RICHARD A. YETTER is Professor of Mechanical Engineering at the Pennsylvania State University. He received his B.S. from Syracuse University, M.S. from Cornell University, and M.A. and Ph.D. from Princeton University. His current research interests include propellant and nano energetic materials combustion, high temperature / high-pressure combustion chemistry, heterogeneous combustion, and micro propulsion and power systems.

He was previously a Research Engineer at the Scientific Research Laboratories of Ford Motor Company, a Senior Research Scientist and Lecturer at Princeton University, and a Research Collaborator at the Brookhaven National Laboratory.

He is an editor of *Combustion Science and Technology*, co-editor of the 30th and 31st *Proceedings of the Combustion Institute*, associate editor of *International Journal of Energetic Materials and Chemical Propulsion*, section editor of *Frontiers of Energy and Power Engineering in China*, and currently serves on the editorial board of *Progress in Energy and Combustion Science* and *Journal of Propulsion and Power*.

Dr Yetter is an author or co-author of over two hundred scientific publications, two books, and two US patents. He is the recipient of the Silver Medal and Distinguished Paper Awards from the Combustion Institute, and the Martin Summerfield Best Paper Award and Best Poster Paper Award from the Sixth and Eighth International Symposium on Special Topics in Chemical Propulsion, respectively.

Nanopropellants

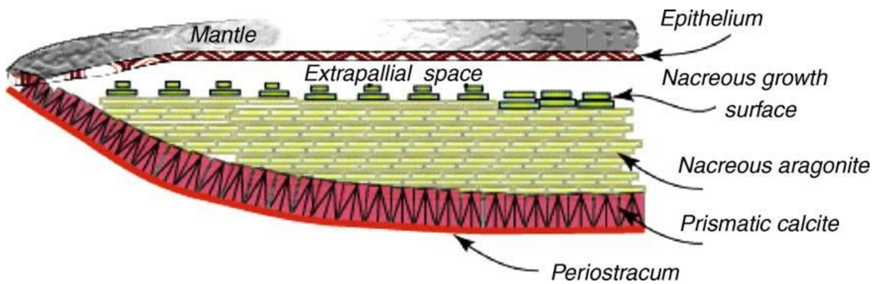
- Energy density vs. sensitivity.
- Nanopropellants will not necessary provide higher energy densities, but can provide improved usage of the stored chemical energy. Nanoingredients could produce new gelled and solid propellants. Nanopropellants may be used in non-conventional applications.
- NASA Nanotechnology Roadmap: “Passivation chemistries must be developed to prevent premature oxidation of the nanoparticles and synthesis methods, including self-assembly based techniques, are needed to tailor the shape and size of the nanoparticles in order to control burn rates.”

Critical Technology Issues

- Self-assembly and supramolecular chemistry of the fuel and oxidizer elements of energetic materials have lagged far behind chemistries in other disciplines (such as pharmaceuticals, microelectronics, microbiology).

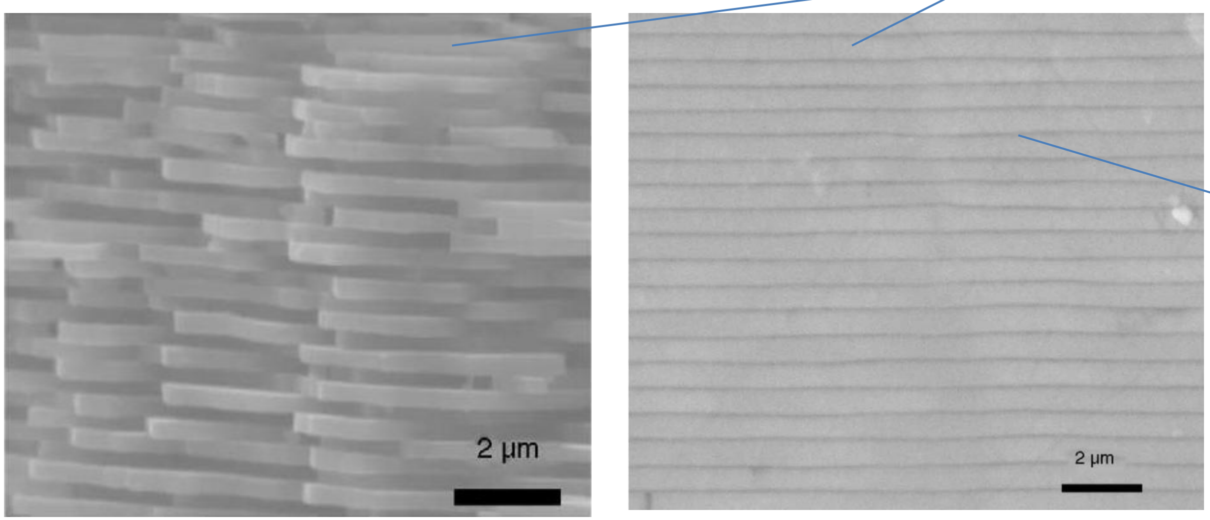
- There is limited fundamental understanding of what type of supramolecular structures provide desirable performance in combustion, mechanical, and hazard characteristics.

Structure of the Abalone Shell



Structure of the *nacre:*
95 wt.% inorganic material
5 wt.% organic material

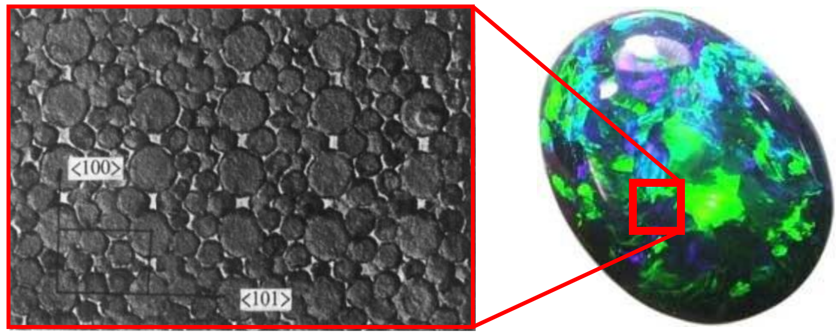
inorganic layers: $CaCO_3$ - aragonite



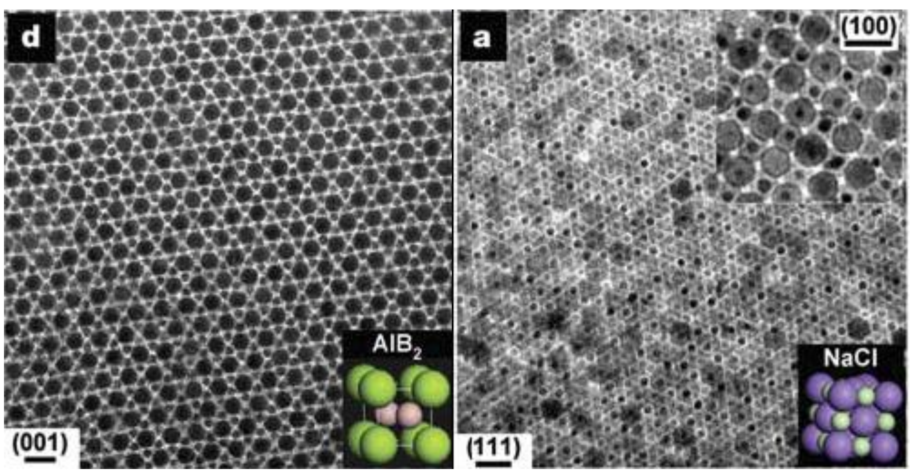
organic layers:

A. Lin and A. Meyers, *Mat. Sci. Eng. A* 390, 27-41, 2005.

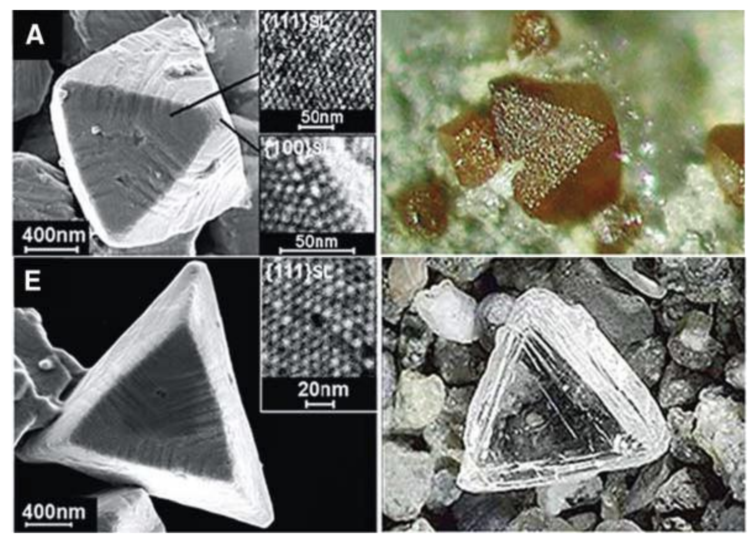
Nanoparticle Self-Assembly



Sanders, J. V., Murray, M. J., *Nature* v275, 1978.

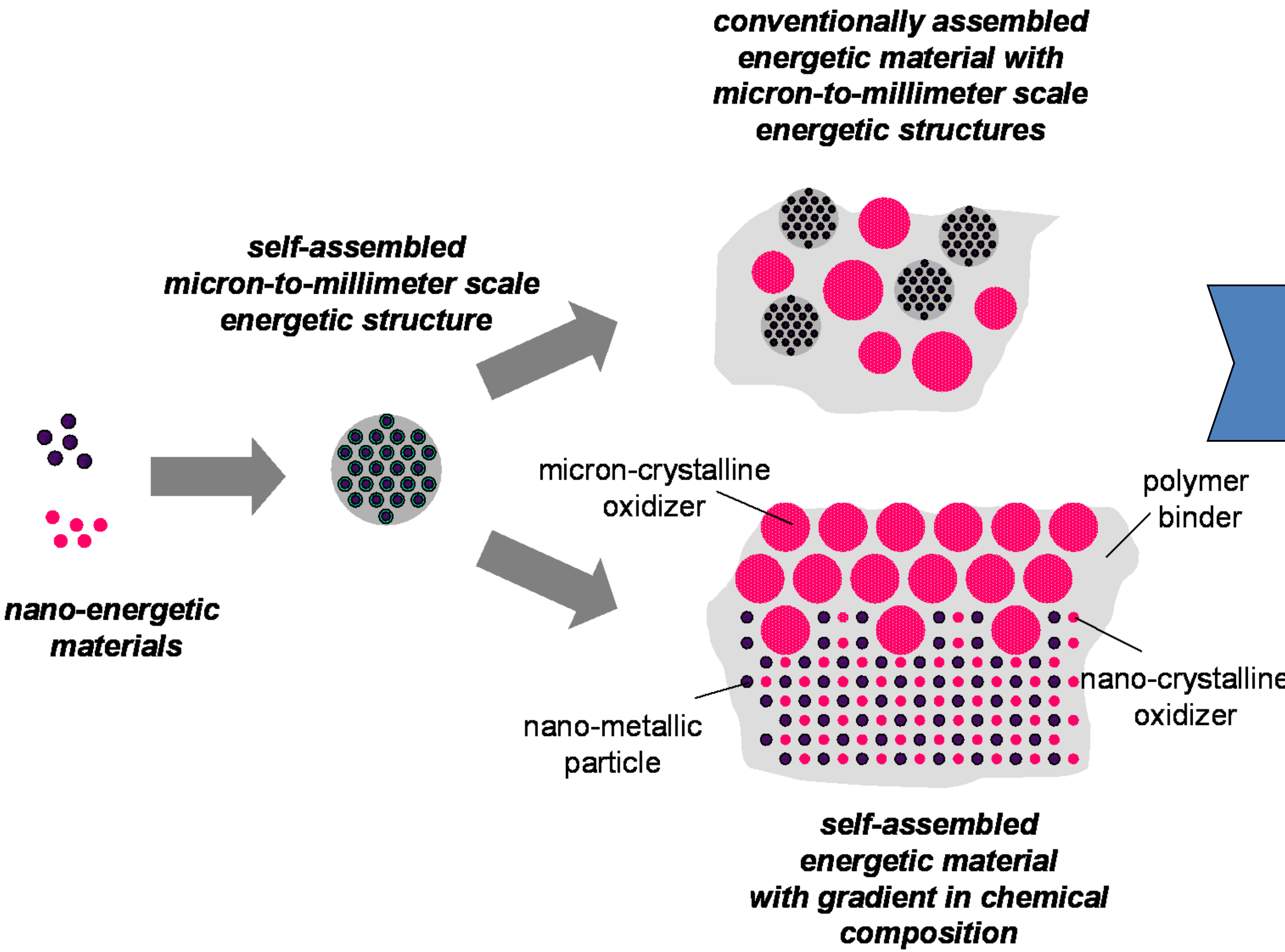


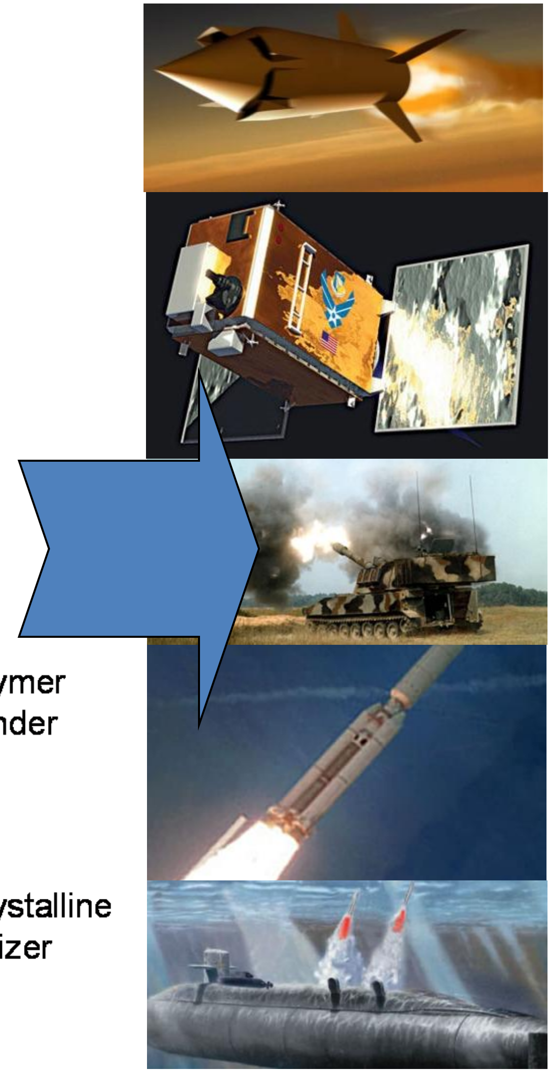
Shevchenko, E. V., Talapin, D. V., Kotov, N. A., O'Brien, S., Murray, C. B., *Nature* v439, 2006



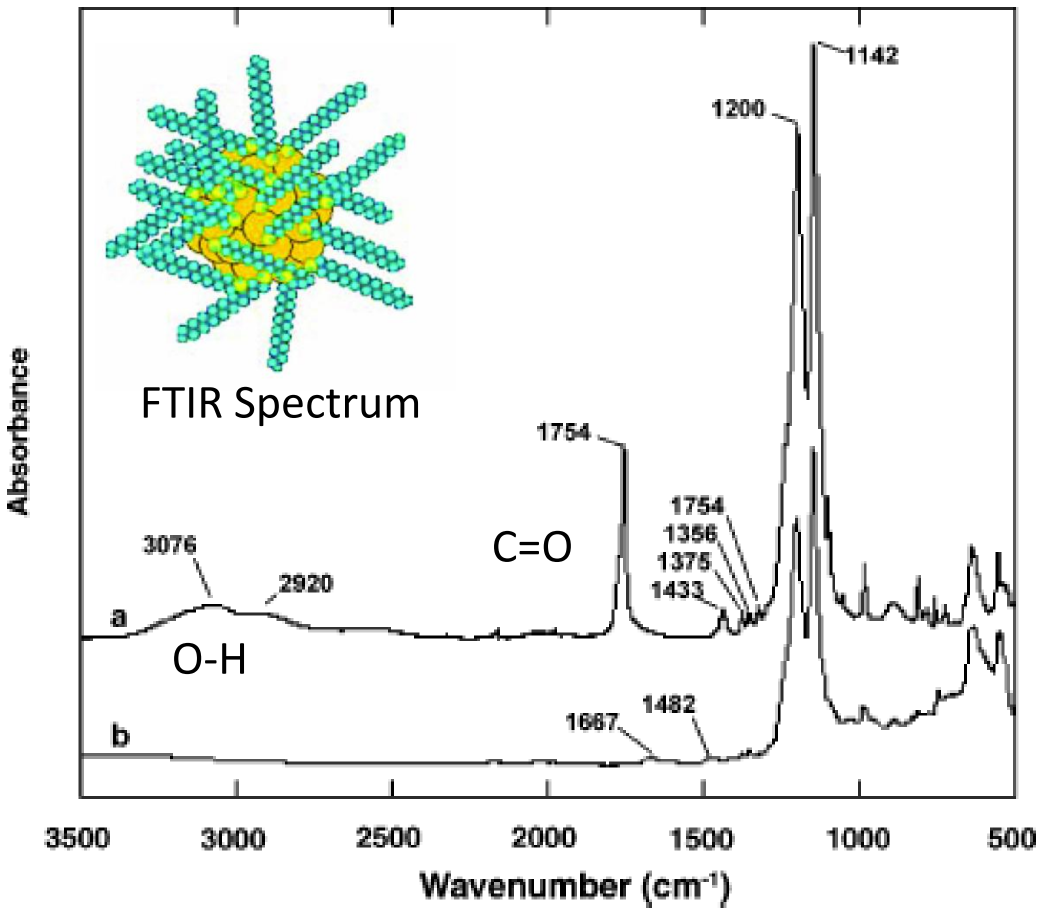
Kalsin, A. M., Fialkowski, M., Paszewski, M., Smoukov, S. K., Bishop, K. J., Grzybowski, B. A., *Science* v312, 2006

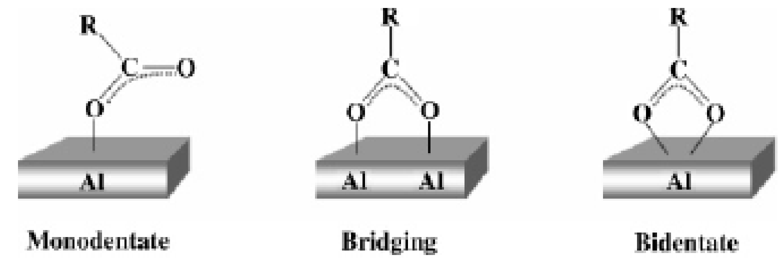
Organization and Assembly at the Nanoscale

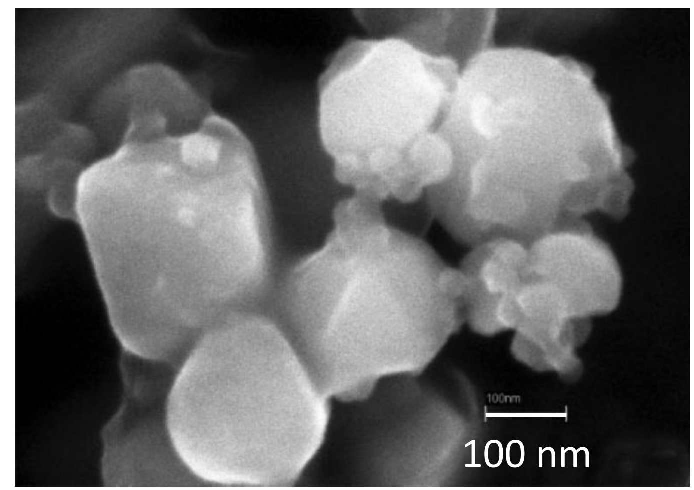




Surface Passivation of Bare Al Nanoparticles Using Perfluoroalkyl Carboxylic Acids ($C_{13}F_{27}COOH$)





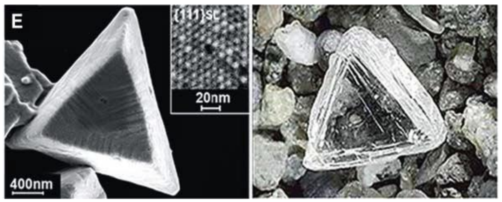


SEM (225 000 magnification) of Al-$C_{13}F_{27}COOH$

R.J. Jouet, A.D. Warren, D.M. Rosenberg, V.J. Bellitto, K. Park, and M.R. Zachariah, Chem. Mater. 17 (2005) 2987-2996.

R.J. Jouet, J.R. Carney, R.H. Granholm, Sandusky, H.W. and A.D. Warren, Mater. Sci. Technol. 22 (2006) 422-429.

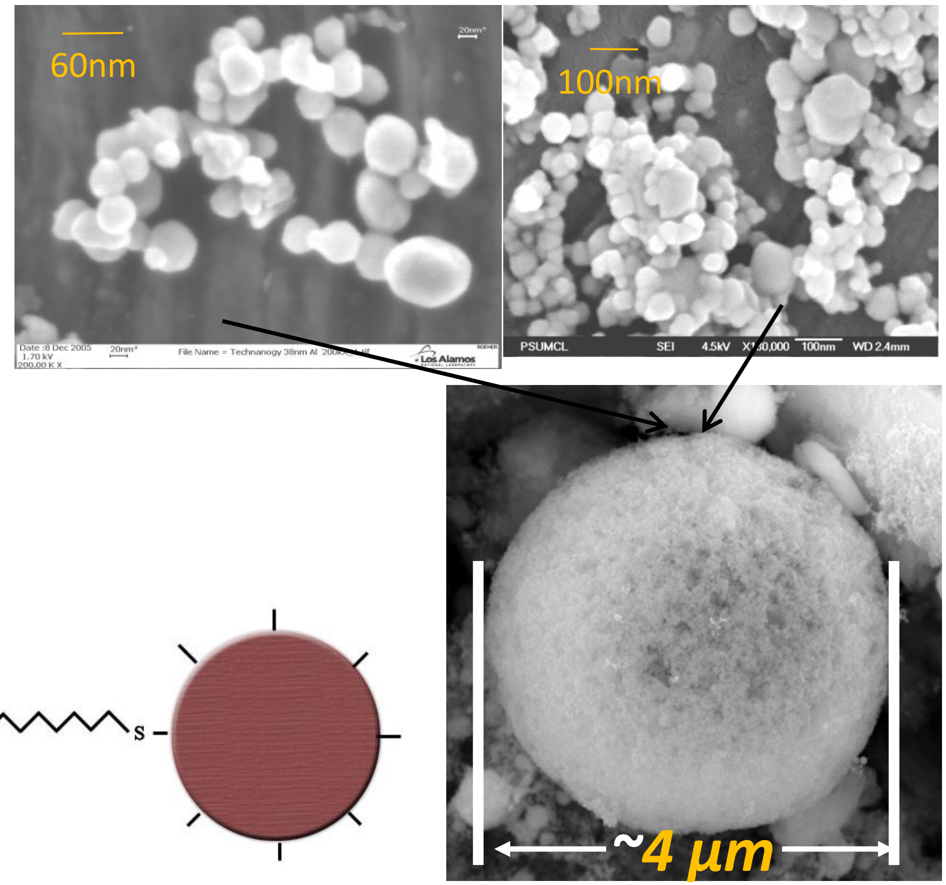
Self-Assembled Nanoscale Thermite Microspheres

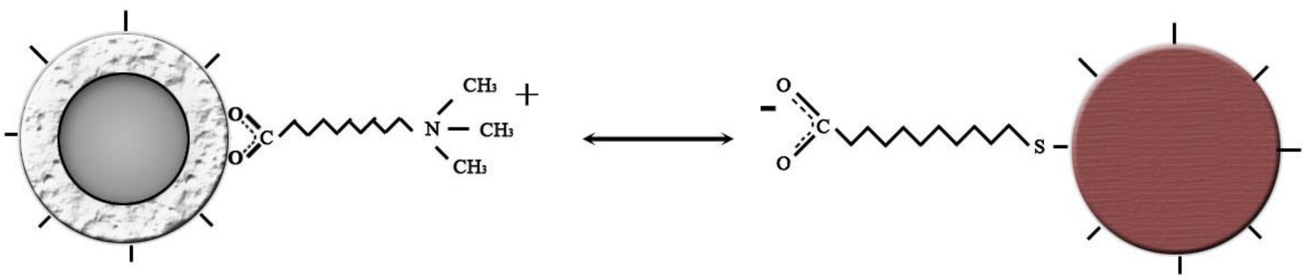


Kalsin *et al*., *Science,* v312, 2006

- Create Self-Assembled Monolayer (SAM) on surface of individual particles
- Monolayers contain a functionalized group at tail end (either + or – charged)
- When mixed in a diluted and slightly elevated temperature they form macroscale structures with nanoscale constituents

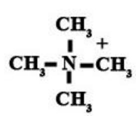
nAl (38nm) nCuO(33nm)





nAl-TMA
(trimethyl(11-mercaptoundecyl) ammonium chloride

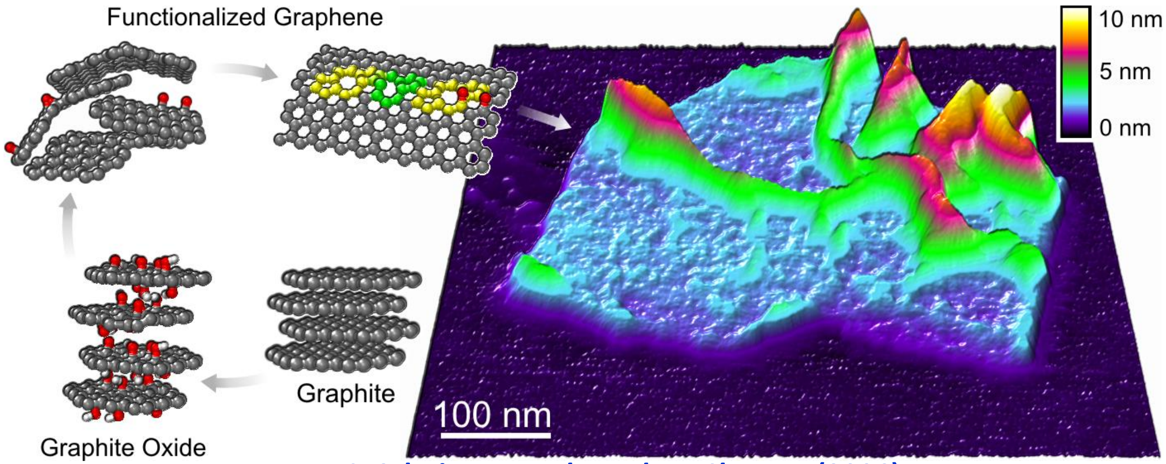
Cl-



nCuO-MUA
(11-mercaptoundecanoic acid)

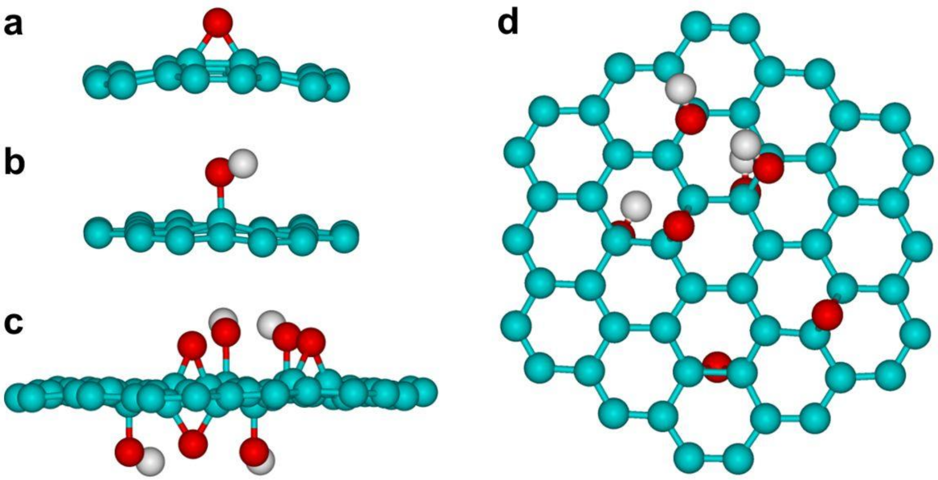
Malchi, J., Foley, T., Yetter, R.A., ACS APPLIED MATERIALS & INTERFACES, 1, 11, 2420, 2009

Functionalized Graphene Sheets as Catalysts Supports for Liquid Propulsion



H.C. Schniepp, *et al.*, *J. Phys. Chem. B* (2006)

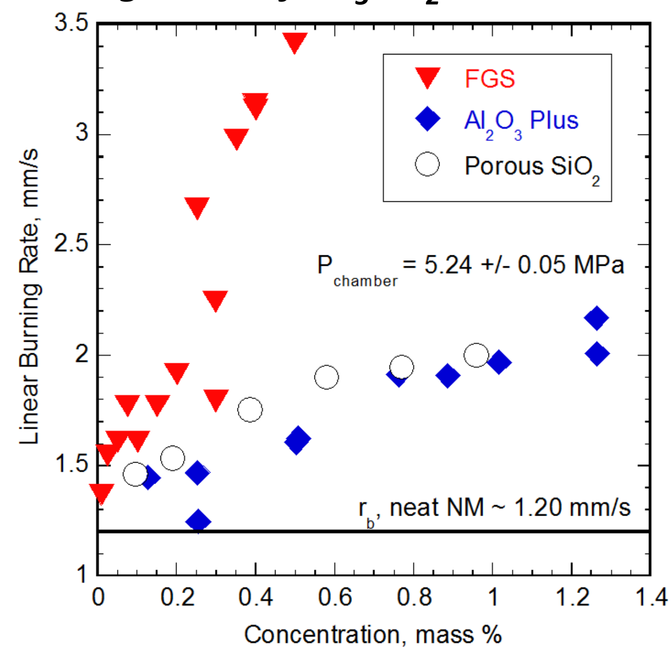
- **FGS active sites:**
  - defects as radical sites
  - carboxylate (edge), epoxide and hydroxyl (surface) functionalities
  - The C/O ratio is adjustable from 2 to 500, i.e., FGS_2 to FGS_{500}



a: epoxide on graphene, b: hydroxide on graphene
c, d: in-plane and overhead view of a FGS

J. L. Sabourin, D. M. Dabbs, R. A. Yetter, F. L. Dryer, and I. A. Aksay, *ACS Nano*, 3,12,3945,2009.

Burning Rates of CH_3NO_2 Enhanced



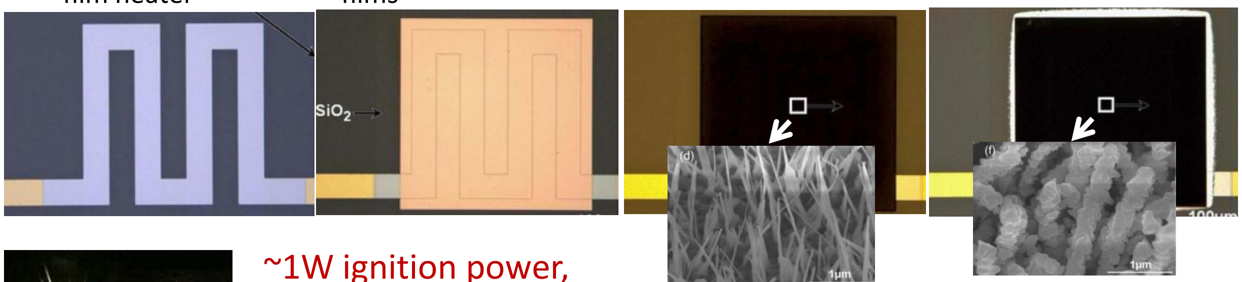
Nanoengineered Energetic Materials

- At the microscale: nanoenergetics on a chip
  - Heat, pressure, specific gases on demand => propulsion, power, actuation, instrument calibration, pumping, switches, initiators
  - Conventional MEMs fabrication methodology: soft lithography, screen and inkjet printing, PVD, etc.
  - New fuels and oxidizers: porous silicon, nanothermites, and intermetallics
- Scale-up to the macroscale

MEMS Device Integrating Nanothermite Al/CuO

Micro initiator/ Micodetonator → CuO/Al nanothermite on igniter chip (1mm²)

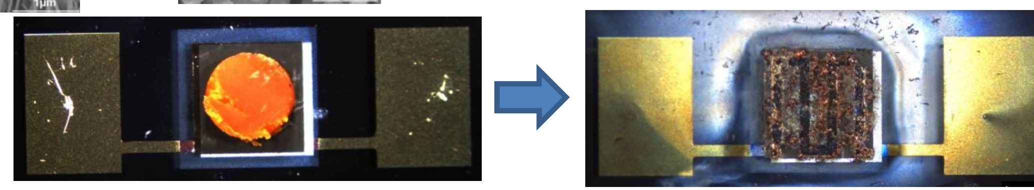
Au/Pt/Cr thin film heater | Patterned SiO2 & Cu films | CuO nano wires | Al/CuO nEM



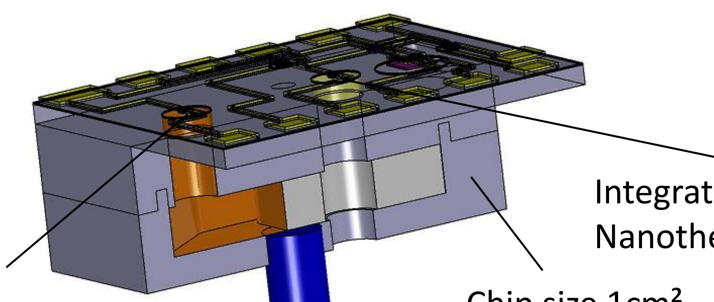
Ignition of a propellant has been demonstrated

Zhang, et al, *Nanotechnology 18 (2007)*
Zhang, et al, *J. of Micro ElectroMechanical Systems, 2008*

~1W ignition power,
0.1 ms ignition delay,
0.12 mJ ignition energy
60 mJ output energy



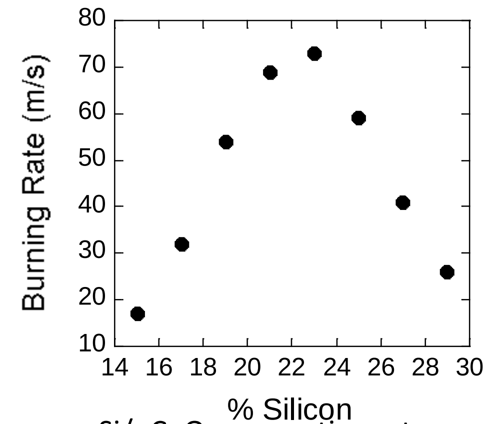
1 cm³ MEMS Safe Arm Fire → MEMS integrate sensors, circuitry, actuator, electrical protections (pyrotechnical switches), highly energetic material ($[Co(NH_3)_6]_2[Mn(NO_3)_4]_3$, Al/CuO nanothermite), moving barrier….



Pezous et al*J. Phys & Chem. Solids 71, (2010)*
Pezouset al, *Sensors and Actuators A159, 2010*

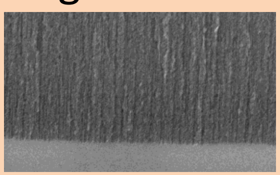
PSi as a Nanostructured Fuel

- McCord et al observed fast combustion reaction of PSi with nitric acid (1992)
- Explosive oxidation of PSi in liquid oxygen by Kovalev et al (2001)
- Composite solid state system based on PSi pores filled with gadolinium nitrate at room temperature by Mikulec et al. (2002)
- Clement et al (2004) and du Plessis (2006) study various oxidizers and begin construction of MEMs devices
- Examples of pore fillers: NaClO4 x 1H2O, Ca(ClO4)2 x 4H2O, Magnesium Perchlorate, Sulfur, PFPE

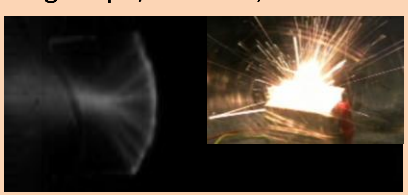


nSi/nCuO propagation rates; PVD of CuO on pSi, Gesner, J. and Yetter, RA

Psi-oxidizer energetic materials

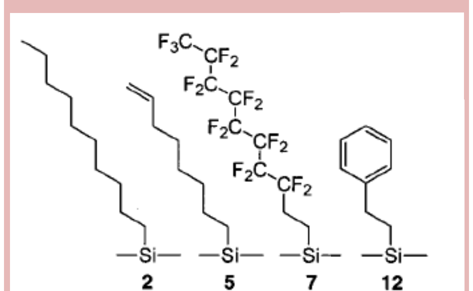


Cross-section SEM image of PSi etched 60mA/cm^2 at x35k magnification (Parimi, S.V., Tadigadapa, S. Yetter, R.A.



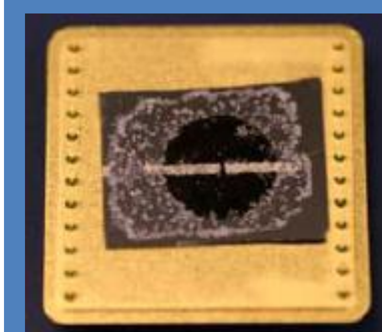
$NaClO_4$ x $1H_2O$ loaded PSi burn (Son, SF)

Functionalization of Si Surfaces



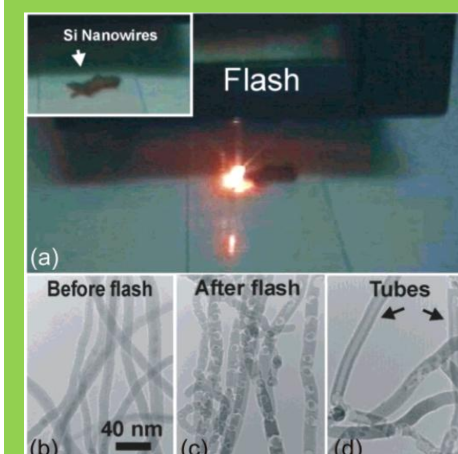
Surfaces prepared through white light promoted hydrosilyation on pSi (Stewart, MP, and Buriak, JM, J. Am. Chem. Soc. 2001, 123, 7821). Thermally induced hydrosilylation with perfluoro-1-octene and perfluoro-1decene (Son, SF)

Packaged nanoporous silicon energetic devices



Churaman et al., Chem. Phys. Letts. 464, 198, 2008 .

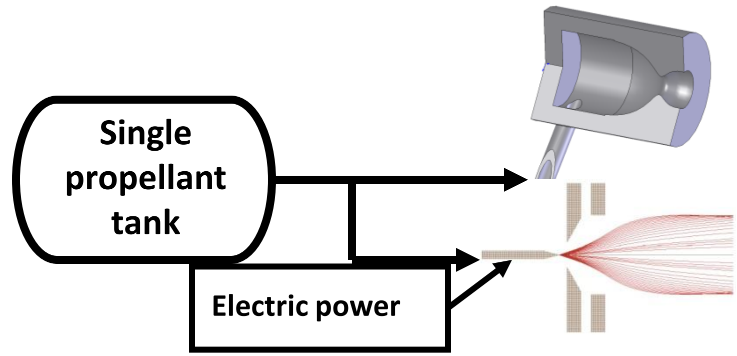
Light-Activated Ignition of Si Nanowires

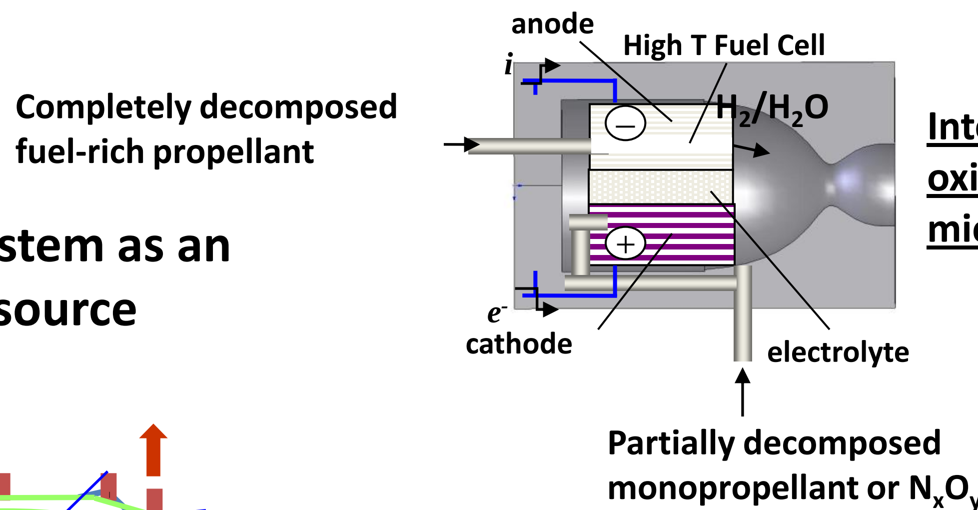


N. Wang,* B. D. Yao, Y. F. Chan, and X. Y. Zhang, Nano Letters, 2003, 3, 475n

Multifunctional Micropropulsion

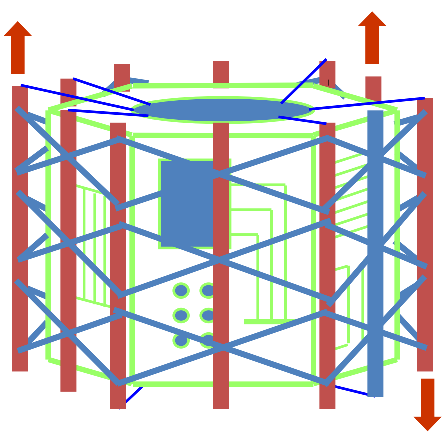
- **Bi-modal propulsion system with single propellant => chemical micro-propulsion and MEMs electro-spray, micro resistojets**





Integrated solid oxide fuel cell / microthruster

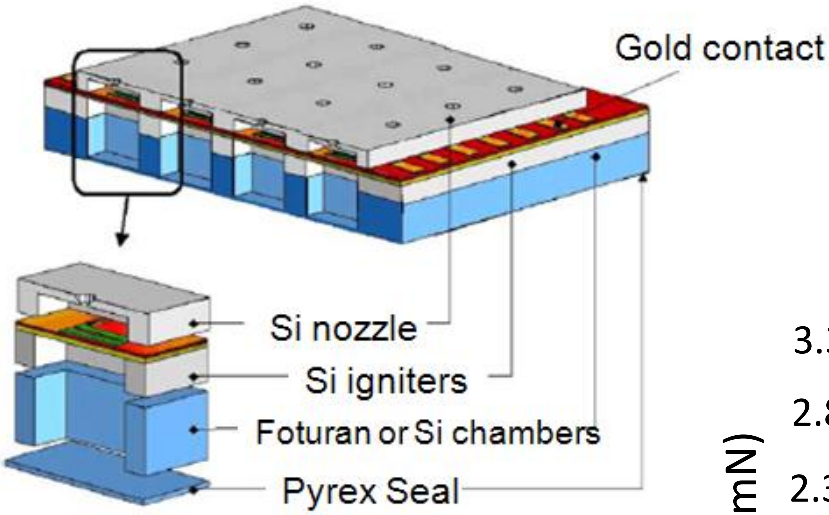
- **Propulsion system as an electric power source**



- **Propulsion system as a satellite structural component (self-consuming satellites) => improved spacecraft mass ratio**

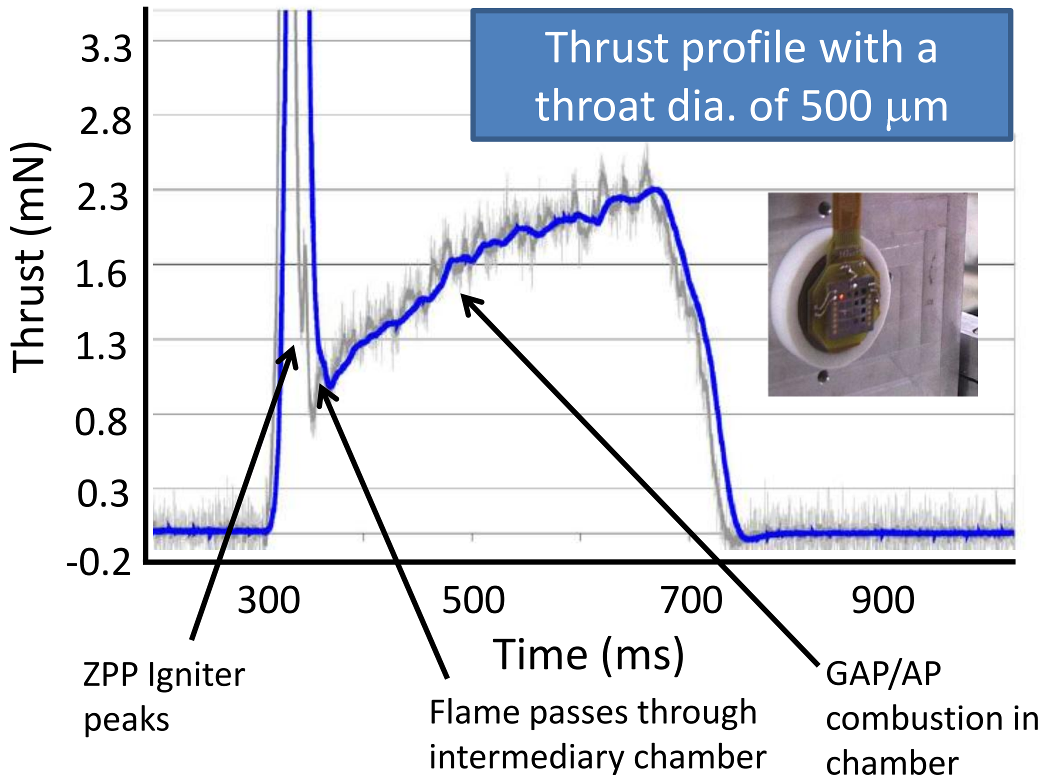
MEMS-based Pyrotechnical Microthrusters

LAAS-CNRS



- Polysilicon resistor igniter at nozzle
- Insulating groves to eliminate cross-talk
- Main grain was screen printed under vacuum
- 100% ignition success with 250 mW
- Thrusts ~0.3-2.3 mN

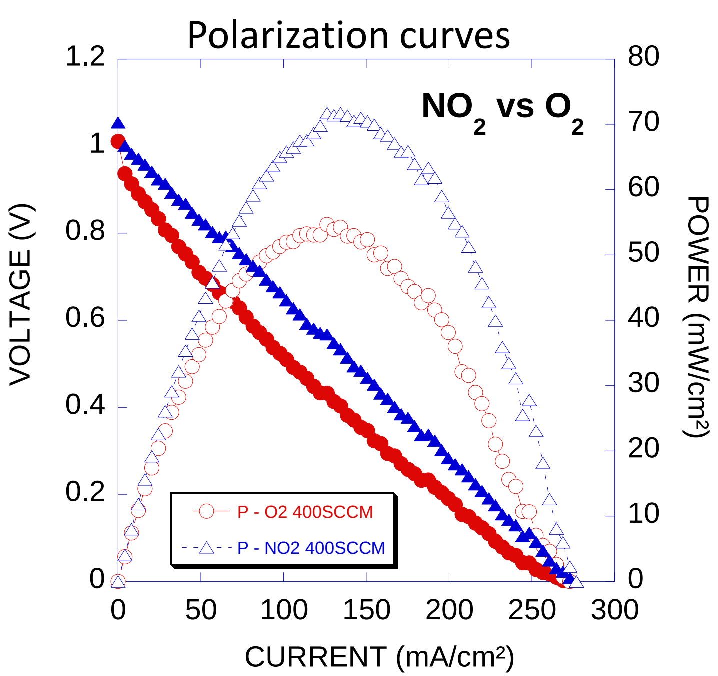
- 100 addressable microthrusters with 3 main micromachined layers
- Combustion chamber 1.5 x 1.5 x 1 mm
- glycidyle azide polymer (GAP) mixed with AP and Zr particles propellant
- zirconium perchlorate potassium primer

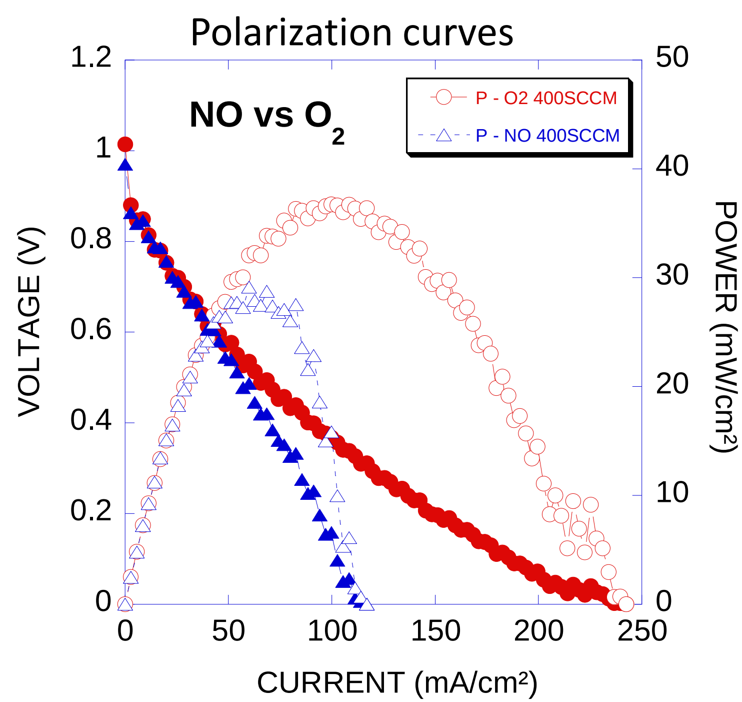


Rossi et al., Sensors and Actuators A, 121, 508-514, 2005, Sensors and Actuators A, 126, 241-252, 2006. Journal of MEMs, 15, 6, 1805-1815, 2006.

Micropropulsion system as an electric power source

- Direct Flame Solid Oxide Fuel Cells (DF-SOFC) provide one approach for incorporating power generation within the thruster combustion chamber.
- Ideal for incorporation into LTCC and HTCC combustors.
- Partially decompose liquid monopropellant to achieve NxOy gases for selective cathode.
- Completely oxidized liquid monopropellant for hydrogen rich gases to anode.
- Successful operation with partially decomposed HAN-based monopropellant.





Solid Electrolyte: Yttria-Stabilized Zirconia; Anode: metallic Ni; Cathode: Strontium-Doped Lanthanum Manganite

- **Benefit**
  - *May enable new missions; improvements in performance (15-40% = likely: factor of 2+ = risky)*
- **Alignment with NASA Needs**
  - *Low cost to space, long term storage of propellants in space, robotic sample return, sounding rockets, scramjets, upper stage engines, booster stages, launch abort stages, nano and pico satellites*
- **Alignment with non-NASA aerospace technology needs**
  - *Direct synergy with DoD in the areas of propulsion and energetic materials.*
- **Alignment with non-aerospace national goals**
  - *Possible impact on alternate fuels and emissions, nanoenergetics on chips for power generation, actuation, micro welding and fusing, long term energy storage shelf life, etc. [pressure (kPa-GPa), heat (200-3000^{o}C), chemical species (neutral and ionized gas)]*
- **Technology risk and reasonableness**
  - *For development of new energetic materials (i.e., synthesis of new molecules-risk is extremely high); for development of new passivation and assembly methodologies- risk is high, for inclusion of nanomaterials in energetic materials – risk is low to moderate)*

- What are the top technical challenges in the area of your presentation topic?
  - *Particle passivation and assembly*
  - *Scale-up of materials and manufacturing*
  - *System implementation (e.g., for metalized gels, pumping and injection)*
  - *Replacements for cryogenic hydrogen*
- What are technology gaps that the roadmap did not cover?
  - *Integration of nanoenergetics with sensors, electronics, etc.*
  - *Graphene as a fuel, catalyst, high energy material, e.g., with polymeric nitrogen*
  - *Health and handling issues*

- What are some of the high priority technology areas that NASA should take?
  - *Passivation of nano aluminum with reactive component and assembly to the micron scale.*
  - *Gelled hydrogen.*
  - *Application of nanoenergetics beyond propulsion.*
- Do the high priority areas align well with the NASA’s expertise, capabilities, facilities and the nature of the NASA’s role in developing the specified technology?
  - *Yes*

- In your opinion how well is NASA's proposed technology development effort competitively placed? *Nanomaterials for propulsion important to both propellants and propulsion systems; Nanoengineered energetic materials also of importance and under study by DoD and DOE*
- What specific technology can we call as a "Game Changing Technology"? *Achieve performance of cryogenic hydrogen and oxygen with non-cyrogenic propellants or exceed cyrogenic hydrogen with nano ingredients. Other measures may produce game changing technology as well, such as cost.*

- In your opinion what is the time horizon for technology to be ready for insertion (5-30yr)?
  - *5-10 years for inclusion of nanomaterials as gelling agents or ingredients in solid propellants*
  - *5-10 years for organized assembly of nanoenergetics on chip-sized devices*
  - *10+ years for organized assembly of macroscale propellant grains*

Nano-Aluminum/Ice Propellants for Replacement of Cryogenic Hydrogen

Motivation

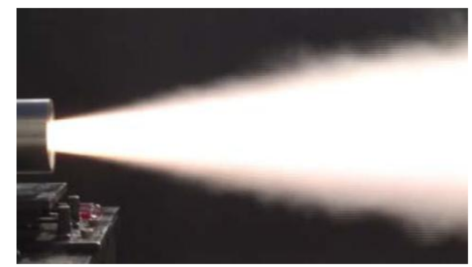
- Cyro-propellant performance without cryo shortcomings
- Nanotechnology for designing and assembling future propellants
- Multi-functionality for both propulsion and power applications

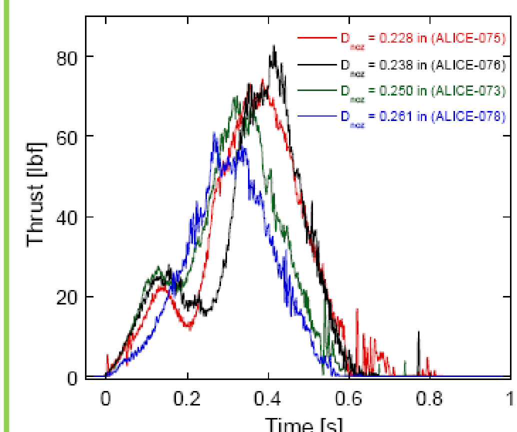
$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$

Research

- $nAl\text{-}H_2O$ composites are studied as a means to generate hydrogen at high temperatures and at fast rates
- Composites have high energy density and low sensitivity
- Combustion occurs without heat releasing gas phase reactions & thus many flame spreading and instability problems of conventional propellants are eliminated.

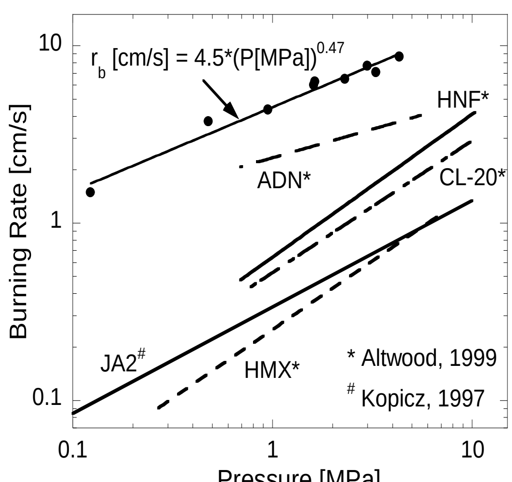
1.5” dia. x 1.5” long center perforated 80nAl-ice grain



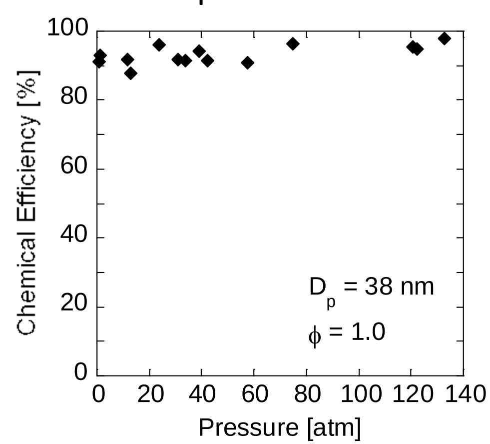


nAl-ice grain in phenolic tube

Burning rates of 38 nAl & liq. H_2O



Efficiency of H_2 production



Risha, G.A., Son, S.F., Yang, V., & Yetter, R.A., 2008