Objectives

- Develop new macroscale (micron-sized or larger) energetic materials with nanoscale features that provide improved performance and ease of processing and handling, managed energy release, reduced sensitivity, and potential for internal/external control and actuation.

- Obtain fundamental understanding of the relationship between the integrated multi-length scale design of newly developed energetic materials and their reactive and mechanical behaviors.
Program Organization

(a) Processing Nanoenergetic Materials
   Aksay, Eichhorn, Zachariah
   Cluster Assembled Metal Mesoparticles
   Linked Tetrazines
   Functionalized Graphene Sheet

(b) Multiscale Processing
   Aksay, Eichhorn, Zachariah
   Energetic Bridging Molecules
   Tetrazine bridge
   Graphene Sponge
   Nanostructured Catalysts
   Metal NPs on FGS

Pennsylvania State Maryland Purdue Princeton Georgia Tech

(c) Modeling
   Quantum Mechanics
   Nanoparticles on Graphene
   Propellants and FGS
   Molecular Dynamics
   Car, Selloni, Yang
   Modeling at the Mesoscale

(d) Kinetics and Propulsion
   Combustion Wave Structure
   Heterogeneous solid
   Probing Reaction Dynamics
   Son, Thynell, Yetter
Materials Research Emphasis

- Bottom up approaches boosting the energetics of functionalized graphene via chemisorption of high nitrogen-containing molecules and/or replacing carbon atoms in the network with nitrogen and boron atoms.
- Metal-based cluster composites with energetic organic ligands (such as high nitrogen molecules).
- Decorated graphene with nano metal-based composites.
- Analogous systems produced through top down approaches via encapsulation and porous materials.
Participating MURI Team Members

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- Michael R. Zachariah, Mechanical Engineering and Chemistry, University of Maryland (mrz@umd.edu)
Metallic Clusters and Mesoscopic Aggregates

Strategy: Develop a mesoparticle comprised of ultra-small nanostructures that can be rapidly disassembled releasing highly reactive nanostructures (B. Eichhorn and M. Zachariah, UMD)

- Gas generator
  - Al Cluster (e.g. Al\textsubscript{77})
Metallic Clusters and Mesoscopic Aggregates

- Various types of nano-structured mesoscale particles prepared for initial processing and characterization (M. Zachariah, B. Eichhorn)
  - polyoxometallate clusters (POMs) and two types of gas generators ($C_2N_{10}$, $SN_4CH_3$)
  - core-shell microspheres of 5-AT / $Na_{12}H[Fe(HPW_{7}O_{28})_2]$ composites through spray pyrolysis
  - microspheres of 15 nm silica nanoparticles with both $Na_2C_2N_{10}$ and KIO4 gas generators
  - microspheres of Al NP/nitrocellulose through electrospray synthesis

- Reactivity and combustion analyses performed (M. Zachariah, B. Eichhorn, R. Yetter):
  - T-jump MS: reactivity for the Al NP/NC microspheres greatly exceeds simple mixtures of the individual components
  - Droplet combustion: disruptive burning of the Al/NC microspheres in toluene. AlCl solutions showed decreases in droplet combustion time.
Graphene as an Energetic Scaffold

Unit Cell Models of FGS
C. Zhang, A. Selloni, R. Car (2013)

- The approach is to use functionalized graphene sheets (FGSs) as high surface area scaffolding.
  - The wrinkled sheets inhibit restacking, while maintaining high surface area.
  - High energy topological and lattice defect sites (including carbon vacancy defects).
  - Oxygen-containing reactive sites: epoxides, hydroxides, carboxides.
  - The FGS itself is a combustible source.
- Template for nanoparticle nucleation
  - Maintains stable dispersion of catalysts and energetic particles.
  - Pinning prevents particle coarsening and sintering
- Sheets linked using energetic molecules
  - Tetrazine bridges add nitrogen, maintain sheet spacing for high surface area structures.

Tetrazine Decomposition on FGS

Cyclic voltammograms of Tz, FGS, and Tz bound to FGS

Decomposition of pure tetrazine (top) and tetrazine on FGS (middle); dichlorotetrazine sublimes and does not decompose (bottom)

- Cyclic voltammetry, infrared spectroscopy and thermal analysis show that some tetrazines may be covalently attached to FGS.
- Modeling studies confirm that covalent bonds are energetically favored over physisorption.
- Tetrazines bound to FGSs decompose more completely at high temperature and thus release more energy.
Nanoscale Inclusions

- **Strategy:** Fabricate micron-scale particles with nanoscale features via rapid crystallization with nano-catalysts as nucleation sites or mechanical activation (MA) to incorporate nanoscale inclusions in aluminum (S. Son, Purdue)

AP crystals w/ inclusions of nanoscale catalysts (Son, Purdue)

Fuel-rich Al+ PTFE Powder Mixture

EDS map of Al/PTFE particle high energy milled (60 min) indicating uniform distribution of PTFE within particles. Al = red, F = green, C = blue. (Son, Purdue)

- **Other top-down material examples**

Porous silicon (Vesta Sciences, ARDEC)

Porous aluminum (Rosenberg, V. and Gany, A., IJEMCP, 10, 9, 2011)
(S. Son, Purdue) Encapsulated nanoscale catalysts are more effective than catalysts powders, and yields less viscous propellants so less binder could be used to improve performance. Details of the effect of the flame structure and microscale combustion dynamics is characterized used high-speed PLIF and visible imaging. Coarse particle ejection can be seen at lower pressures for catalyzed propellants.

(S. Son, Purdue) Solid propellant pellet (left) and burning surfaces of pellets containing sieved spherical, flake, 80 nm nAl, Al/PTFE 90/10 wt.%, and Al/PTFE 70/30 wt.% (right). Pressure is 0.1 MPa and all photos were taken with the same exposure setting. Much smaller agglomerates were achieved that will reduce two phase flow losses.
Program Interactions

Interactions within the MURI Program

- Princeton, UMD, and Penn State - Decomposition kinetics of nanocomposite materials (capabilities of research groups range from heating rates on the order of seconds, $10^3 \text{ s}$, and $10^6 \text{ s}$).
- Princeton, UMD, Purdue, Penn State - Fabricated nanocomposite materials being transferred for combustion analysis in liquid and solid propellants.

External Interactions

- Greg Young (NSWC-IH, Incorporation of microparticles in polymer, boron PTFE mixtures)
- Scott Weigarten (ARL, simulation of cluster aggregate decomposition)
- Chad Stoltz (NSWC-IH, energetic materials and reactive characterization)
- Dennis Mayo (NSWC-IH, cluster synthesis and reactive materials)
- Kit Bowen (Johns Hopkins, cluster synthesis and characterization)
- Purdue Material transferred to Chris Crouse at Eglin, David Dye at Crane, Bryce Tappan at Los Alamos, Nick Glumac at UIUC (shock tube studies), EMPI for AFOSR SBIR
- Pierre Audebert and Fabien Miomandre (ENS)
- Thomas M. Klapötke (Visiting Professor, UMD)
- Alex Gash and Thomas Lagrange (LLNL)
- Dave Adams and Robert Reeves (SNL)
- Chris Bunker (AFRL, Propulsion Directorate, Wright-Patterson Air Force Base)
- Jonathan Essel (NAVAIR China Lake)
Meeting Presentations

- **10:20-10:40 MURI Program Overview**  
  Rich Yetter, Pennsylvania State University

- **10:40-11:10 Metallic Clusters, Mesoscopic Aggregates, and their Characterization**  
  Bryan Eichhorn, University of Maryland

- **11:10-11:40 Graphene as a Reactive Material and Carrier of Energetic Materials**  
  Ilhan Aksay, Princeton University

- **11:40-12:15 Decomposition, Ignition, and Combustion Studies on Nanoenergetic Composite Ingredients and Mixtures**  
  Steve Son, Purdue University
Additional sides
Impact

- New storable energetic propellants, additives, or catalysts to achieve on-demand, on-time, tailorable, and affordable propulsion and munition capabilities not currently available.

- Methodologies to create smart and functional nanoenergetics for incorporation into various systems ranging from MEMs devices to rocket propellants to explosives that permit new functions to be performed ultimately enhancing the performance of the system.