

SMART FUNCTIONAL NANOENERGETIC MATERIALS

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Abstract

Given the constraints on typical bond energies and the commonality of final products produced from combustion of C-H-N-O-Cl-Al based energetic materials, the possibilities for increased stored potential energy and increased thermodynamic performance from these classes of materials are limited, but still possible. Table 1 provides a few illustrative examples. Baseline propellants consisting of ammonia perchlorate and hydroxyl terminated polybutadiene without and with aluminum have typical specific impulse metrics of approximately 243 and 265 s, respectively. Measured specific impulses of real motors achieve approximately 96-98 and 94-96% of the theoretical values for nonaluminized and aluminized propellants, respectively, depending on the size of the motor. Two-phase flow losses for aluminized propellants may account for approximately two percent of these losses (or equivalently ~5 s of I_{sp}). Methods to increase the specific impulse (as well as the density specific impulse) either through the development of new propellants or by reducing the losses of current propellants are significant goals. An increase of several seconds in I_{sp} is considered an important achievement. In the present effort, our goal is to study hierarchically structured nanocomposite fuels that could be additives or replacements of fuel particles in current or future propellant formulations. The foundations of the composites are based on either metal or carbon fuels (for example in the form of metallic clusters such as aluminum, boron, and magnesium, and functionalized graphene sheets, FGSs) that use high nitrogen compounds as scaffolds to assemble the ingredients into composite fuel particles of controllable size with high energy density. The

Table 1. Performance Calculations with Nanoenergetic Composites

Propellant Formulation	I_{sp}^1 (s)	$\phi_{overall}$	T_c (K)	$X_{condensed\ phase}$
Baseline without Al ²	243.0	1.37	2779	0
Baseline with Al ³	265.1	1.8	3532	0.100
Metal Cluster Composites				
<i>Al/DAATO3.5 Composites</i>				
20wt% DAATO3.5/80wt% Al	266.4	1.82	3520	0.095
40wt% DAATO3.5/60wt% Al ⁴	268.3	1.85	3498	0.085
50wt% DAATO3.5/50wt% Al	269.4	1.89	3489	0.081
<i>Al/BTAT Composites</i>				
40wt% BTAT/60wt% Al	266.0	1.73	3566	0.089
<i>Al/5-ATZ Composites</i>				
40wt% 5-ATZ/60wt% Al	264.0	2.01	3312	0.083
Graphene Composites				
75wt% DAATO3.5/25wt% C ⁵	244.0	1.37	2844	0
50wt% N-/50wt% C	247.0	1.40	2926	0
75wt% N-/25wt% C	252.0	1.34	3058	0

¹ $P_c = 1015\text{psia}$, $P_c/P_e = 69$; Calculations performed with NASA CEA

²Baseline Propellant Composition without Al: 85 wt% AP, 15 wt% HTPB

³Baseline Propellant Composition with Al: 20wt% Al, 68 wt% AP, 12 wt% HTPB

⁴Example Formulation: 17.6 wt% Al, 11.8 wt% DAATO3.5, 59.9 wt% AP, 10.6 wt% HTPB

⁵Example Formulation: 2 wt% C, 6 wt% DAATO3.5, 80 wt% AP, 12 wt% HTPB

structural organization will be designed to provide additional desirable features other than energy density not possible with pure micron-sized metal particles.

Our interest in nanoenergetic composites also arises from previous successes and limitations of adding nanoparticles to propellants.^{i,iii} While the introduction of nanosized fuel and oxidizer particles into solid propellants has provided significant benefits in increasing burning rates and reducing agglomeration,ⁱⁱⁱ there are two major constraints that have limited further investigation, characterization, and implementation of nanomaterials: (i) Their nanometer scale dimensions and the inherently high surface areas reduce their usability, e.g., similar solids loading cannot be achieved, and (ii) Particle-particle interactions dominate making dispersion of such particles nearly impossible. Thus, in order to realize the benefits of nanoparticles in future propellants, new approaches must be undertaken.

Table 1 illustrates that by constructing aluminum and graphene high nitrogen composites, improvements of a few seconds may be achievable. These calculations were based on the properties of bulk aluminum and do not account for the potential for additional energy stored in the surfaces of very small particles or in clusters. For example, Chung *et al.* have recently estimated that heats of reaction for aluminum nanoparticle oxidation could increase from 1-7% when the nanoparticle diameter is less than 10 nm and the particle is oxidized to produce substantially agglomerated products.^{iv} This will require a structured nanoparticle so an oxide layer would not be formed. In Table 1, the compositions were based on attempting to maintain a similar overall equivalence ratio of the mixture while substituting the composites for the aluminum fuel. For the aluminized propellants, the amount of condensed products was also reduced when the composite fuels were considered. If highly energetic polymeric nitrogen stabilized in a graphene matrix could be produced, a greener propellant that approaches the performance of a metalized propellant may be achievable. The thermochemical calculations suggest that the addition of 6 wt% of graphene-nitrogen nanocomposite (with a C/N ratio of 0.86) to a conventional AP/HTPB solid propellant could increase the Isp by 4 s and as much as 9 s if the nitrogen loading is even higher. Formulations with newly developed energetic materials such as SMX^v with graphene based-high nitrogen composites could be used to produce greener propellants with even higher Isp than current aluminized propellants. The theoretical specific impulse ($P_c = 1015$ psia, $P_c/P_e = 69$) of SMX is about 266 s. If this could be made into a feasible propellant, it would have an Isp much higher (10-20 s higher) than current greener propellants. This could be accomplished by co-crystallization or blending in other materials. Graphene-nitrogen nanocomposites further increase the Isp. Since these propellants will not have two-phase flow losses, the gains would be expected to even be greater, and the introduction of nanoenergetics could further tailor the properties obtainable. While the examples of Table 1 are for solid propellants, considerations of composite particles dispersed in liquid fuels and propellants are also predicted to achieve performance gains in Isp and even greater gains in density specific impulse. More importantly, from a materials design perspective, much is yet to be gained in the actual performance, multi functionality, and controllability of energetic materials. Integrated multiscale organization of energetic materials from the molecular and nanometer scales to the micron and millimeter scales will provide design rules for synthesis and assembly at even larger scales.

The successful development of multiscale nanoengineered energetic materials may also provide a means to unravel and control the strong correlation that exists between the energy density of a propellant (or explosive) and its sensitivity. In addition to Isp, the addition of nanostructured additives has been shown in the literature^{vi} to decrease agglomeration/slag and increase combustion efficiency. In some cases, the measured Isp increased by up to 8%, in large part due to the increased combustion efficiency. Because of relatively higher burning rates at lower pressures with nanostructured particles, it was shown that controlling pressure exponents of propellants is possible. In addition to performance gains, integrating other functionality can also be game-changing.

From a materials design perspective much is yet to be gained in the actual performance, multi functionality, and controllability of energetic materials. Integrated multiscale organization of energetic materials from the molecular and nanometer scales to the micron and millimeter scales will provide design rules for synthesis and assembly at even larger scales. We recognize that many biological and physical objects derive their unique properties through an integrated multilength scale organization of their constituent nano and microscale structures. Such multiscaled structures are being increasingly exploited to engineer devices such as adhesives mimicking spatulae of a gecko, porous silicon drug delivery systems, to adaptive porous materials that mimic the multifunctionality of bone.^{vii,viii} A common

feature in all these structures is that nanoscale units are all integrated into micron to macro scale structures and are accessible as individual modules for rapid response, usually through the use of porous structures. Such design principles are crucial to the goals of our work.

While there has been tremendous progress in the energetic materials community in the synthesis and fabrication of nanosized reactive materials, the progress on the fabrication of micron scale energetic materials, with integrated nanoscale features, capable of yielding desirable, responsive, and controllable traits have lagged behind due to lack of integration with nanoenergetic materials. With new options for nanoscale reactive materials and advances in multiscale chemical modeling, and materials characterization and diagnostics, the development of integrated multistructure energetic materials is now possible.

For example, functionalized graphene sheets that have unique electrical and chemical properties are now available in tons/year quantities and can provide new directions for the development of reactive materials at both the nano- and microscales. FGS not only can function as a nanoscale catalyst itself but may also be decorated with energetic materials such as energetic organics or metallic nanoparticles to produce hybrid reactive materials. Graphene has also been proposed as a means to stabilize highly energetic polymeric nitrogen, e.g., between graphene sheets^{ix} or bound within the carbon matrix,^x to produce highly energetic materials. To ensure rapid and controlled access to the nanoscale energetic units, as one of main goals of this effort, we will develop graphene-based sponge structures as shown in Figure 1(b) and use them as templates for energetic polymeric nitrogen and/or nanosized metallic clusters. Metallic clusters have been shown to exhibit unique properties with regards to their reactivity and size, while also capturing the beneficial physical and energetic properties of nanoparticles less than 10 nm in diameter. We will also develop procedures to assemble highly energetic clusters into stable organized multiscale structures usable in energetic materials. Our approach will be to combine state-of-the-art theoretical modeling and experimental diagnostic techniques with novel nanotechnology fabrication

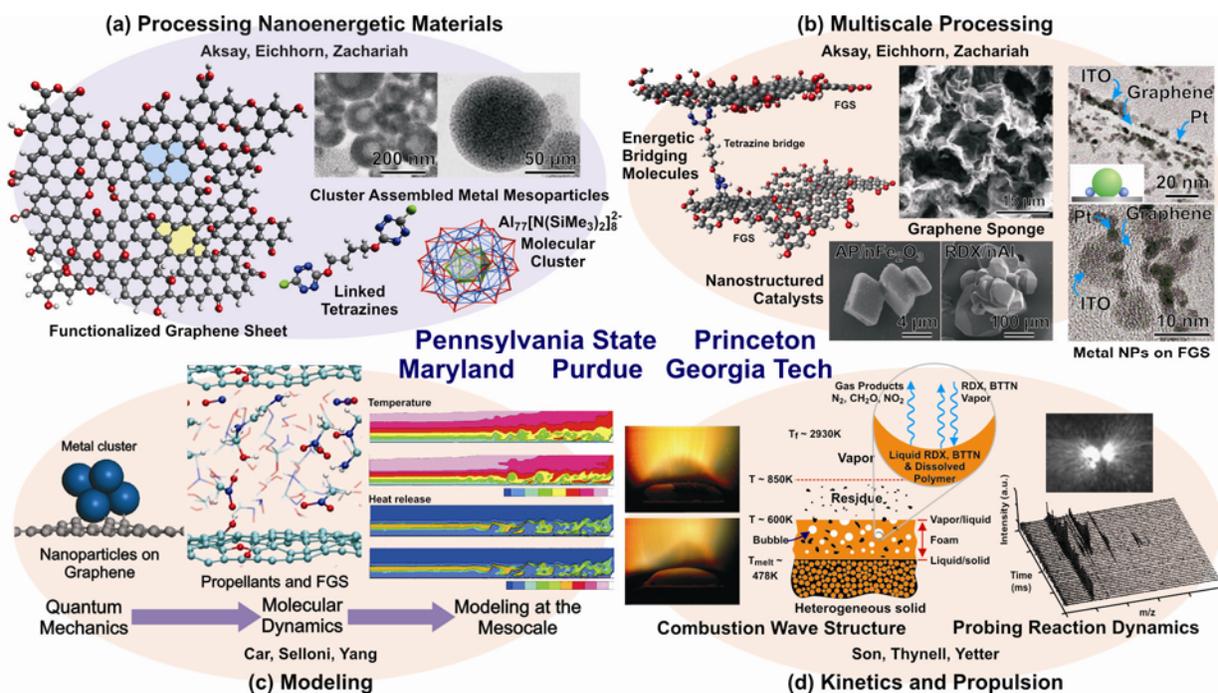


Figure 1: Overview of the proposed research. (a) The energetics of FGSs will be boosted through the addition of nitrogen such as tetrazine-based molecules. Molecular clusters such as the $Al_{77}[N(SiMe_3)_2]_{20}^{2-}$ cluster shown will be used to further boost the energetics of C-H-N-O materials. These can be grouped into cluster assembled metal mesoparticles to further stabilize and desensitize the cluster until needed. (b) Cluster composites and metal nanoparticles will be dispersed on graphene sheets for further stability and to provide a fuel source in proximity to energetic or catalytic particles. The graphene sheets themselves will be linked together to form high surface area matrices; linkages will be energetic molecules of high nitrogen content. (c) The reactions of energetic materials range across length scales, requiring modeling efforts that combine QM and MD simulations to provide information on mechanisms observed at the mesoscale. (d) Characterization techniques will be developed for measurements on the micro- and meso-scales.

techniques. The outcome will be a new class of smart and functional nanostructured energetic materials that will enhance the performance and controllability of future propellants and explosives.

Our program is divided into four major inter-related areas as outlined in Figure 1: (a) processing of nanoenergetic materials with graphene and metal nanoclusters, (b) multiscale processing to enable the insertion of nanoenergetic materials into larger units such as graphene sponge, (c) atomistic to mesoscale modeling and design, and (d) experimental analysis and performance characterization for propulsion. Figures 1(a) and (b) summarize the first two areas with emphasis on (i) boosting the energetics of functionalized graphene using the addition of nitrogen via chemisorption of nitrogen-containing molecules (including polymeric nitrogen) and/or replacing carbon atoms in the network with nitrogen atoms; (ii) metal-based cluster composites; and (iii) porous materials and encapsulation.

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