SMART FUNCTIONAL NANOENERGETIC MATERIALS

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Pennsylvania State University

Multidisciplinary University Research Initiative (MURI) Program Review
System Planning Corporation Capital Conference Center – One Virginia Square
3601 Wilson Blvd, 6th Floor
Arlington, VA 22201
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Why Nanoenergetic Materials

Important Components to Energetic Materials

- High Energy Density Fuel Components to Propellants, Fuels, and Explosives (High Concentrations)
- Burning Rate Modifiers (Low Concentrations)
- Gelling Agents for Hazards Reduction, MEMs systems, and others

Unique Properties

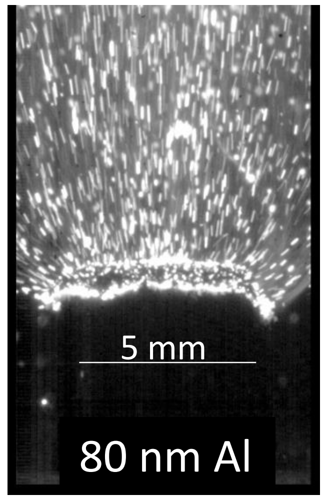
- Increased Specific Surface Area
- Increased Reactivity
- Increased Catalytic Activity
- Lower Melting Temperatures
- Lower Heats of Fusion, Increased Heats of Reaction

Implications to Energetic Materials

- Increased Burning Rates (> factor 5)
- Higher Efficiency (more efficient particle combustion, less two phase flow losses, for solids Isp ↑ 10s)
- Reduced Sensitivity
- Min/low smoke energetic materials

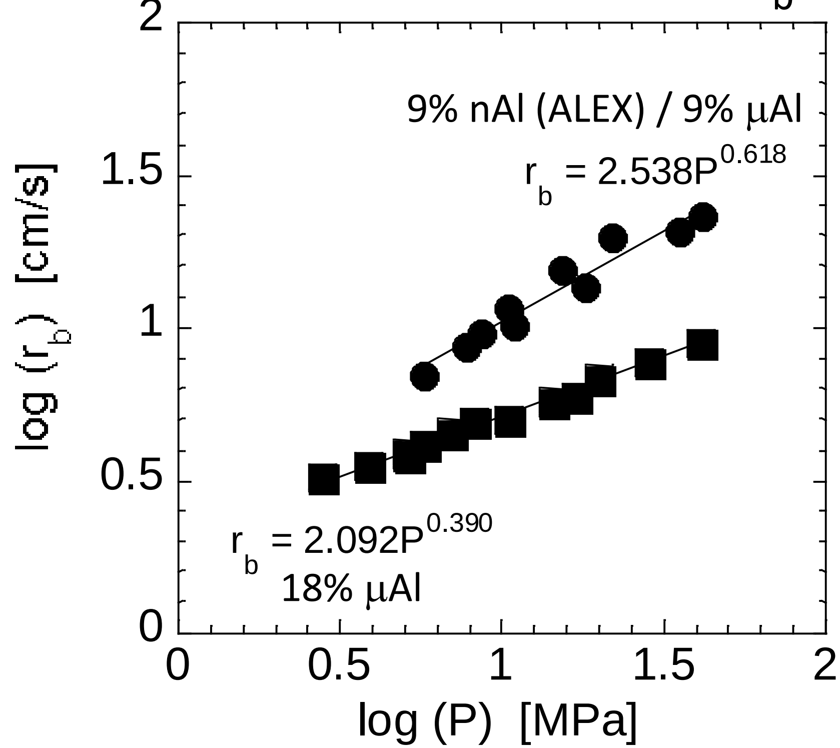
Example of Burning Propellants

Combustion of μm Al far from surface



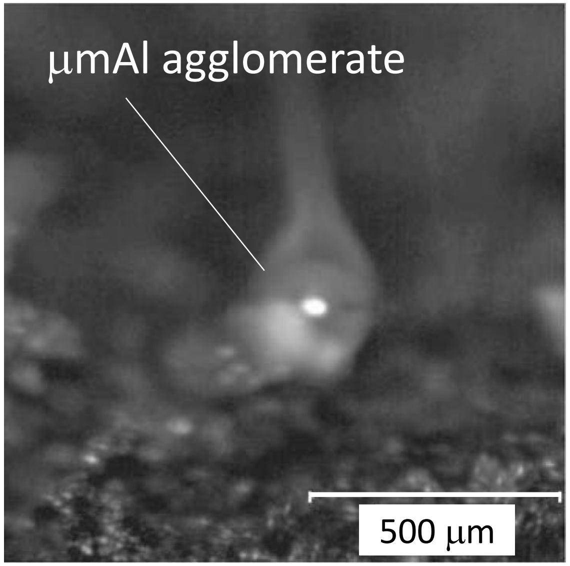
Combustion of nm Al close to surface

~1.8 ×'s increase in r_b

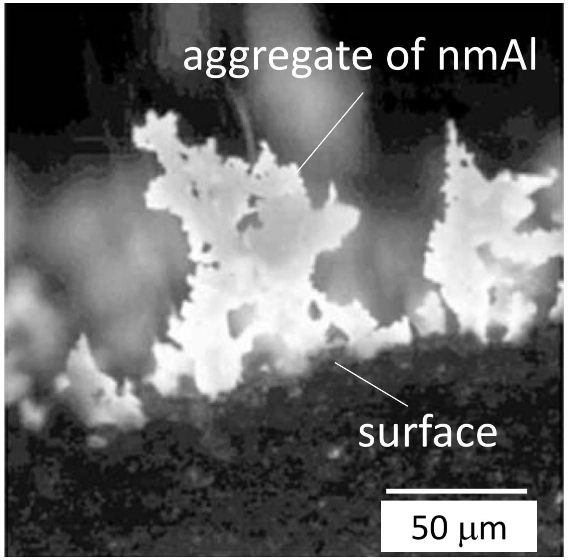


T. R. Sippel, S. F. Son, L. J. Groven, Aluminum agglomeration reduction in a composite propellant using tailored Al/PTFE particles, Combustion and Flame 161 (2014) 311–321.
Mench, M.M., Yeh, C.L., and Kuo, K.K., "Propellant Burning Rate Enhancement and Thermal Behavior of Ultra-fine Aluminum Powders (ALEX)," in Proc. of the 29th Annual Conference of ICT, 1998, pp. 30-1 – 30-15.
G. V. Ivanov, and F. Tepper, Challenges in Propellants and Combustion 100 Years after Nobel, pp.636-645, (Ed. K. K. Kuo et al., Begell House, 1997).

Example of Burning Propellants: the Surface



50 μmAl spherical agglomerate formed by inflammation of an aluminized aggregate



50-250 nmAl emerging from surface as aggregates (pre-agglomerate)

L. T. De Luca, L. Galfetti, F. Severini, L. Meda, G. Marra, A. B. Vorozhtsov, V. S. Sedoi, and V. A. Babuk, Burning of Nano-Aluminized Composite Rocket Propellants, *Combustion, Explosion, and Shock Waves, Vol. 41, No. 6, pp. 680–692, 2005*

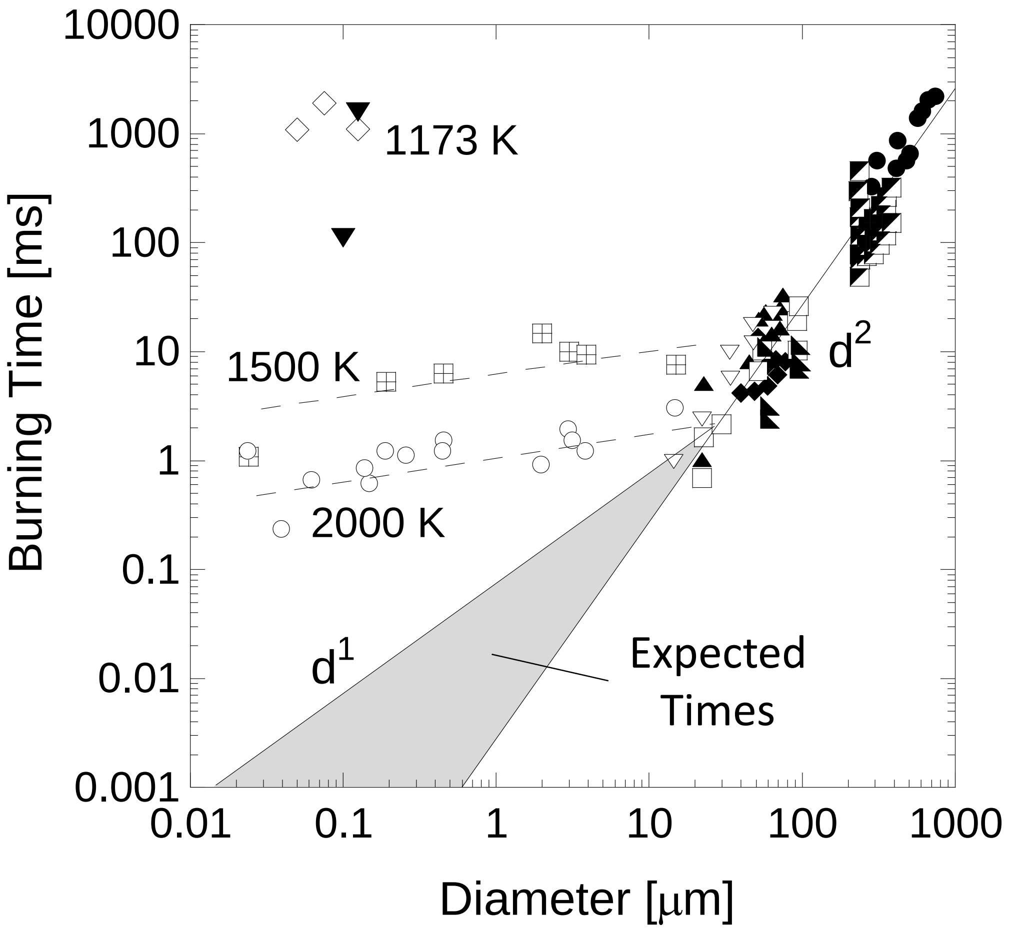
Anticipated Burning Times

Theory

$$t_{b,diff} = \frac{\rho_p d_0^2}{8\rho D\, ln(1 + iY_{O,\infty})}$$

$$t_{b,kin} = \frac{\rho_p d_0}{2MW_p kPX_{O,\infty}}$$

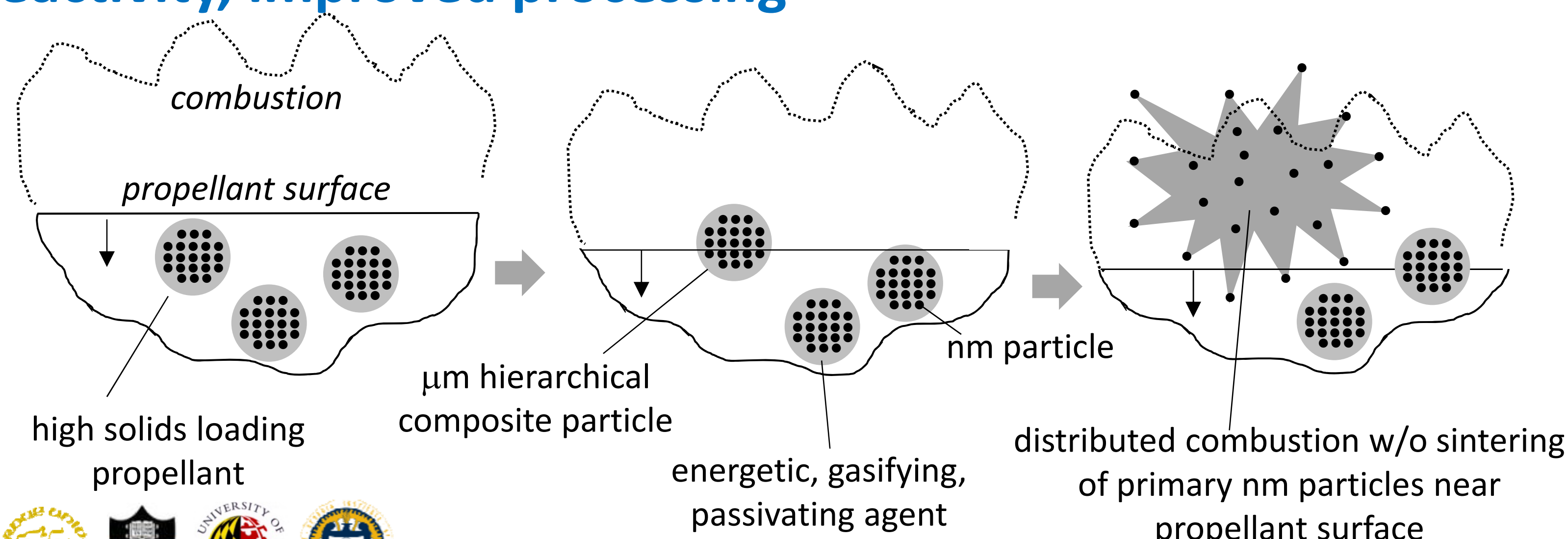
Experiment



Issues and Motivation

Current Status: **The full extent of the anticipated gains from nanoscale energetic materials has not been realized** in large part due to: *Low sintering temperatures, High surface area leading to large aggregates , Limited solids loading with nanoparticles, Oxide coatings lowering active metal content, Lack of fundamental understanding of burning process*

Motivation: **3-D, hierarchical, ordered structures, controlled reactivity, improved processing**

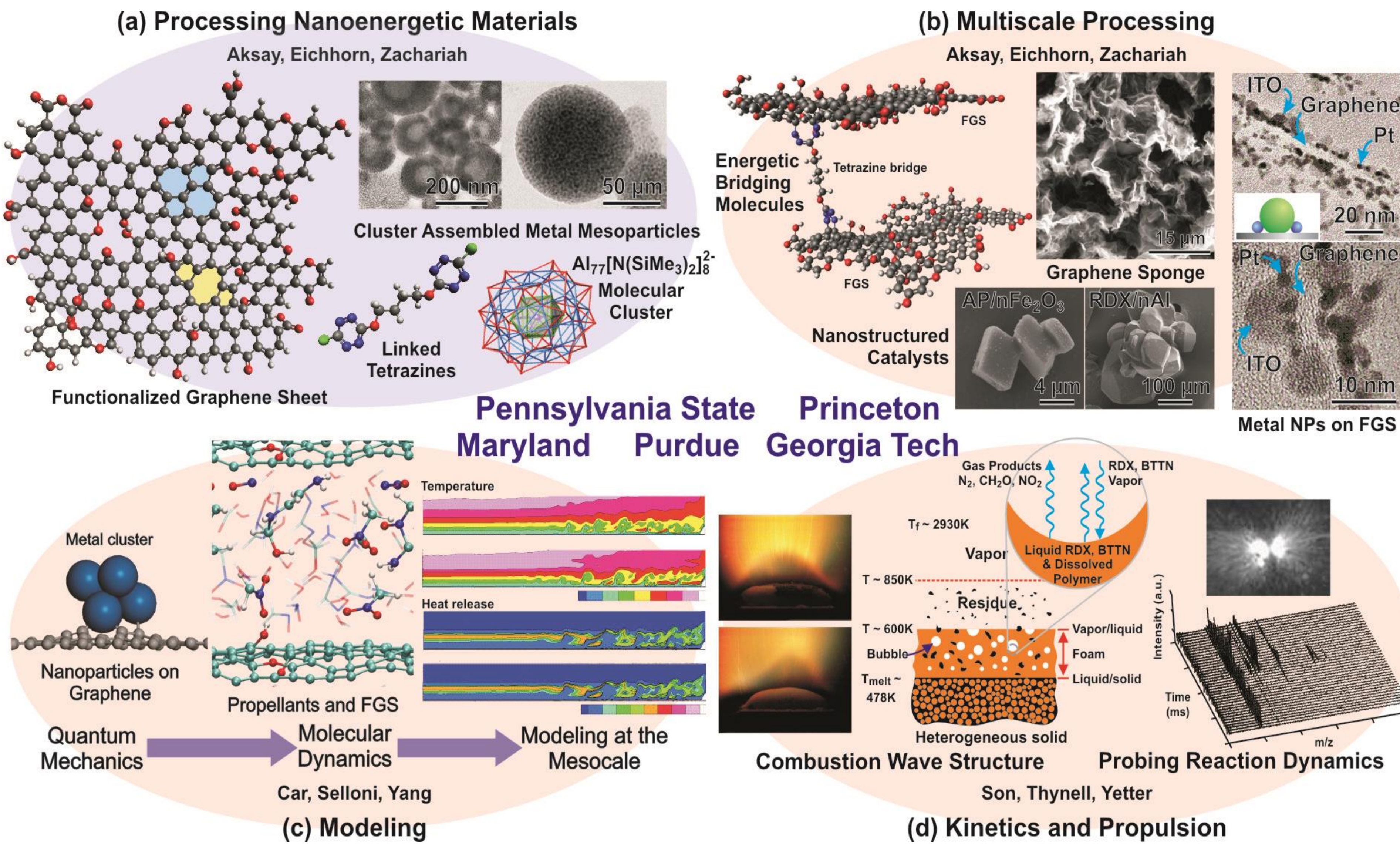


Objectives

- **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 and reactive and mechanical behaviors**.

Approach and Organization



MURI Team Members

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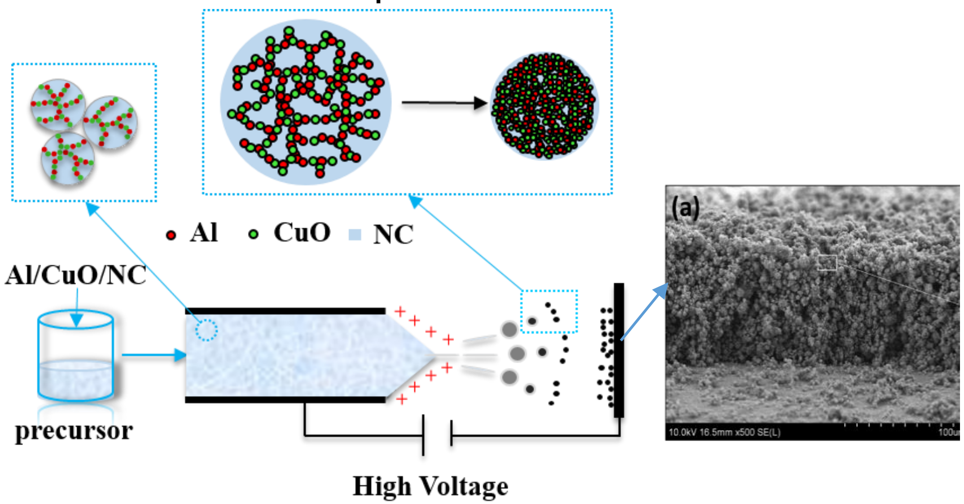
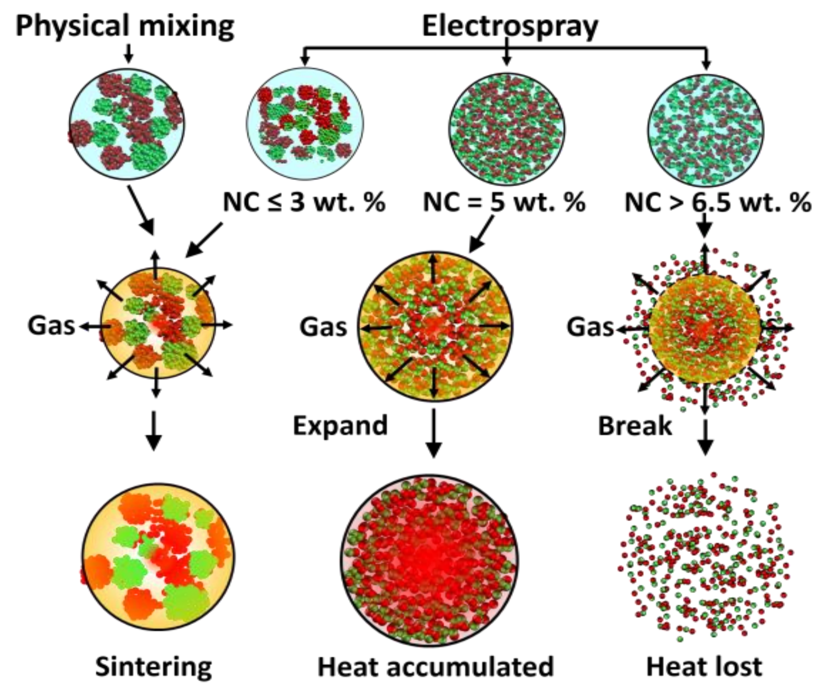
Richard A. Yetter, Mechanical and Nuclear Engineering, The Pennsylvania State University (rayetter@psu.edu)

Michael R. Zachariah, Mechanical Engineering and Chemistry, University of Maryland (mrz@umd.edu)

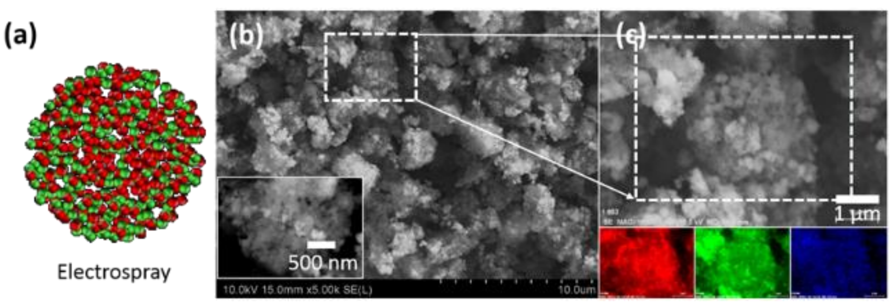
Processing of Nanoenergetic Materials to Create Mesoscale Structures with Enhanced Reactivity

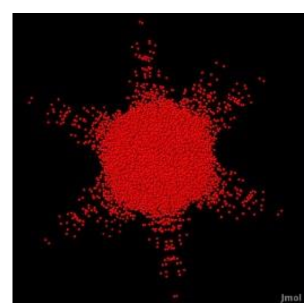
Approach: Material assembly that maximizes interfacial contact between fuel and oxidizer and minimizes sintering effects. Employ electrospray to create a multi-component structure.





Electrospray formed mesoparticle



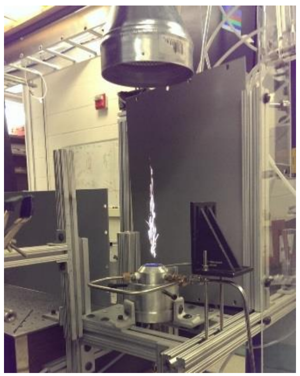


MD simulation nanoparticle ejection from a gas generating mesoparticle.

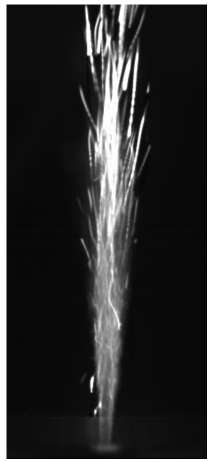
Zachariah and Eichhorn, UMD

Combustion Performance of nAl NC Mesoparticles

Methane Air Diffusion Flame
$CH_4:O_2:N_2$ = 1:14:7
T_{ad} = 1365 K

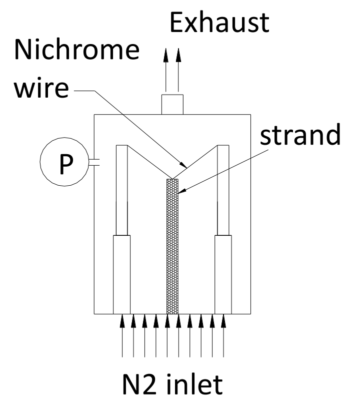


50 nAl

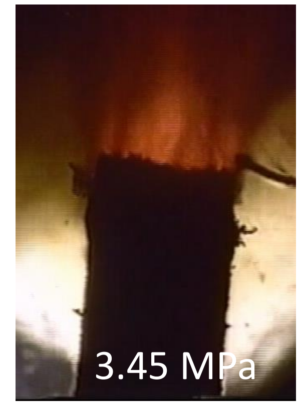


nAl 10%NC microparticle

Strand Burner

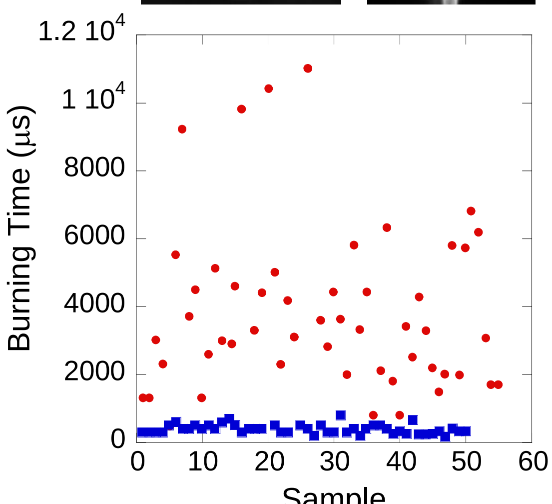


Valimet H2 Al



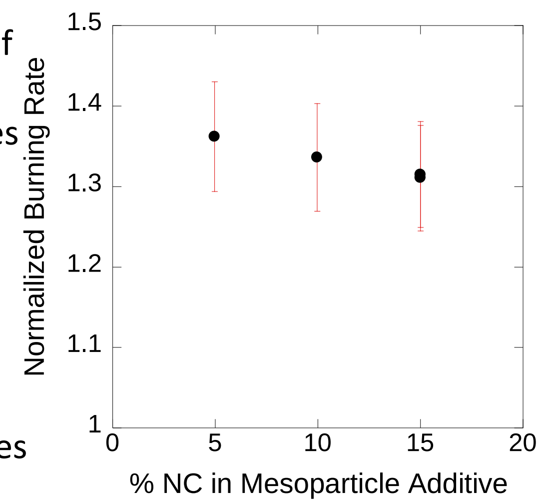
nAl 15% NC microparticle

Preliminary results show low T (500K) NC dissociation prevents early sintering and improves burning rate



Combustion near surface of propellant appears more vigorous with mesoparticles

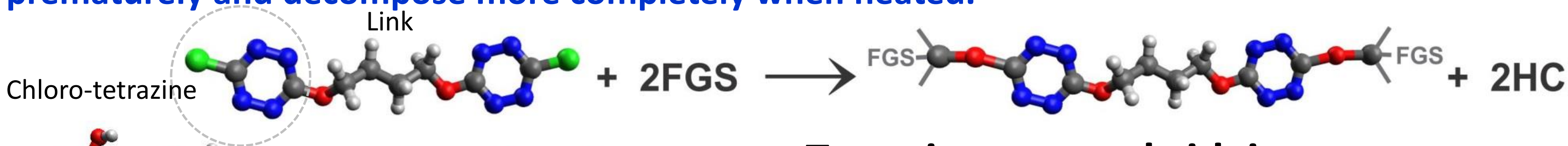
Preliminary results show burning rate enhancement along with processing benefits appear to make mesoparticles attractive alternatives to nanoparticles

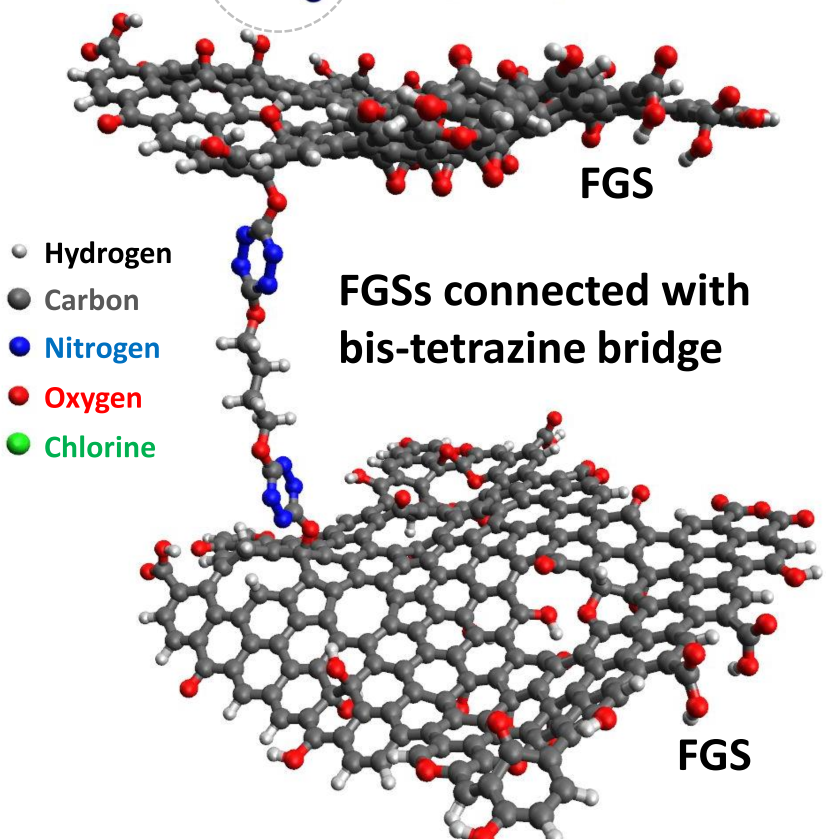


Zachariah, UMD, and Young, NSWC-IH

Energetic Tetrazines Covalently Bound to Functionalized Graphene Sheets

Quantum modeling shows covalent bonding is energetically favored via substitution of chloro-tetrazine onto FGSs; this has been verified experimentally. Tetrazines bound to FGS (Tz-FGS) do not vaporize prematurely and decompose more completely when heated.





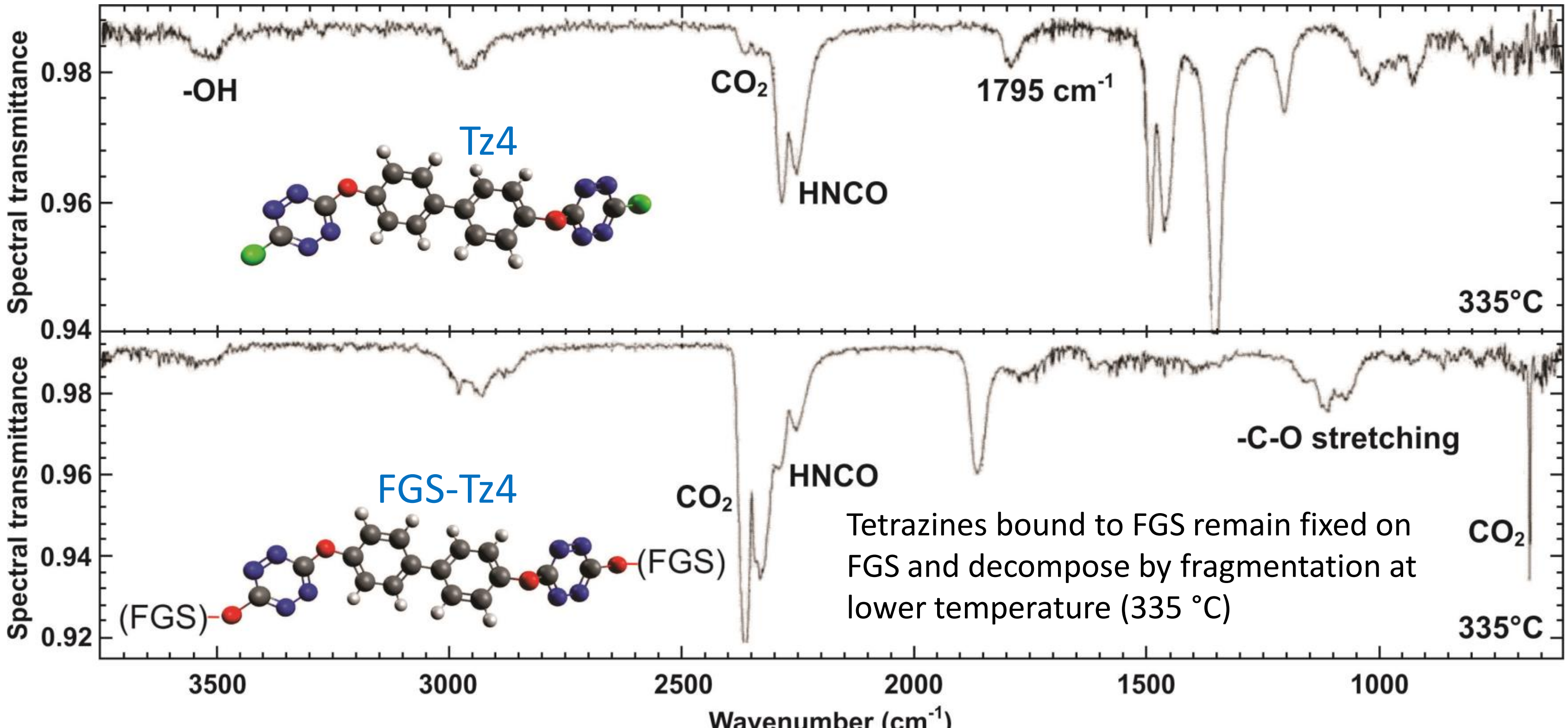
- **Tetrazines act as bridging agents** to maintain spacing between FGSs for higher surface area and accessible interlayer volume
  - Energetic spacer to increase energy density in a graphene-based foam
  - Uniform distribution across FGS for uniform heating of tetrazine molecules
- **Increased nitrogen content** to raise energy content of FGS-based porous structures

	FGS_2	FGS_2 - Tz2	FGS_2 - Tz3	FGS_2 - Tz4
At% N	0	12.4	5.8	18.0
At% O	31.0	10.9	14.3	10.7

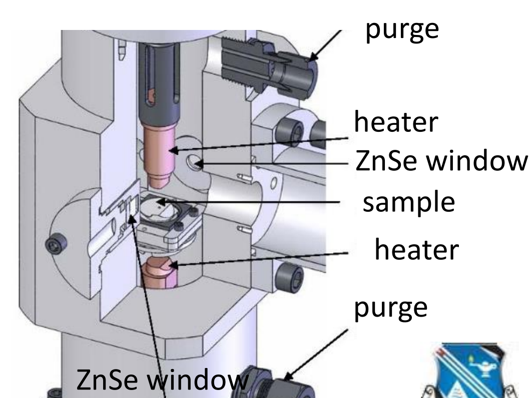
ENS Cachan 2014

Aksay and Selloni, Princeton, Zachariah, UMD, & Thynell, PSU

Covalent Bonds Stabilize Tetrazines for More Complete Decomposition



- Confined rapid thermolysis of pure tetrazines show tetrazines vaporize well before decomposition **unless stabilized on FGS (corroborated by T-Jump MS)**
- Modeling studies on the **decomposition of tetrazines** in vapor and when bound to FGS now underway



Aksay, Princeton, Thynell, PSU, and Zachariah, UMD

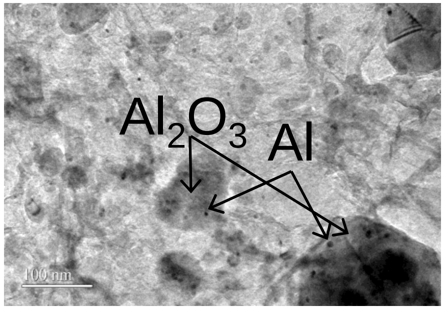
Nanoparticles on Graphene Supports

nAl on Graphene

- Reduction of AlCl solutions with $LiAlH_4$ at very low temperatures (-78 C, 30 min) in the presence of graphene yields, highly pyrophoric Al-graphene nanocomposites.

$AlCl + LiAlH_4 \rightarrow$ Al/graphene $+ 2H_2 +$ LiCl

- Passivation yields an Al_2O_3 shell with small 10 – 20 nm Al cores.
- XRD analysis shows crystalline Al and LiCl indicating the Al_2O_3 is amorphous.

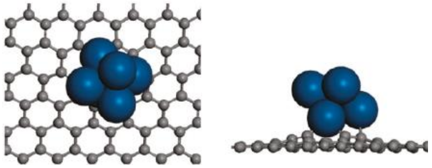


TEM image showing Al NPs (dark) and Al_2O_3 (gray) particles on graphene (light)

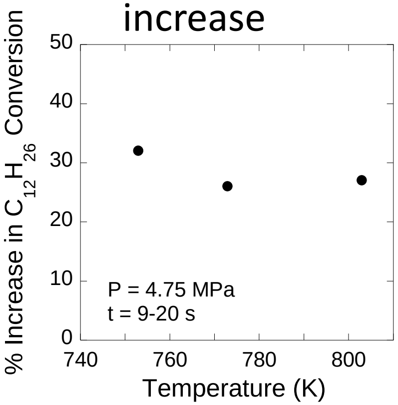
- Developing methods for controlling passivation, particle size and direct reduction of Al NPs on graphene oxide.

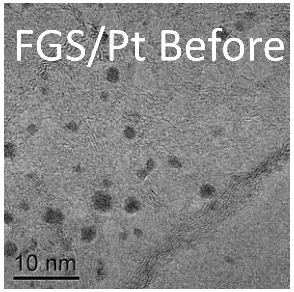
nPt on Graphene

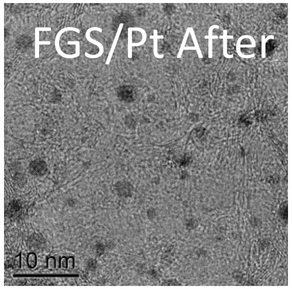
- Pt nanoparticles were uniformly pinned onto FGSs by impregnation method.
- Defects and functional groups on FGS lead to enhanced activity and stability of Pt particles.



- Thermal Decomposition of 50 ppmw FGS/Pt in $C_{12}H_{26}$ at 4.75 MPa yields 30% conversion increase





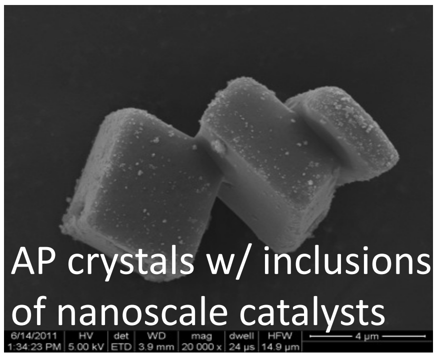


- Higher selectivity to H_2 observed with FGS/Pt

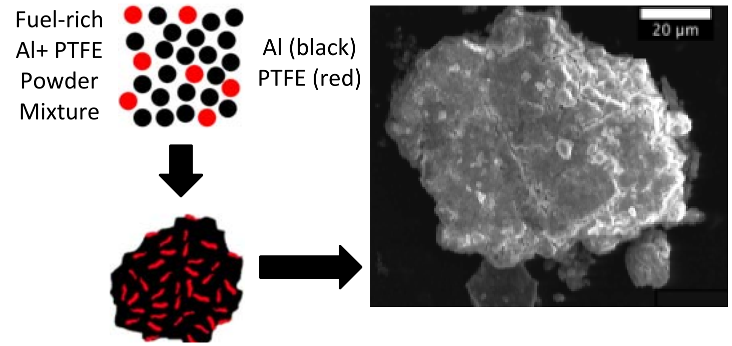
Eichhorn, UMD, Aksay, Princeton, and Yetter, PSU

Nanoscale Inclusions or Encapsulation

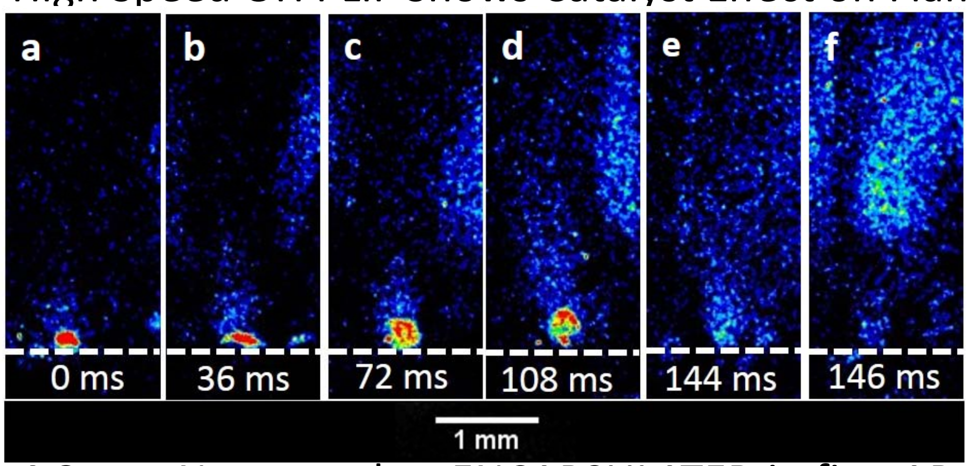
Approach: Use rapid crystallization with nano-catalysts as nucleation sites or mechanical activation (MA) to incorporate nanoscale inclusions in aluminum



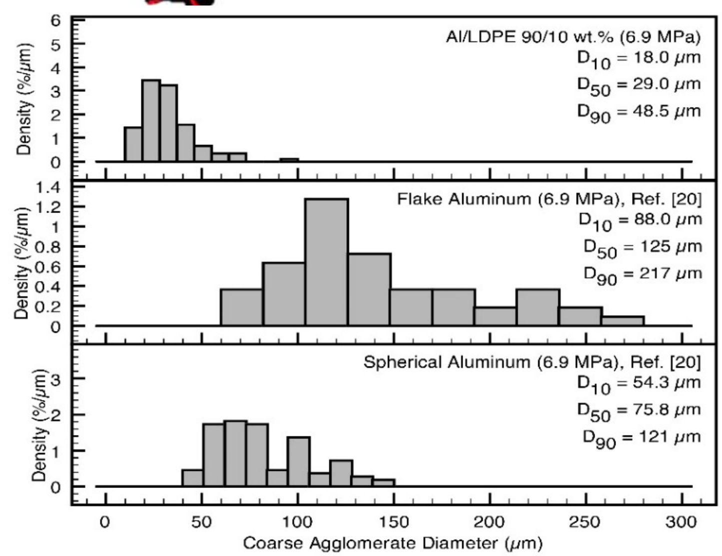
- Encapsulated nanoscale catalysts are MORE effective than catalyst powders added to propellants
- Burning rate 44% greater than micron-catalyzed propellant
- Yields less viscous propellants -> less binder could be used to improve performance!



High Speed OH PLIF Shows Catalyst Effect on Flames



4.8 atm Nano catalyst ENCAPSULATED in fine AP



Son, Purdue

Significant Accomplishments

1. Successfully assembled energetic microparticles with very narrow size distribution (**UMD**).
2. Assembled energetic microparticles of Al show enhanced burning rate, relative to NP counterparts (**UMD**).
3. Assembled energetic microparticles of Al when incorporated in propellant mix show enhanced burning relative to micron Al (**UMD**).
4. When assembled as thermites, microparticles show enhanced pressurization rate relative to standard formulated systems (**UMD**).
5. Prepared small Al NPs (~10 nm) that are significantly smaller that commercial Al particles (50-90 nm) (**UMD**).
6. **Synthesized and studied clusters of $Al_4Br_4(NEt_3)_4$ for combustion acceleration in toluene solutions** (**UMD**).
7. Prepared graphene-supported Al NPs without passivation (**UMD**).
8. For a *condensed phase*, showed that results from *ab initio* quantum chemistry calculations on transition states can be used in a continuum **model to describe thermal decomposition of a complex ionic compound (Guanidinium 5-amino-tetrazolate**) (**PSU**).
9. Investigated the effect of hydrogen peroxide on combustion of aluminum and water mixtures (**GeorgiaTech**)
10. Explored the effect of packing density on combustion of metal-based heterogeneous materials (**GeorgiaTech**)
11. **Studied effects of entrainment & agglomeration of particles on burning properties** of nanoaluminum-water mixtures (**GeorgiaTech**)

Significant Accomplishments

12. **Investigated heat transport in metal-based nano-energetic materials** (**GeorgiaTech**)
13. Synthesized FGS gels using covalently bound cross-linking energetic compounds (**Princeton**)
14. Performed controlled thermal decomposition of energetic gels (**UMD, PSU, Princeton**)
15. Performed molecular simulations to determine reaction paths and mechanisms of decomposition (**Princeton**)
16. Evaluated FGS as propellant catalyst and catalyst support (**PSU** and **Princeton**)
17. **Synthesizing conductive inks and gels for addressable devices** (igniters) (**Princeton**)
18. Analyzed porous silicon particle combustion and propagation mechanisms (**PSU**)
19. Encapsulation of nanocatalysts and graphene oxide in ammonium perchlorate, and characterizing the performance (**Purdue**)
20. Application of high speed OH PLIF to catalyzed ammonium perchlorate composites and SMX (**Purdue**)
21. **Development of 3D OH PLIF applied to multiphase combustion** (**Purdue**)
22. Fabrication and characterization of nanoscale inclusion materials (PTFE, LDPE, PMF) in micron sized aluminum or aluminum-silicon eutectic alloys (**Purdue**)
23. Performed single particle ignition experiments of composite particles and showed conditions needed for microexplosions (**Purdue**)
24. Fabricated SMX/HTPB propellant and characterized its performance to show that sensitivity is comparable with min/low smoke propellants and theoretical performance is better (**Purdue**)

Publications/Presentations

1. D.S. Sundaram and V. Yang, "Effect of Packing Density on Flame Propagation of Nickel-Coated Aluminum Particles," Combustion and Flame, DOI: 10.1016/j.combustflame.2014.05.014.
2. D.S. Sundaram and V. Yang, "Combustion of Micron-Sized Aluminum Particle, Liquid Water, and Hydrogen Peroxide Mixtures," Combustion and Flame, DOI: 10.1016/j.combustflame.2014.03.002.
3. D.S. Sundaram and V. Yang, "Effects of Entrainment and Agglomeration of Particles on Combustion of Nano-Aluminum and Water Mixtures," Combustion and Flame, Vol. 161, 2014, pp. 2215-2217.
4. T.L. Connell, Jr., G.A. Risha, R.A. Yetter, C.W. Roberts, G. Young, Boron and Polytetrafluoroethylene as a Fuel Composition for Hybrid Rocket Applications, J. Prop. Power, DOI: 10.2514/1.B35200, 2014.
5. N. Kumbhakarna, and S.T. Thynell, "Development of a reaction mechanism for liquid-phase decomposition of guanidinium 5-amino tetrazolate," Thermochimica Acta, Vol. 582, 2014, pp. 25-34.
6. N. R. Kumbhakarna, K. J. Shah, A. Chowdhury, and S. T. Thynell, "Identification of liquid-phase decomposition species and reactions for guanidinium azotetrazolate," Thermochimica Acta, Vol. 590, 2014, pp. 51-65.
7. T. R. Sippel, S. F. Son, and L. J. Groven, "Aluminum Agglomeration Reduction in a Composite Propellant Using Tailored Al/PTFE Particles," Combustion and Flame, Vol 161(1), pp. 311-321 (2014). http://dx.doi.org/10.1016/j.combustflame.2013.08.009
8. D. A Reese, S. F. Son, and L. J. Groven, "Composite Propellant Based on a New Nitrate Ester," Propellants, Explosives, Pyrotechnics, (2014), online version available, http://dx.doi.org/10.1002/prep.201300157
9. K. Y. Cho, A. Satija, T. L. Pourpoint, S. F. Son, and R. P. Lucht, "High-Repetition-Rate Three-Dimensional OH Imaging Using Scanned Planar Laser-Induced Fluorescence System for Multiphase Combustion," Applied Optics, Vol. 53(3), pp. 316-326 (2014). http://dx.doi.org/10.1364/AO.53.000316
10. S. C. Shark, T. L. Pourpoint, S. F. Son, and S. D. Heister, "Performance of Dicyclopentadiene/H2O2-Based Hybrid Rocket Motors with Metal Hydride Additives," Journal of Propulsion and Power, Vol. 29(5), pp. 1122-1129 (2013). http://dx.doi.org/10.2514/1.B34867
11. T. R. Sippel, S. F. Son, L. J. Groven, S. Zhang, and E. L. Dreizin, "Exploring Mechanisms for Agglomerate Reduction in Composite Solid Propellants with Polyethylene Inclusion Modified Aluminum," accepted for publication in Combustion and Flame, 2014.
12. H.S. Sim, R.A. Yetter, D.M. Dabbs, I.A. Aksay, Colloidal Platinum-Decorated Graphene Sheets for Enhanced Fuel Decomposition Under Supercritical Conditions, Proceedings of the Combustion Institute, 35, 2013, in revision.
13. D.S. Sundaram and V. Yang, "Combustion of Nano Aluminum Particles: A Review," Combustion, Explosion, and Shock Waves, submitted, 2014.
14. V. S. Parimi, S. A. Tadigadapa. R. A. Yetter, Reactive Wave Propagation Mechanisms in Energetic Porous Silicon Composites, Combustion Science and Technology, submitted for review 2014.

Publications/Presentations

15. D.S. Sundaram and V. Yang, “A General Theory of Ignition and Combustion of Aluminum Particles,” Combustion and Flame, to be submitted.
16. D.S. Sundaram, V. Yang, and R.A. Yetter, “Metal-Based Nanoenergetic Materials: Synthesis, Properties, and Applications,” Progress in Energy and Combustion Science, to be submitted.
17. C. Zhang, D. M. Dabbs, L.-M. Liu, I. A. Aksay, R. Car, A. Selloni “Infrared Spectra of Graphene Oxide”, to be submitted, 2014.
18. Y. Li, V. Alain-Rizzo, L. Galmiche, P. Audebert, F. Miomandre, G. Louarn, M. Bozlar, M. A. Pope, D. M. Dabbs, I. A. Aksay“Functionalization of graphene oxide by tetrazine derivatives: a versatile approach toward covalent bridges between graphene sheets”, to be submitted, 2014.
19. N. R. Kumbhakarna, K. J. Shah, A. Chowdhury, and S. T. Thynell, "Identification of liquid-phase decomposition species and reactions for triaminoguanidinium azotetrazolate,“ in preparation.
20. H.S. Sim, R.A. Yetter, D.M. Dabbs, I.A. Aksay, Colloidal Platinum-Decorated Graphene Sheets for Enhanced Fuel Decomposition Under Supercritical Conditions, 35th International Symposium on Combustion, San Francisco, California, USA, August 3-8, 2014.
21. S. F. Son, “High-speed OH PLIF and Imaging of Propellant Combustion,” Invited Lecture at University of Texas at El Paso, El Paso, Texas (Jan., 2014).
22. S. F. Son, “High-speed OH PLIF and Imaging of Propellant Combustion,” Invited Lecture at Iowa State University, Ames, IA (Oct, 2013).
23. S. F. Son, “Overview of Energetic Materials Research at Purdue,” Invited lecture at the U.S./France Working Group 1 Meeting at China Lake, CA (Sept. 2013).
24. S. F. Son, “Playing With Fire,” Two invited classes lectures to professionals and business leaders at Mickey’s Camp http://www.mickeyscamp.com (Aug. 2013).
25. S. F. Son, “Solid Propellant Combustion Enhancement Using Fluorocarbon Inclusion Modified Aluminum,” Crane Naval Laboratory (Aug. 2013).
26. S. F. Son, “High-speed OH PLIF and Imaging of Propellant Combustion,” Invited Plenary Lecture at the International Pyrotechnic Society Meeting in Valencia, Spain (May, 2013).
27. S. F. Son, “Tailored Energetic Material Particles,” Invited seminar for the Center for

Internal Collaborations/Interactions

1. **UMD** (Zachariah) analyzing reactions of energetic gels under high heating rates produced by **Princeton** (Aksay)
2. **PSU** (Thynell) studying thermal decomposition of energetic gels analyzing fabricated materials by **Princeton** (Aksay)
3. **PSU** (Thynell) analyzing decomposition reactions of encapsulated nanocatalysts and graphene oxide in AP produced by **Purdue** (Son)
4. **Purdue** (Son) evaluating combustion properties of nanoaluminum – nitrocellulose composite particles fabricated by **UMD** (Zachariah)
5. **PSU** (Yetter) collaborating with **UMD** (Zachariah and Eichhorn) on droplet combustion experiments of Al cluster precursors and mesoscopic particles.
6. **PSU** (Yetter) collaborating with **Purdue** (Son) on particle size effects in propellants.
7. Collaborations of molecular simulations to determine reaction paths and mechanisms of decomposition energetic gels (Aksay, A. Selloni, and R. Car) **Princeton**

External Collaborations/Interactions

1. **PSU** (Yetter) collaborating with Professor Adri van Duin on ReaxFF of aluminum particles.
2. **UMD** (Eichhorn) collaborating with Andreas Schnepf (**University of Tubingen**) on Si and Ge cluster synthesis.
3. **UMD** (Eichhorn) collaborating with Kit Bowen (**Johns Hopkins**) on mechanistic combustion studies of clusters.
4. **UMD** (Eichhorn) collaborating with Dennis Mayo and Chad Stoltz (**NSWC Indian Head**) on cluster synthesis and characterization.
5. **UMD** (Zachariah) collaborating with Greg Young (**NSWC-IH**) on combustion of composite mesoparticles.
6. **UMD** (Zachariah) interacting with Scott Weingarten and Jennefer Gottfried (**ARL**) via transfer of energetic materials and molecular computations.
7. **UMD** (Zachariah) transferred reactive materials to Dana Dlott (**UIUC**)
8. **UMD** (Zachariah) collaborating with Tom LeGrange (**LLNL**) on Dynamic TEM of composite energetic materials via *UMD student* visitor
9. **Princeton** (Aksay) collaborating with **Ecole Normale Supérieure de Cachan** (France) on synthesis of FGS gels using covalently bound cross-linking energetic compounds.
10. **Purdue** (Son) sent composite aluminum with inclusion materials for testing to: **EMPI**, **AFRL (Eglin AFB)**, **LANL**, and **Navy Crane** *Laboratory*.
11. **Purdue** (Son) collaborated on shock tube and explosive experiments with **UIUC** (Glumac)

Emphasis on Education

19 Graduate Students, 3 Postdoctoral Students, 2 Undergraduates

1. Mr. Murali Gopal Muraleedharan, Graduate Student, School of Aerospace Engineering, Georgia Institute of Technology, Atlanta, GA
2. Mr. Hung Sub Sim, Graduate Student, Department of Mechanical and Nuclear Engineering, Pennsylvania State University, PA
3. Mr. Venkata Sharat Parimi, Graduate Student, Department of Mechanical and Nuclear Engineering, Pennsylvania State University, PA
4. Mr. Phil Guerieri , Graduate Student, Department of Mechanical Engineering, University of Maryland, MD
5. Mr. Jeff Delisio , Graduate Student, Department of Chemistry, University of Maryland, MD
6. Ms. Samantha DeCarlo, Department of Chemistry, University of Maryland, MD
7. Ms. Lauren Stevens, Department of Chemistry, University of Maryland, MD
8. Mr. Ameya Sohani, Chemical and Biological Engineering, Princeton University, NJ
9. Mr. Kevin Sallah, Chemical and Biological Engineering, Princeton University, NJ
10. Ms. Michail Alifierakis, Chemical and Biological Engineering, Princeton University, NJ
11. Mr. Betul Uralcan, Chemical and Biological Engineering, Princeton University, NJ
12. Mr. N. Kumbhakarna, Graduate Student, Department of Mechanical and Nuclear Engineering, Pennsylvania State University, PA
13. Mr. K. Zhang, Graduate Student, Department of Mechanical and Nuclear Engineering, Pennsylvania State University, PA
14. Dr. Chris Snyder, Postdoctoral Fellow, Department of Chemistry, University of Maryland, MD
15. Dr. Dilip Srinivas Sundaram, Postdoctoral Fellow, School of Aerospace Engineering, Georgia Institute of Technology, Atlanta, GA
16. Dr. Cui Zhang, Postdoctoral Research Associate, Department of Chemistry, Princeton, NJ
17. Ms. S. Isert (also NSF Fellow, attended Princeton combustion summer school), Department of Mechanical Engineering, Purdue University, IN
18. Mr. D. Kittell (Ph.D. candidate), Department of Mechanical Engineering, Purdue University, IN
19. Mr. A. McBain (M.S. Student), Department of Mechanical Engineering, Purdue University, IN
20. Dr. D. Reese (completed Ph.D., working at Aerospace Corp.), Department of Mechanical Engineering, Purdue University, IN
21. Dr. T. Sippel (completed Ph.D., Assistant Prof. at Iowa State U.), Department of Mechanical Engineering, Purdue University, IN
22. Mr. B. Terry (Ph.D. candidate and NDSEG Fellow), Department of Mechanical Engineering, Purdue University, IN
23. 2 students were partially supported at Purdue University

Research Scientists

Dr. Daniel M. Dabbs, Research Scientist, Chemical and Biological Engineering, Princeton University, NJ

Dr. Cem Ustundag, Visiting Scientist, Yildiz Technical University, Istanbul, Turkey

Dr. Lori Groven, formerly Purdue University, now Professor at SDSM&T, South Dakota

Dr. E. Gunduz, Research Scientist, Purdue University, IN

Dr. Nasir Memon, Visiting Professor, Purdue University, IN

Budget

Start Date: November 1, 2012

3 years at 1.5 million per year
Optional 2 years at 1.5 million per year

Extras

Approach

AREA 1: Multiscale Processing of Nanoenergetic Materials

- Processing of nanoenergetic materials
  - Solution based combustion accelerators (low valent Al precursors)
  - Non-aluminum clusters (bimetallic mass analogs of aluminum, Ti-B)
- Energetic Metallic Cluster/Nanoparticle Composites
  - Mesoscopic aggregates (electrospray)
  - Encapsulated crystals (rapid crystallization)
  - Nanoscale inclusions (mechanical activation)
- Functionalized Graphene Sheets
  - Decorated FGS with high nitrogen ligands, energetic nanoparticles, and nanocatalysts
  - Linked FGSs with high nitrogen ligand bridges
- Activation Methods
  - Piezoelectric energetic materials
  - FGS-based RF transponders
  - Photostimulation and low temperature plasma

Approach (continued)

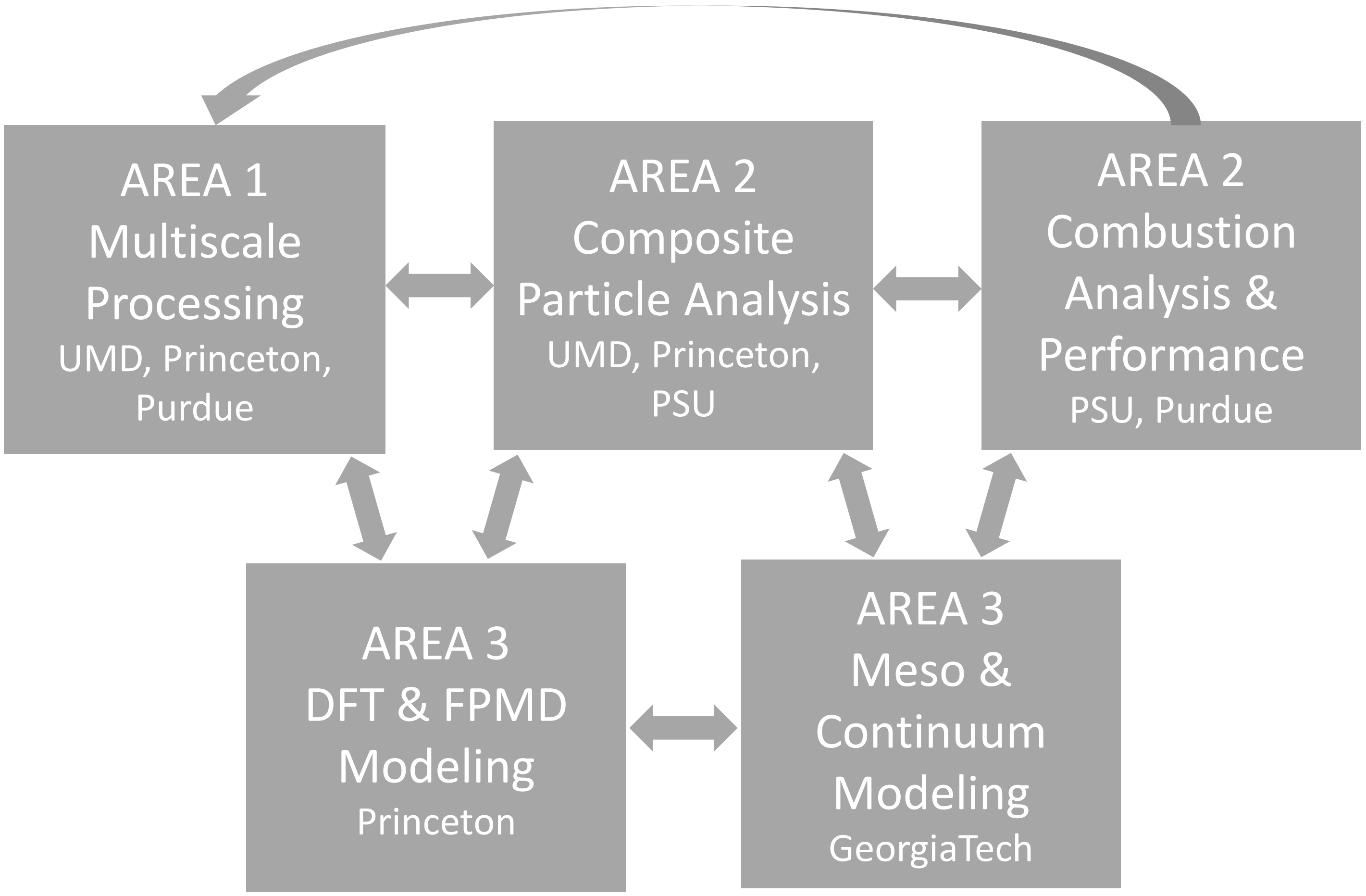
AREA 2: Experimental Analysis and Performance Characterization

- Kinetic Analyses (Time resolved MS, Emission, FTIR, Dynamic TEM)
  - T-Jump Filament (10^6 K/s)
  - Confined Rapid Thermolysis (10^3 K/s)
  - Thermogravimetric and Differential Scanning Calorimetry (10 K/s)
- Combustion and Performance Analyses (1 – 500 bar)
  - Burning Rates for Solids and Liquid Propellants (strands and droplets)
  - Constant Volume Bomb Ignition Energy and Delay Times
  - Flame Structure via Femtosecond Planar Laser Induced Fluorescence, High Speed Shadowgraphy and Photography
- Sensitivity Measurements
  - Electrostatic Discharge, Drop-Weight Impact, Friction

AREA 3: Multiscale Modeling and Simulation

- Density Functional Theory electronic structure calculations - properties
- First Principles Molecular Dynamics simulations – reaction mechanisms
- Continuum Mechanics Simulations – combustion of composite particles, strands

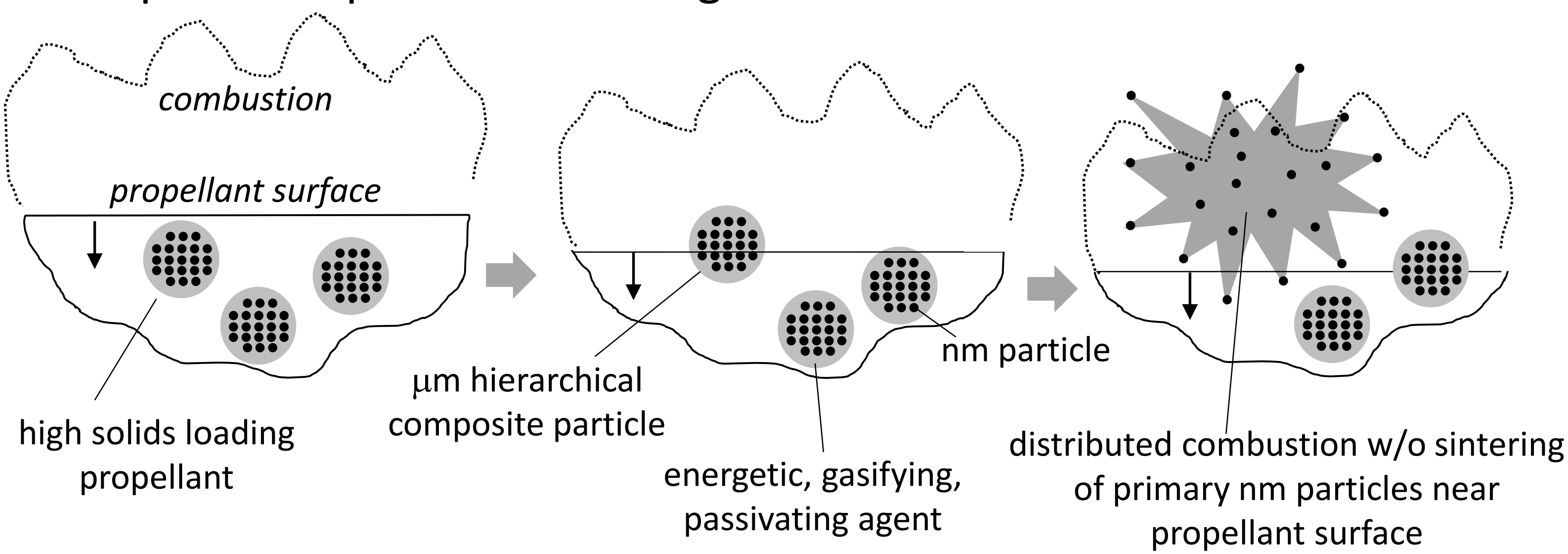
Program Structure and Interactions



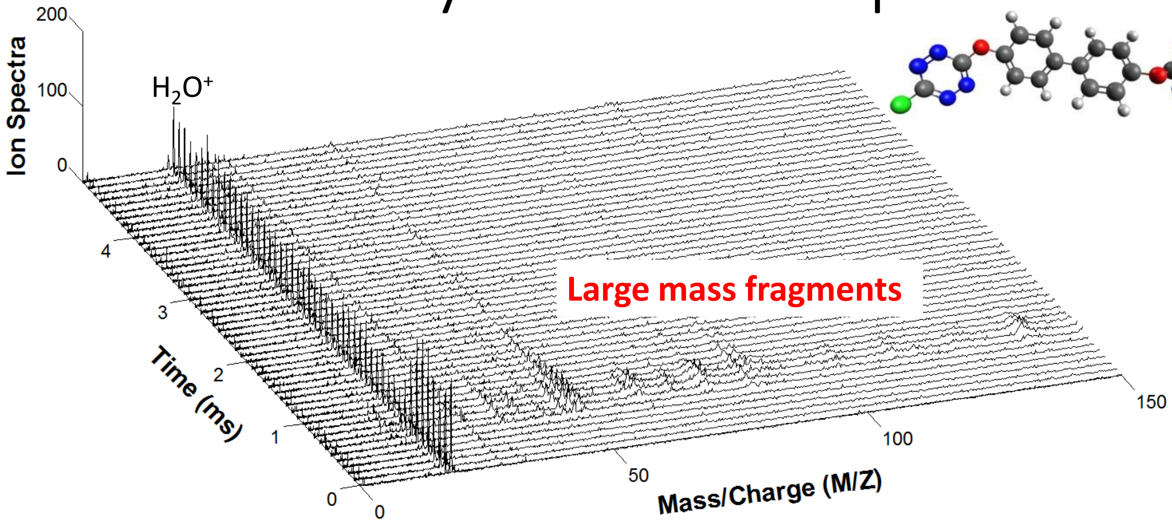
Critical Technology Issues

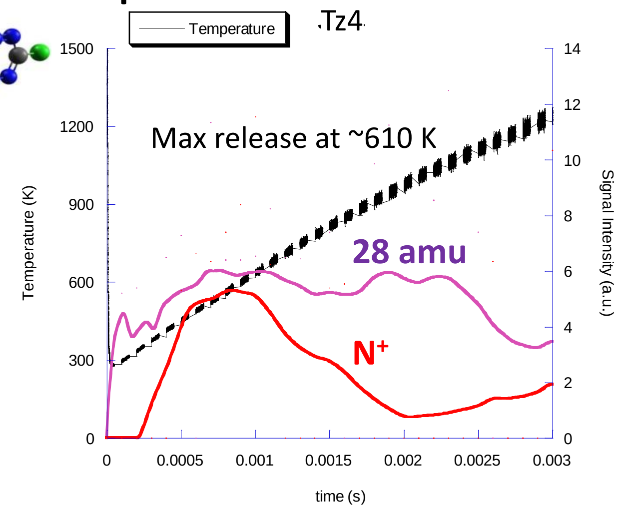
- Integrated multiscale organization of energetic materials have lagged far behind chemistries in other disciplines.
- There is no fundamental understanding of what type of nano and micron scale hierarchical structures provide desirable performance in combustion, mechanical, and hazard characteristics.

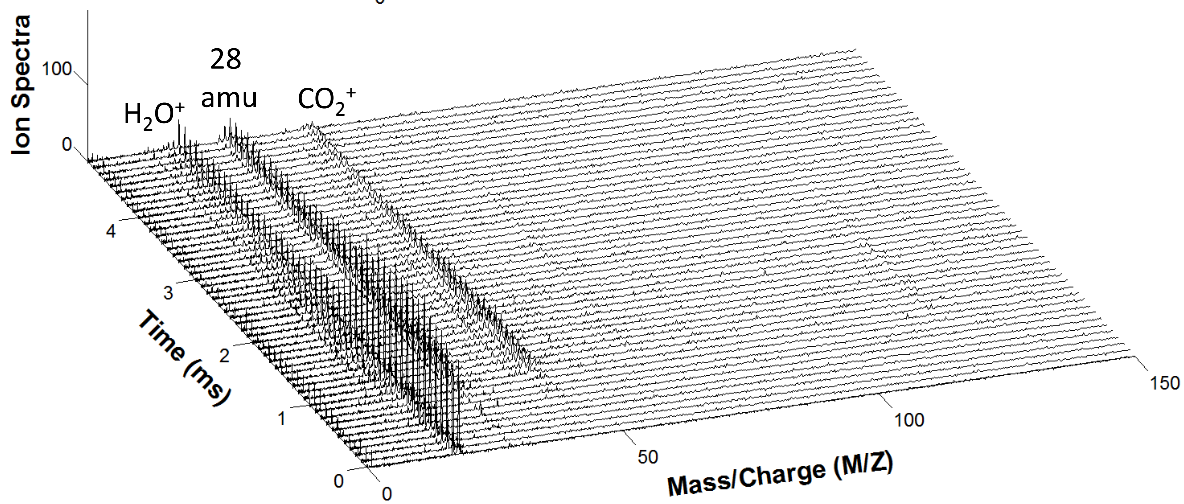
Example of Propellant with Integrated Multiscale Hierarchical Structure

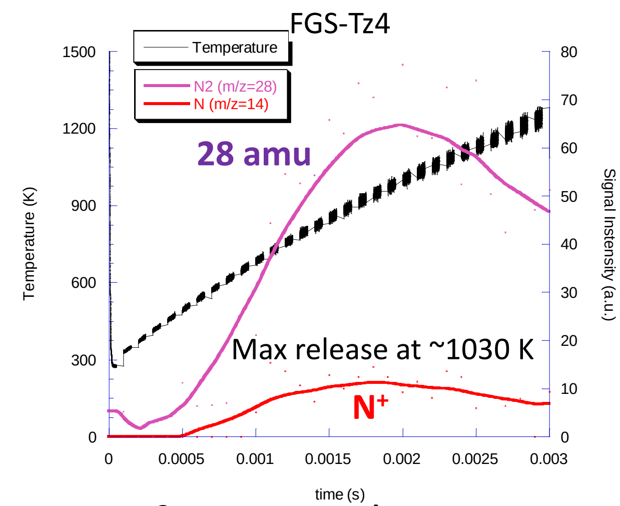


FGS-Tetrazine Compound Stabilizes Tetrazine with Delayed but Complete Decomposition









- Pure tetrazine volatilizes before decomposition (large mass fragments)
- High nitrogen-content decomposition products from **FGS-tetrazine** compounds

Aksay, Princeton, and Zachariah, UMD

Future Studies:

- **Effect of Tz-FGS on AP decomposition: mixtures of AP/Tz-FGS as composite energetic materials**
  - **“Inks” → printable energetic materials; compare with other additives (nanoparticles)**
  - **Porous FGS-based networks (gels and foams) → hosts for propellant**
  - **Patterned 3-dimensional structures**

Goal: Fabricating structures designed for enhanced control of propellant combustion

- **Couple with FGS-based RF transponders → remote controlled igniters**