamos NATIONAL LABORATORY

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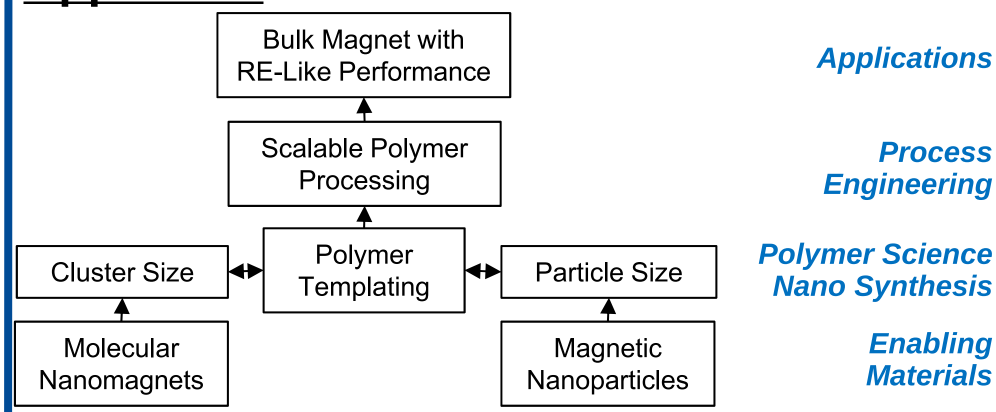
Scaling Transition-Metal Nanomagnets by Polymer Templating

Challenge/Motivation

- **Problem:** Best magnets are rare earth (RE) based using critical materials such as Dy and Nd
- **Opportunity:** Magnets built from doped iron oxide nanoparticles can offer competitive performance
- **Challenges:**
  - Engineering of magnetic nanoparticle / molecular nanomagnet properties
  - Scalability

Approach:



Goal/Deliverable

- Demonstrate RE-like performance from a non-RE magnetic nanomaterial
- Demonstrate process scalability to application relevant quantities

Team & resources required

- MST-7 Polymers
- In collaboration with:
  - NHMFL
  - Lujan Neutron Scattering Center
  - MPA-MC
  - MPA-CINT
  - T

Point of Contact: Robert Gilbertson (MST-7)
rgilbert@lanl.gov

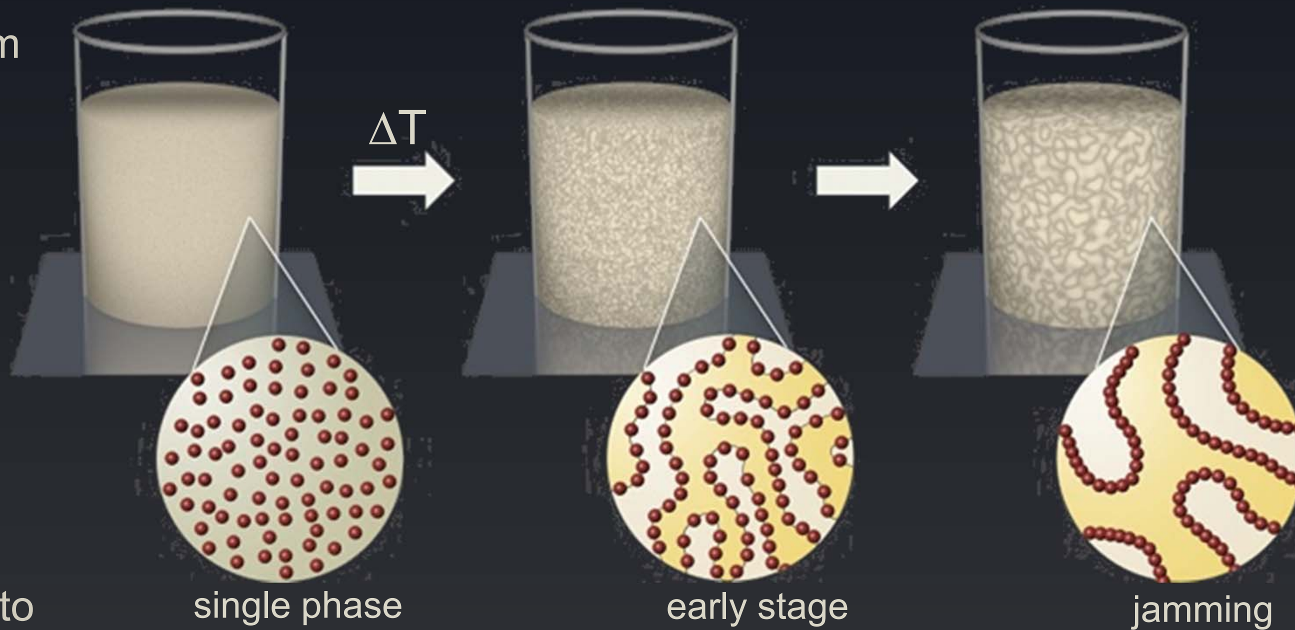
Bicontinuous Interfacially Jammed Emulsion Gels (Bijels)

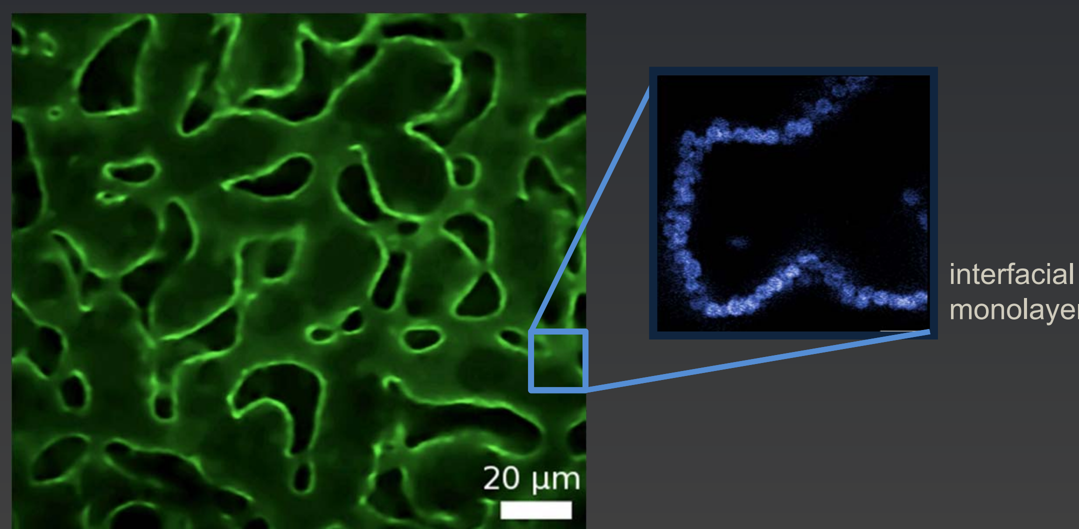
A new class of non-equilibrium soft materials formed by arrested
spinodal decomposition of binary fluids

Neutrally-wetting colloidal particles jam a percolating interface shared by two continuous fluid phases

Confocal microscopy is used to visualize the (fluorescent) particle monolayer at the interface

Potential applications in separations, controlled release, foods/consumer products, and **advanced materials synthesis**

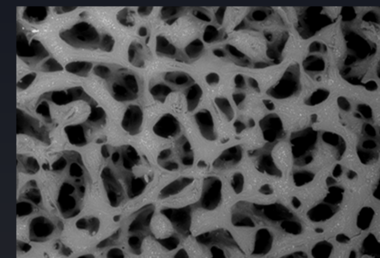




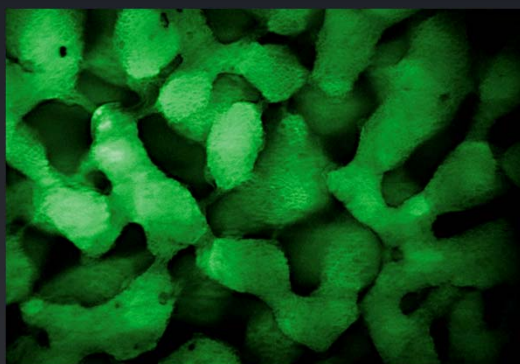
Using Bijels for Advanced Materials Synthesis

Bijels can serve as robust scaffolds for 3-D bicontinuous macroporous and hierarchically porous materials with tunable chemistry

Potential applications in energy systems (batteries, fuel cells, photovoltaics), separations, catalysis, and tissue engineering

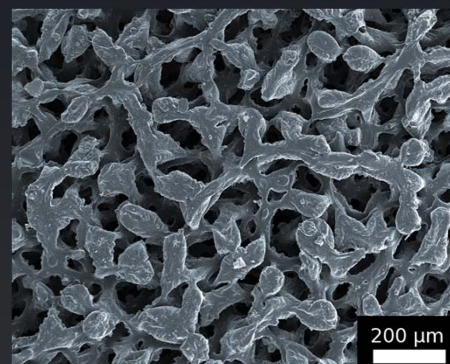


PEG hydrogel

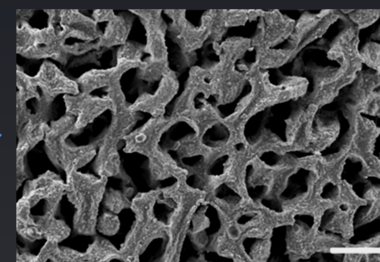


Fluid-fluid bijel (confocal)

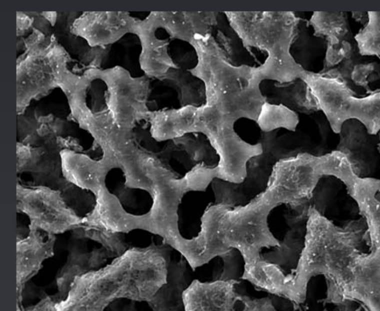
Polymerize



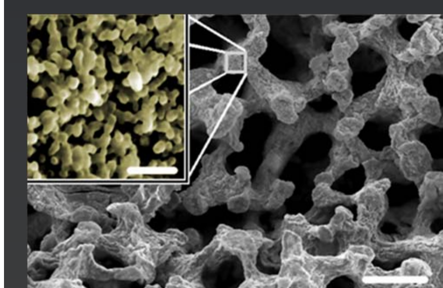
Polymer template (SEM)



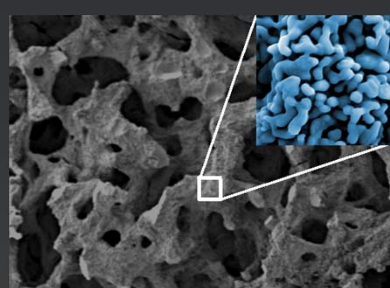
SiC monolith



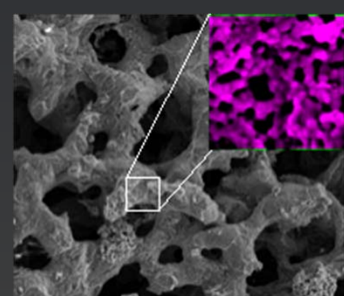
Carbon monolith



Hierarchically porous Ni



hydroxyapatite



ZnO

[1] Lee *et. al.*, *Advanced Materials*, 2010
[2] Lee *et. al.*, *JACS*, 2011

EXPLORATION OF URANIUM DIOXIDE / MACROPOROUS SiC NUCLEAR FUELS FOR HIGH BURNUP APPLICATIONS

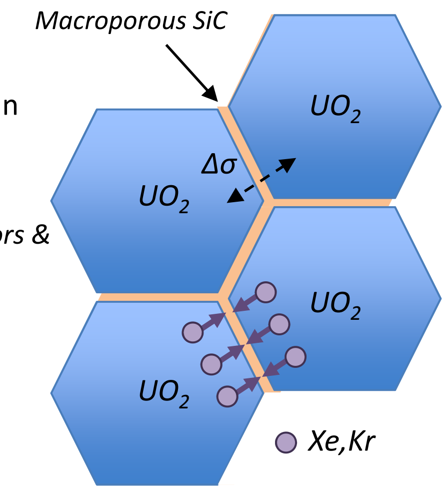
A.T. Nelson, MST-7

OBJECTIVE

- Development of improved nuclear fuels has gained international priority following Fukushima
- Economics favors evolutionary improvements constructed on conventional UO_2 framework
  - *Licensure of completely new fuel requires > 15 years*
  - *Entirety of commercial infrastructure build upon UO_2*
- Fundamental question: can minor changes to the structure / chemistry of UO_2 result in improved performance?
- Incorporation of intergranular macroporous SiC within UO_2 matrix may offer appreciable performance gains with minimal modification to existing fuel processing or losses in other performance areas

APPROACH

- Objective is pellet microstructure containing macroporous SiC on grain boundaries of UO_2 prepared using conventional processing
- *Coat UO_2 feedstock with SiC precursors & polymer phase*
  - *Press / sinter pellet using conventional route*
  - *Macroporous architecture is synthesized during sintering*
- Characterize performance of UO_2/macroporous SiC as a function of structure and chemistry variables



IMPACT

- Development of 'drop in' UO_2 derivative with enhanced properties compatible with existing fuel fabrication infrastructure would be extremely attractive to industry
- Macroporous SiC could offer a range of benefits
  - *Enhanced toughness (pellet fracture is a reality of current fuels and significantly limits performance)*
  - *Limit fuel swelling due to fission gas production (fuel swelling is major factor limiting operation to high burnup)*
  - *Improved thermophysical properties (λ_{SiC} >> λ_{UO2}; higher thermal conductivity lowers fuel centerline temperatures & increases safety margin)*

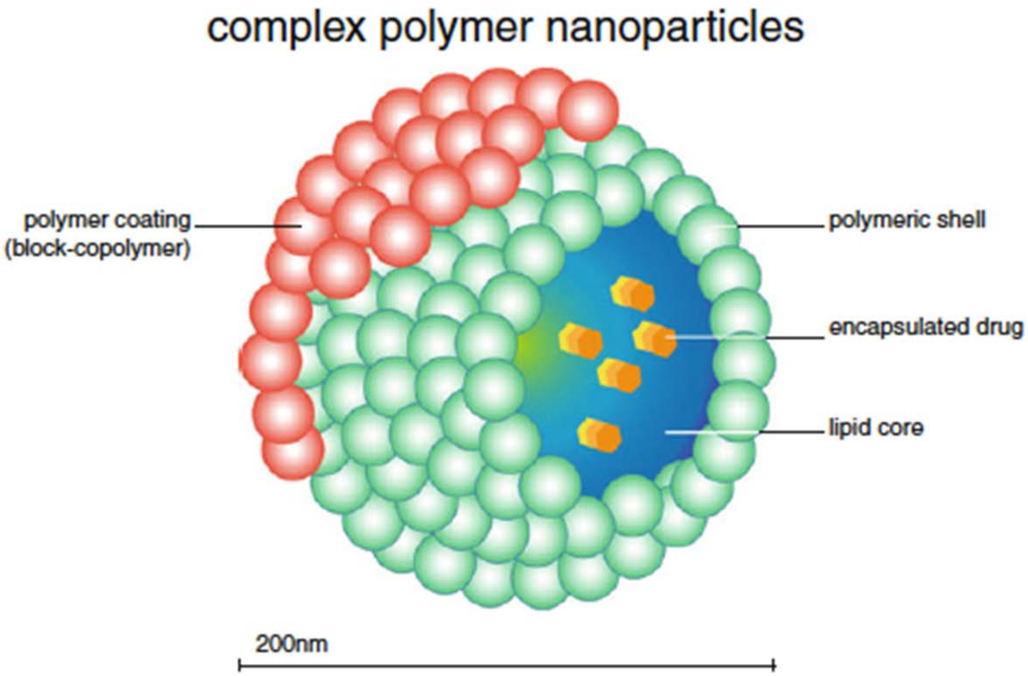
PATH FORWARD

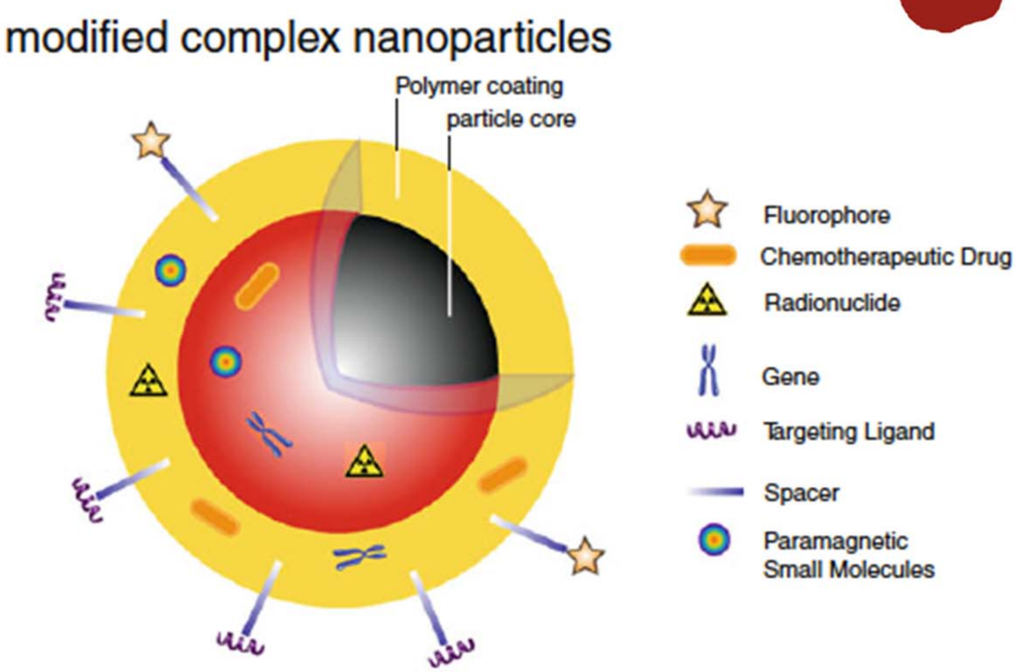
- PHASE I: Synthesis of surrogate (CeO_2) / macroporous SiC feedstock and dense bodies as feasibility study
- PHASE II: Synthesis of UO_2 / macroporous SiC samples
  - *Refinement of processing-structure relations*
  - *Characterization of mechanical performance*
  - *Characterization of thermophysical properties*
  - *Characterization of fuel oxidation behavior*
- PHASE III: Optimization of structure given assumed property & neutronics tradeoffs
  - *Incorporate reactor design and fuel loading feasibility work*
  - *Characterize fission product mobility during steady state / transient scenarios*
- PHASE IV: Link to programmatic support for test irradiation

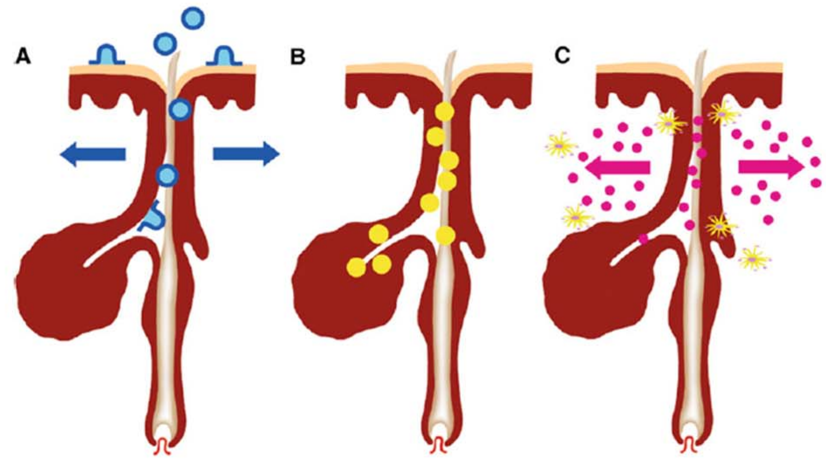
APPF: Technological applications-Biomedical

- Polymeric nanostructures
  - Reduces solubility requirements-potentially doubles number of chemical compounds that could be formulated into pharmaceuticals
  - Nano/microgel structures for drug carrying devices
  - Advanced tumor targeting/treatment:
    - Passive (size only-50 to 100 nm)
    - Active (target ligands on NPs to enhance selectivity)
    - Cancer detection at the cellular level
    - NP based radio-therapy sensitisers
  - Radio-synthesis of fine compounds
    - New synthetic pathways
    - Controlled stereoselectivity

Nanoparticles for medical applications







Papakostas etl al, Arch Dermatol Res, 303, 2011, 533-550

Capability Road Map: Polymeric Functional/Adaptive Materials

End state:

- Have Advanced Polymer Processing Facility proposal
- Have Industrial support core e.g. P&G, Chevron type CRADAs
- Enlarge computation resources for inclusion of process modeling
- Integration of materials for multifunctionality and/or emergent properties
- Realize and implement self-assembly, self-healing concepts in functional materials across scales

5 yrs:

- Develop strategy for industrial partnerships thru licensing outreach
- Improved modeling of structure-property rel'n for nanocomposites and nanogels
- *In-situ* synthesis and growth diagnostics (tie to M4 or precursors, CINT, LANSCE, etc.)

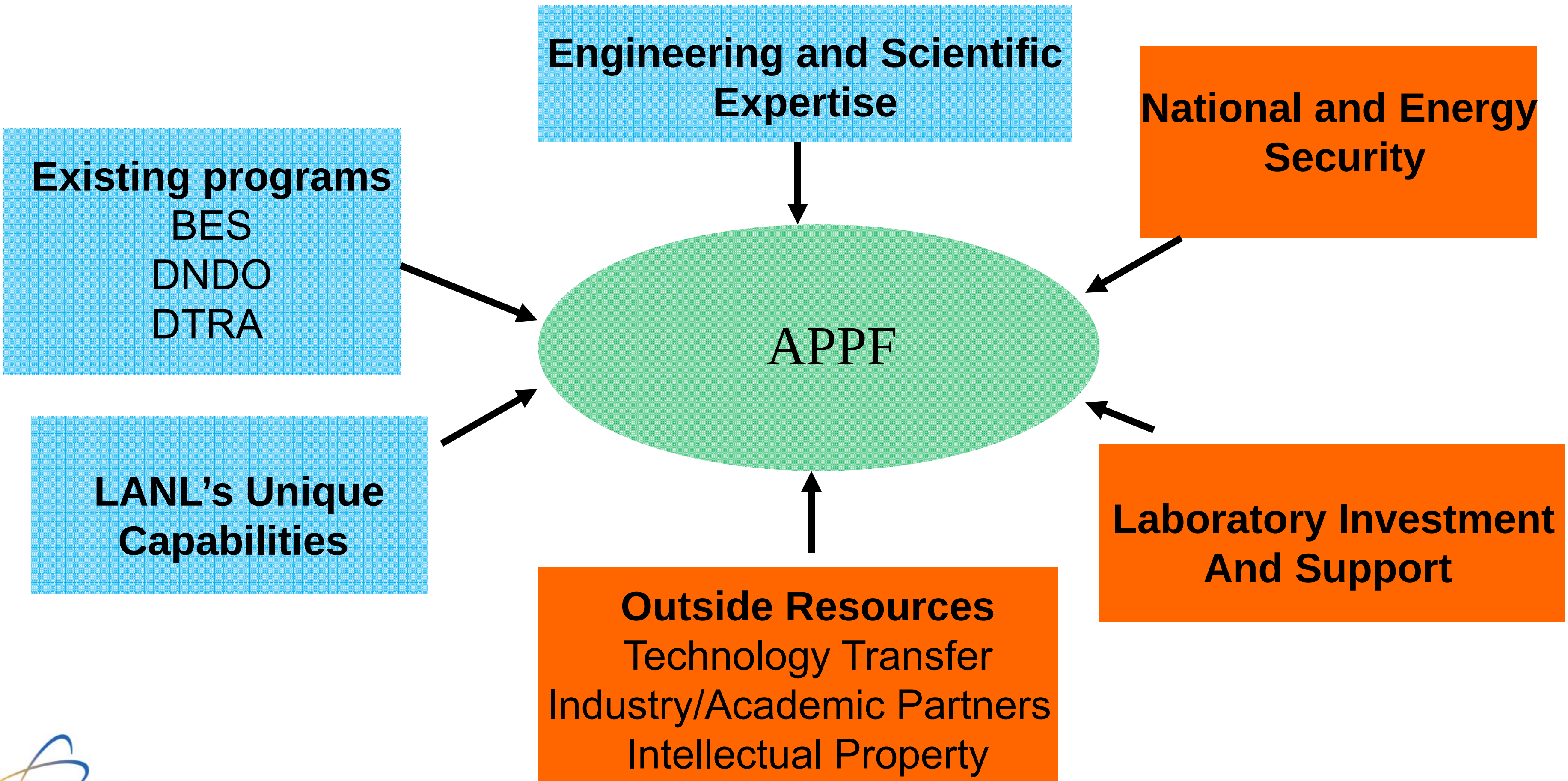
2 yrs:

- Begin process toward improving computational ability for predictive control of radiation chemistry synthesis of polymers
- Improve interface between experiments and models
- Develop capability to synthesize polymeric nanogels

Current State

- Identify unique chemical transport mechanisms, chemical reactivity in polymeric heterogenous systems.
- Exploit Inorganic-organic nanocomposites emergent optical and structural properties.
- Explore polymeric gels potential for large-scale adaptive material applications (sensors, delivery systems)

A Business Case for Investment



Radiolytic Processes for Nanomaterials are Inherently Green

- **The Twelve Principles of Green Chemistry***

- *Anastas, P. T.; Warner, J. C. Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998, p.30. By permission of Oxford University Press.

Prevention

Atom Economy

Less Hazardous Chemical Syntheses

Designing Safer Chemicals

Safer Solvents and Auxiliaries

Design for Energy Efficiency

Use of Renewable Feedstocks

Reduce Derivatives

Catalysis

Design for Degradation

Real-time analysis for Pollution Prevention

Inherently Safer Chemistry for Accident Prevention

Advanced Manufacturing Based on these Processes is also Inherently Green

- **The Twelve Principles of Green Engineering***

- * Anastas, P.T., and Zimmerman, J.B., "Design through the Twelve Principles of Green Engineering", Env. Sci. and Tech., 37, 5, 94A-101A, 2003.

Inherent Rather Than Circumstantial
Prevention Instead of Treatment
Design for Separation
Maximize Efficiency
Output-Pulled Versus Input-Pushed
Conserve Complexity
Durability Rather Than Immortality
Meet Need, Minimize Excess
Minimize Material Diversity
Integrate Material and Energy Flows
Design for Commercial "Afterlife"
Renewable Rather Than Depleting

APPF: Conclusions

- Radiation-assisted nanotechnology applications will continue to grow. See, for example *"Emerging applications of radiation in nanotechnology"* (IAEA-Tecdoc-1438, March 2005.)
- The APPF will provide a unique focus for radiolytic processing of nanomaterials in support of DOE-DP, other DOE and advanced manufacturing initiatives.
- γ, X-ray, e-beam and ion beam processing will increasingly be applied for "green" manufacturing of nanomaterials and nanocomposites.
- Biomedical science and engineering may ultimately be the biggest application area for radiation-assisted nanotechnology development.