



**AFRL-RW-EG-TR-2016-036**

**Cross Directorate Proposal: Nanostructured  
Materials for Munitions and Propellants –  
Production, Modeling, and Characterization**

---

**Claron J. Ridge  
Brian K. Little  
C. Michael Lindsay**

**Air Force Research Laboratory  
Munitions Directorate/Ordnance Division  
Energetic Materials Branch (AFRL/RWME)  
Eglin AFB, FL 32542-5910**

**July 2016**

**Interim Report**

**Distribution A:** Approved for public release; distribution unlimited.  
Approval Confirmation 96TW-2016-0128

**AIR FORCE RESEARCH LABORATORY  
MUNITIONS DIRECTORATE**



## NOTICE AND SIGNATURE PAGE

Using Government drawings, specifications, or other data included in this document for any purpose other than Government procurement does not in any way obligate the U.S. Government. The fact that the Government formulated or supplied the drawings, specifications, or other data does not license the holder or any other person or corporation; or convey any rights or permission to manufacture, use, or sell any patented invention that may relate to them.

Qualified requestors may obtain copies of this report from the Defense Technical Information Center (DTIC) (<http://www.dtic.mil>).

AFRL-RW-EG-TR-2016-036 HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION IN ACCORDANCE WITH ASSIGNED DISTRIBUTION STATEMENT.

FOR THE DIRECTOR:

//SIGNED//

//SIGNED//

//SIGNED//

HOWARD G. WHITE, PhD  
Chief Engineer  
Ordnance Division

DOUGLAS R. SMITH  
Branch Chief  
Energetic Materials Branch

MICAH PAUL, Capt., USAF  
Work Unit Manager  
Energetic Materials Branch

This report is published in the interest of scientific and technical information exchange, and its publication does not constitute the Government's approval or disapproval of its ideas or findings.

This page intentionally left blank

| REPORT DOCUMENTATION PAGE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |              |                           |                            | Form Approved<br>OMB No. 0704-0188                                     |                                                           |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|---------------------------|----------------------------|------------------------------------------------------------------------|-----------------------------------------------------------|
| Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.                                                                                                                                                                              |              |                           |                            |                                                                        |                                                           |
| 1. REPORT DATE (DD-MM-YYYY)<br>15-07-2016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |              | 2. REPORT TYPE<br>Interim |                            | 3. DATES COVERED (From - To)<br>10-01-2014 - 09-30-2015                |                                                           |
| 4. TITLE AND SUBTITLE<br><br>Cross Directorate Proposal: Nanostructured Materials for Munitions and Propellants – Production, Modeling, and Characterization                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |              |                           |                            | 5a. CONTRACT NUMBER                                                    |                                                           |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |              |                           |                            | 5b. GRANT NUMBER                                                       |                                                           |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |              |                           |                            | 5c. PROGRAM ELEMENT NUMBER<br>61102F                                   |                                                           |
| 6. AUTHOR(S)<br><br>Claron J. Ridge, Brian K. Little, C Michael Lindsay                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |              |                           |                            | 5d. PROJECT NUMBER<br>3002NW14                                         |                                                           |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |              |                           |                            | 5e. TASK NUMBER                                                        |                                                           |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |              |                           |                            | 5f. WORK UNIT NUMBER<br>W0QE                                           |                                                           |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br>Air Force Research Laboratory<br>Munitions Directorate<br>Ordnance Division<br>AFRL/RWME<br>Eglin AFB FL 32542-5910                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |              |                           |                            | 8. PERFORMING ORGANIZATION REPORT NUMBER<br><br>AFRL-RW-EG-TR-2016-036 |                                                           |
| 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)<br>Air Force Research Laboratory, Munitions Directorate<br>Ordnance Division<br>Energetic Materials Branch (AFRL/RWME)<br>Eglin AFB FL 32542-5910<br>Technical Advisor: C. Michael Lindsay, PhD                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |              |                           |                            | 10. SPONSOR/MONITOR'S ACRONYM(S)<br>AFRL-RW-EG                         |                                                           |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |              |                           |                            | 11. SPONSOR/MONITOR'S REPORT NUMBER(S)<br>AFRL-RW-EG-TR-2016-036       |                                                           |
| 12. DISTRIBUTION / AVAILABILITY STATEMENT<br><br>DISTRIBUTION A – Approved for public release; distribution unlimited. Approval Confirmation 96TW-2016-0128                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |              |                           |                            |                                                                        |                                                           |
| 13. SUPPLEMENTARY NOTES<br><br>DISTRIBUTION STATEMENT INDICATING AUTHORIZED ACCESS IS ON THE COVER PAGE AND BLOCK 12 OF THIS FORM.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |              |                           |                            |                                                                        |                                                           |
| 14. ABSTRACT<br>Over the past few years RWME has been investigating the use of the liquid helium droplet beam technique to generate of single component and composite nanoclusters at low temperature, deposit the clusters onto various substrates, and then investigate the stability, chemical, and physical properties of the subsequent cluster-based material. This report provides an annual status update in the understanding of the environment of the clusters prior to, during, and after collision of the doped droplet with a surface. To do this, we fabricate a range of clusters of varying sizes, examine them prior to deposition using mass spectrometry, then examine the properties of the resulting films using spectroscopic, conductivity, electron microscopy, and diffraction techniques. Materials to be discussed include pure magnesium, magnesium- perfluoropolyether composite, copper-magnesium core-shell, and gold nanoclusters. Also included in this interim report are the latest results on studying nanoenergetic materials based on aluminum and iodine oxides at the milligram scale. |              |                           |                            |                                                                        |                                                           |
| 15. SUBJECT TERMS<br>Energetic Materials, nanoenergetics, nanoclusters, core-shell particles, iodine oxide, aluminum, SHeDA, Helium Droplets                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |              |                           |                            |                                                                        |                                                           |
| 16. SECURITY CLASSIFICATION OF:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |              |                           | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES                                                    | 19a. NAME OF RESPONSIBLE PERSON                           |
| a. REPORT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | b. ABSTRACT  | c. THIS PAGE              |                            |                                                                        | Micah Paul, Capt                                          |
| UNCLASSIFIED                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | UNCLASSIFIED | UNCLASSIFIED              | SAR                        | 21                                                                     | 19b. TELEPHONE NUMBER (include area code)<br>850-882-9634 |

This page intentionally left blank

## ANNUAL LABORATORY TASK REPORT

**LRIR #:** 14RW05COR

**Title:** Cross Directorate Proposal: Nanostructured Materials for Munitions and Propellants – Production, Modeling, and Characterization

**Reporting Period:** 1 Oct 2014-30 Sep 2015

**Laboratory Task Manager:** C. Michael Lindsay, AFRL/RWME

**Commercial Phone:** 850-882-1543 **DSN:** 872-1543 **FAX:** 850-882-3540

**Mailing Address:** AFRL/RWME  
Dr. C. Michael Lindsay  
2306 Perimeter Rd  
Eglin AFB, FL 32545-5910

**Email Address:** [c.michael.lindsay@eglin.af.mil](mailto:c.michael.lindsay@eglin.af.mil)

**AFOSR Program Manager:** Dr. Michael Berman

### Research Objectives:

Nanoclusters are promising systems for future energetic materials (explosives and propellants) due to their potentially high-energy densities, ability to resist unintentional oxidation, and customizable properties. In this cross-directorate laboratory task, we continue a joint experimental and theoretical program aimed at exploring the electronic/geometric structure, low-temperature synthesis, reactivity, and macroscale stability of energetic nanoclusters with diameters  $\sim 0.5$ -5 nanometer in search of those that are meta-stable. Fundamental to the effort is a better understanding of the processes involved in bringing atoms together at the nano-scale, stabilizing the system's metastability nanostructure, and preserving such a structure during deposition and as a material under ambient conditions.

Experimentally, over the past year our objectives focused on confirming conclusively that energetic material can indeed be produced by the Superfluid Helium Droplet Assembly (SHeDA) methodology and that the core-shell structure thought to be produced in such clusters in the droplet is attained and maintained upon deposition. This work was done in collaboration with our computational partners at AFRL/RZRP and a summary of their work can be found in a separate annual report prepared by Dr. Jerry Boatz. Additionally, we are engaged in an array of collaborations to leverage the capabilities of state of the art experimental tech developed by our peers at national labs and universities across the country. In particular, this year we have focused attention towards the deposition of well-characterized gold nanoclusters and the mechanical properties, catalytic activity, and sintered growth of such clusters on a variety of substrates in order to establish fundamental behaviors of clusters deposited by the technique.

## Technical Summary:

### Summary of FY15 Progress:

#### *Production of Energetic Nanocomposite Cluster Films*

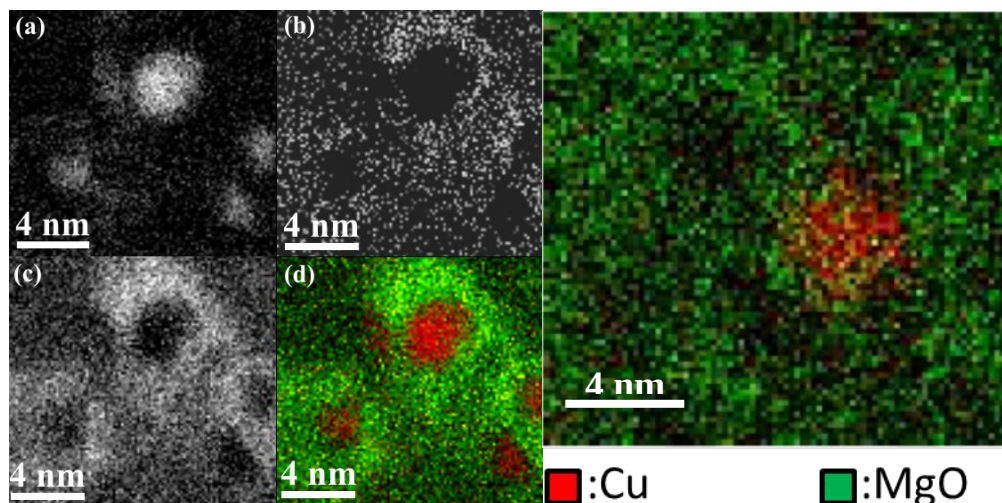
Our first successful energetic nanocomposite material consisted of Mg and perfluoropolyether (PFPE) which we reported on last year and the year previous. This system was useful for our experiments because we were able to evaporate, with relative ease, the reactants and observe combustion products in the mass spectrometer. However, Mg, C, and F are all light elements that are challenging to image and discern with transmission electron microscopy (TEM). This limited our ability to characterize structures at the nanoscale.

This year we have moved on to other materials that will facilitate imaging along with TPD and, potentially, nanocalorimetry (thermites and intermetallics, e.g. Al/CuO, Ni/Al). We are in discussions with Professor Tim Weih's group at Johns Hopkins University who have utilized a nanocalorimetry technique developed at NIST, sensitive to thin films of energetic material [1]. They have also integrated TEM grids with compatible sample substrates so structure and thermal analysis can be performed on the same sample films. The current plan is to prepare samples in SHeDA to send up to JHU for analysis and determine the feasibility of doing nanocalorimetry in SHeDA *in-situ*. While progress on this collaboration is preliminary, it is a high priority because nanocalorimetry has the potential to answer the questions that SHeDA was built to ask.

#### *Characterization of Cu/Mg Core/Shell Clusters*

We have shown and explained in last year's annual report the observation that Mg has the unusual property that it does not form the core of a core/shell structure with Cu. Our recent article discusses the various possibilities for how and at what point in the process, Mg is displaced from the core. Ab initio computations, performed by Jerry Boatz and Robert Buszek, support the theory that the weak Mg-Mg bonds are disrupted by the much more strongly binding Cu atoms. The theoretical calculations are reported in detail in our recent article in JCP [2] and in Dr. Boatz annual report from this and last year. The mechanism of the core inversion is still the subject of some debate in the field, but it is not the only observation of this phenomenon. Two other groups have since observed related behavior with Cr and Ag clusters formed in He droplets and Ti and Pt clusters formed in a magnetron sputter source. However, neither group has published their results. We anticipate that the continued investigation of this behavior, by a variety of research groups, will yield high impact insights into the fundamental properties of bimetallic clusters.

As a continuation of the Mg/Cu cluster study, we prepared samples in which Cu was picked up first. We did not expect significant differences from the core inversion result, but it does display some differences that may shed further light onto how the Mg atom behave in the He droplet. As shown in Figure 1 (on the left), instead of a localized shell around the Cu core that was seen in the core inverted clusters (on the right), we see a Cu core (in red) embed in a film of MgO. So in the previous experiments the MgO was somewhat spread out but still stayed localized around the Cu. In the reverse order depositions, the MgO is forming a more widely distributed film. It is almost as if the presence of the Cu has little or no effect on the Mg deposition and vice versa. As a next step, we are preparing to deposit bimetallic Au/Mg clusters to further probe the unusual behavior of Mg in He droplets.



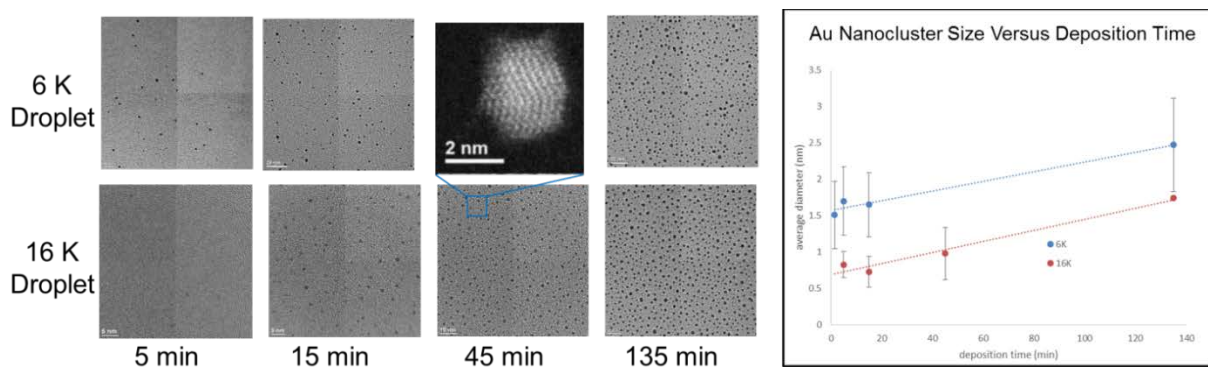
**Figure 1.** (Left) STEM EELS elemental mapping of deposited Mg/Cu clusters with Mg picked up first. Mapped here are (a) copper, (b) magnesium, (c) oxygen, and (d) the composite image (Cu-red, Mg-yellow, and O-green). (Right) STEM EELS map of Cu/Mg clusters with Cu picked up first, with Cu (red) and MgO (green) showing a relatively even coverage of MgO cluster film containing a well-defined Cu core.

### *Vacuum Transfer of Nanocluster Material*

Thus far, we have been limited to investigating only air-exposed cluster material produced in SHeDA by high resolution TEM and it is clear that in most samples, this exposure results in oxidation of the material. To remedy this problem we have constructed a vacuum suitcase capable of transferring our samples from UHV conditions to a glove box environment under high vacuum ( $10^{-6}$  torr) or inert atmosphere. We plan to use this system to transfer water and oxygen sensitive samples (Mg, Al, etc.) to our collaborators for TEM and XPS analysis of the un-oxidized cluster material. We have also designed and are building a UHV suitcase with an integrated pump and battery that we can ship over several days and have it maintain UHV ( $<10^{-10}$  torr). This will allow us to maintain in situ experimental conditions while utilizing state of the art analytical tools to investigate our novel cluster systems.

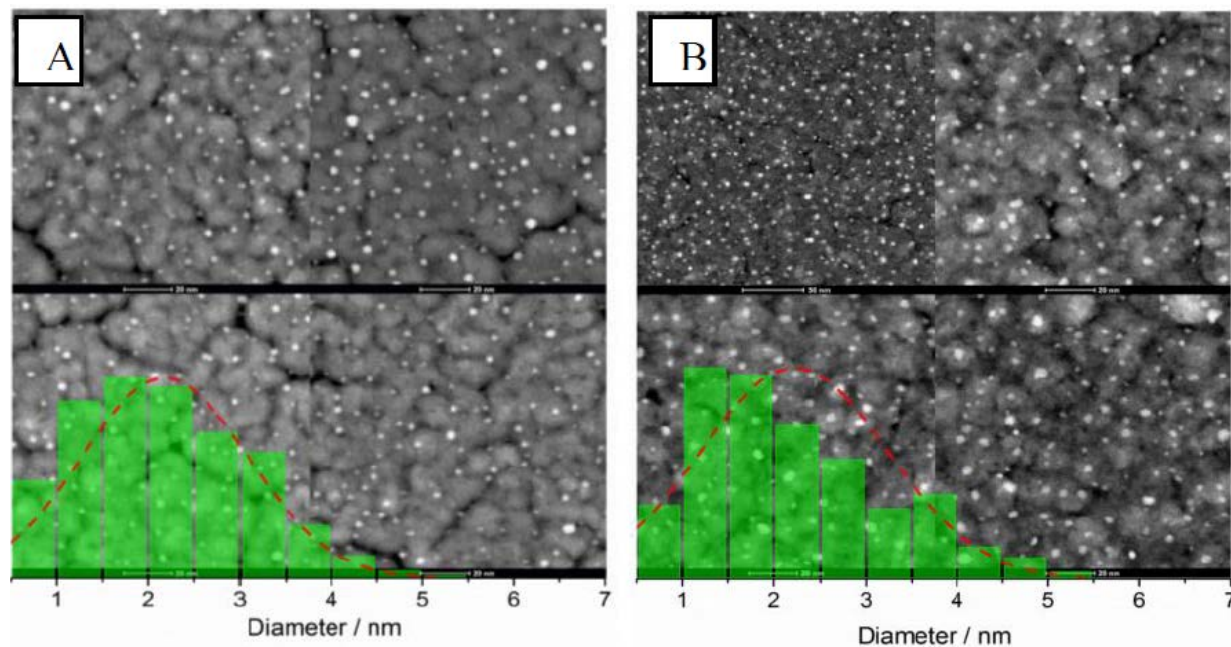
### *Sintering and Reactivity of Catalytic Au Nanoclusters*

In our ongoing collaboration the Orlov group at SUNY Stony Brook we have focused primarily on Au nanoparticles. We started out with a study of the deposition and size distribution characteristics of the Au clusters deposited under different nozzle and oven conditions. In Figure 2 the average cluster size is plotted against the deposition time. Longer deposition times result in larger clusters, which is an indication that sintering is taking place. The mechanism of the sintering is still an open question but we have turned to environmental TEM (ETEM) to allow us to see what is happening to the clusters under high temp, high pressure sintering conditions.



**Figure 2.** TEM images and size plot for Au clusters produced at 6K and 16K for durations of 5, 15, 45, or 135 min.

With specially designed TEM supports and access to an ETEM at Brookhaven National Lab, we were able to deposit Au clusters onto an amorphous  $\text{TiO}_2$  film and image the clusters before and after heating and gas exposure. Figure 3 shows the size distributions before and after heating to 473 K at 0.2 torr  $\text{O}_2$  and 0.8 torr CO. While the average size remains unchanged the shape of the distribution indicates that sintering is happening. The decrease in clusters in the middle of the distribution ( $\sim 2.7$  nm) is accompanied by a commensurate increase in smaller and larger clusters. This is consistent with Ostwald ripening where the larger clusters grow at the expense of smaller clusters. In future experiments we plan to record the process as it happens with the ETEM. It was not possible to do so this time because of instability of the  $\text{TiO}_2$  film.



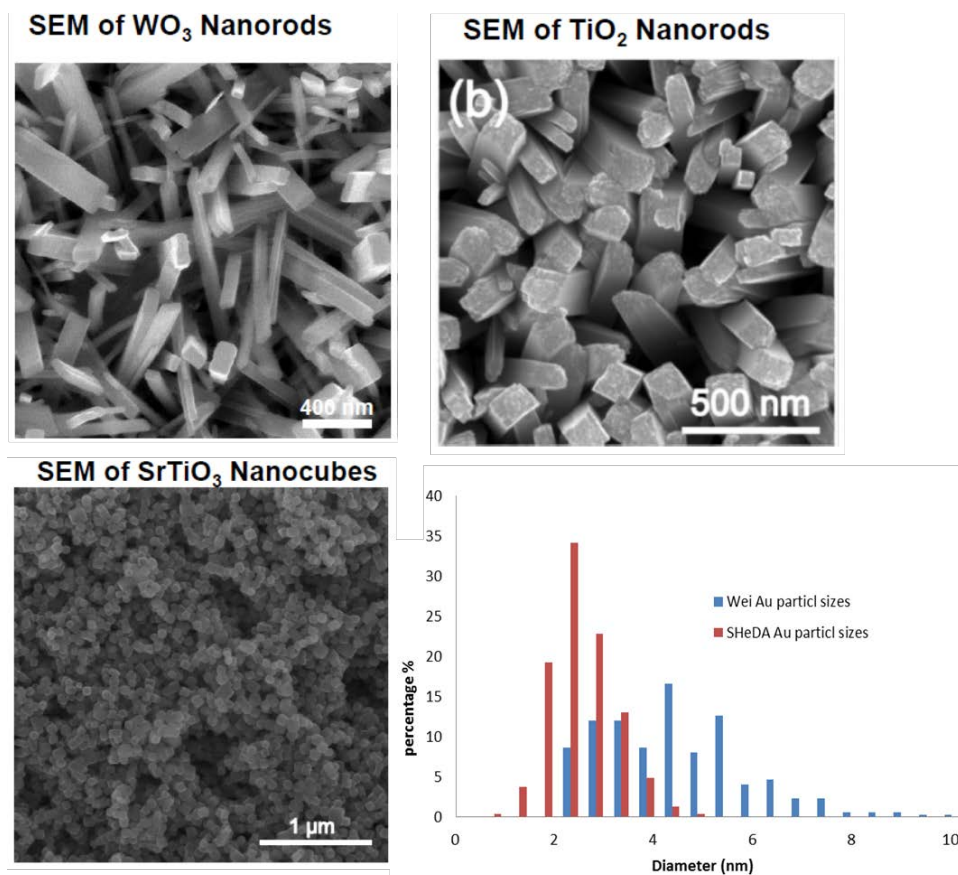
**Figure 3.** (A) TEM image of (6K 135min) Au on amorphous  $\text{TiO}_2$  under vacuum at room temperature. Average size is  $2.2 \pm 0.9$  nm. (B) : TEM image of (6K 135min) Au on amorphous  $\text{TiO}_2$  under 0.2 torr  $\text{O}_2$  and 0.8 torr CO mixed gas atmosphere at 473K. Average size is  $2.2 \pm 1.0$  nm.

In parallel with the ETEM studies we deposited Au clusters onto reduced rutile single crystal  $\text{TiO}_2$  (110) for transfer to a surface science instrument for analysis with X-ray Photoelectron Spectroscopy (XPS) and Temperature Programmed Reaction (TPR) techniques. XPS was consistent with literature spectra for 2 nm Au particles on a support [3] and did not change upon

heating up to 473 K. We also performed CO oxidation TPR with  $^{13}\text{C}$  labeled CO. These results also were consistent with a low temperature activity of small Au nanoparticles for CO oxidation. Interestingly the activity improved on a second TPR run, which may be due to an increase in smaller particles as shown by the ETEM work. This is the first evidence of catalytically active clusters produced by the He droplet mediated method. Two manuscripts are in preparation to publish this work.

#### *Photocatalysis with Nanostructured Oxides Modified with He Droplet Deposited Clusters*

As a result of an interaction and the AFOSR Molecular Dynamics Program Review, we have recently undertaken a new collaboration with the group of Professor David Wei from the University of Florida. They have shown recently that there is a particle size dependent mechanism for the photocatalytic splitting of  $\text{H}_2\text{O}$  by Au particles [4]. However, the Au particle size distributions produced by their methods are much wider than distributions that we produce in SHeDA (Figure 4, bottom right). We are currently depositing Au clusters onto three different oxide supports ( $\text{WO}_3$ ,  $\text{TiO}_2$ , and  $\text{SrTiO}_3$ ) to identify if the higher quality and better controlled clusters produced by SHeDA enhance the photocatalytic activity of the materials.

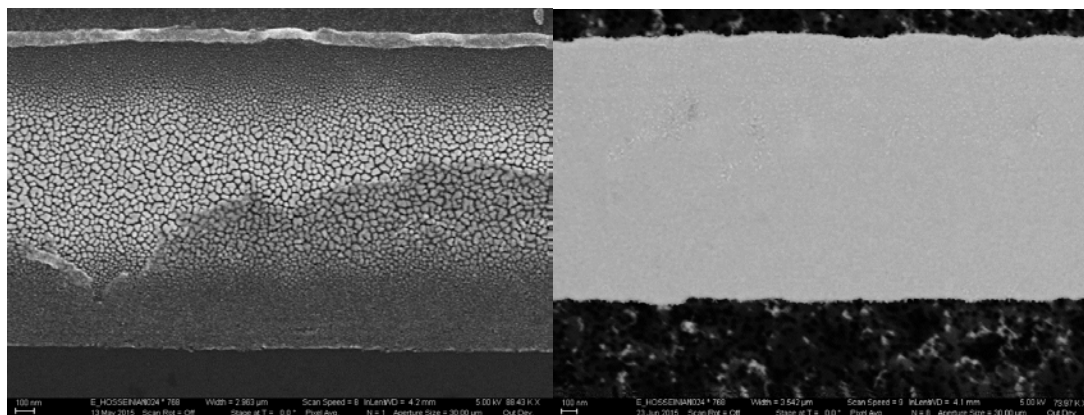


**Figure 4.** SEM micrographs of the oxide supports prepared in the Wei lab. (**Bottom, right**) comparison of size distributions of Au nano particles prepared by the Wei Group (blue) and SHeDA (red)

Our method of cluster deposition should allow the Wei group to narrow down the size dependence of their photocatalytic experiments and provide the information necessary to elucidate the mechanisms for this high impact chemistry. Au clusters are in the process of being deposited onto

### Mechanical Properties of He Droplet Cluster Assembled Films

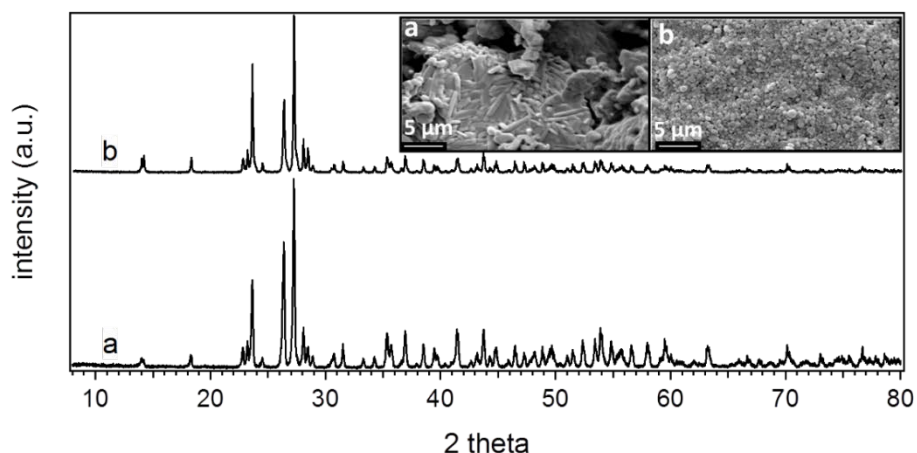
Several samples were prepared in this collaboration, but remarkably, the films made by He droplet deposition appear not to be cohesive enough to be manipulated. As can be seen in Figure 5, The SHeDA film is porous with channels winding between cluster agglomerations. This a fascinating result on its own as it strongly suggests that the He droplets deposit material onto the surface with very little excess energy and undergoes a very weak sintering in contrast to similarly sized particles produced by other means. The clusters appear to simply pile up onto one another with little or no local annealing. This is in stark contrast to a vapor deposited or sputter coated film in which the depositing material lands on the surface with enough energy to locally anneal the film into a polycrystalline bulk material. This is a result that requires further investigation and plans are underway to measure annealed samples of SHeDA produced films to force the material to bind.



**Figure 5.** (Left) SEM image of a  $\sim 30$  nm thick Au cluster film deposited in SHeDA. (right) SEM image of a  $\sim 50$  nm Au film made by physical vapor deposition.

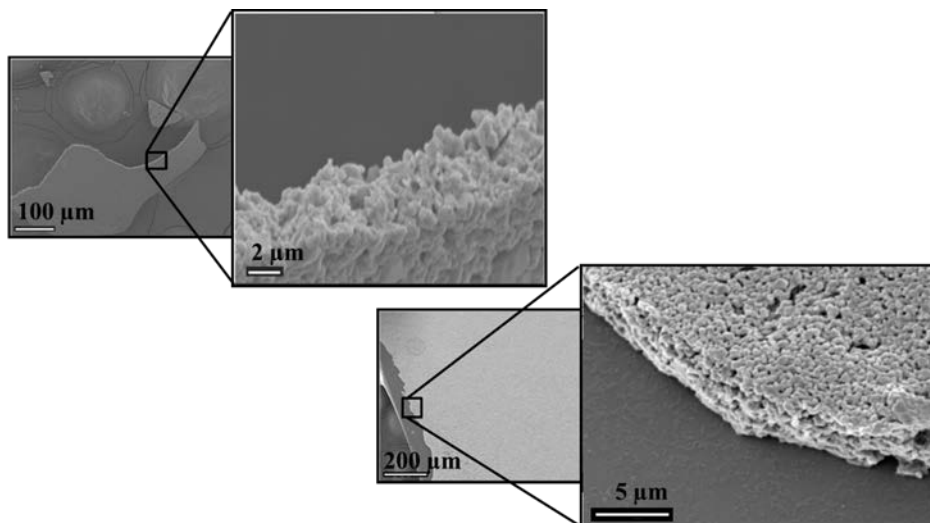
### *Morphology and Crystal Structure of Iodine (V) Oxide Particulate Films*

Efforts to explore novel energetic composites containing gas-generating oxidizers such as iodine (V) oxide have been underway at our group for the last few years and their addition to the AFOSR program has allowed us to examine the materials at a more fundamental level. Building off of our past work in 2014 [5] which identified thresholds for the meta-stability of iodine (V) oxide particles towards hydration and decomposition along with probing their hydration mechanisms, we are now exploring processing and deposition effects for this oxidizer in the form of a film.



**Figure 6.** Powder X-ray diffractograms of (a) as-received powder pulverized with a mortar and pestle and (b) drop cast film from a sonicated suspension of  $\text{HI}_3\text{O}_8$  in denatured ethanol, deposited at  $\sim 2\%$  relative humidity. Inset: Electron microscope images of (a) and (b).

In this study, the production of particulate films of iodine (V) oxides is investigated. The influence that sonication and solvation of suspended particles in various alcohol/ketone/ester solvents have on the physical structure of spin or drop cast films is examined in detail with electron microscopy, powder x-ray diffraction, and UV-visible absorption spectroscopy. Results indicate that sonicating iodine oxides in alcohol mixtures containing trace amounts of water decreases deposited particle sizes and produce a more uniform film morphology while maintaining its crystalline state, as reflected in Figure 6. A UV-visible spectrum of the pre-cast suspensions reveals that for some solvents, the iodine oxide oxidizes the solvent, producing  $\text{I}_2$  and lowering the pH of the suspension. Characterizing the crystals within the cast films reveal their composition to be primarily  $\text{HI}_3\text{O}_8$ , their orientations to exhibit a preferential orientation, and their growth to be primarily along the *ac*-plane of the crystal, enhanced at higher spin rates. Spin coating at lower spin rates produces laminate-like particulate films *versus* higher density, one-piece films of stacked particles produced by drop casting, see Figure 7. The results of this work were accepted for publication in a special edition on energetic materials in the journal of *Crystals* [6].



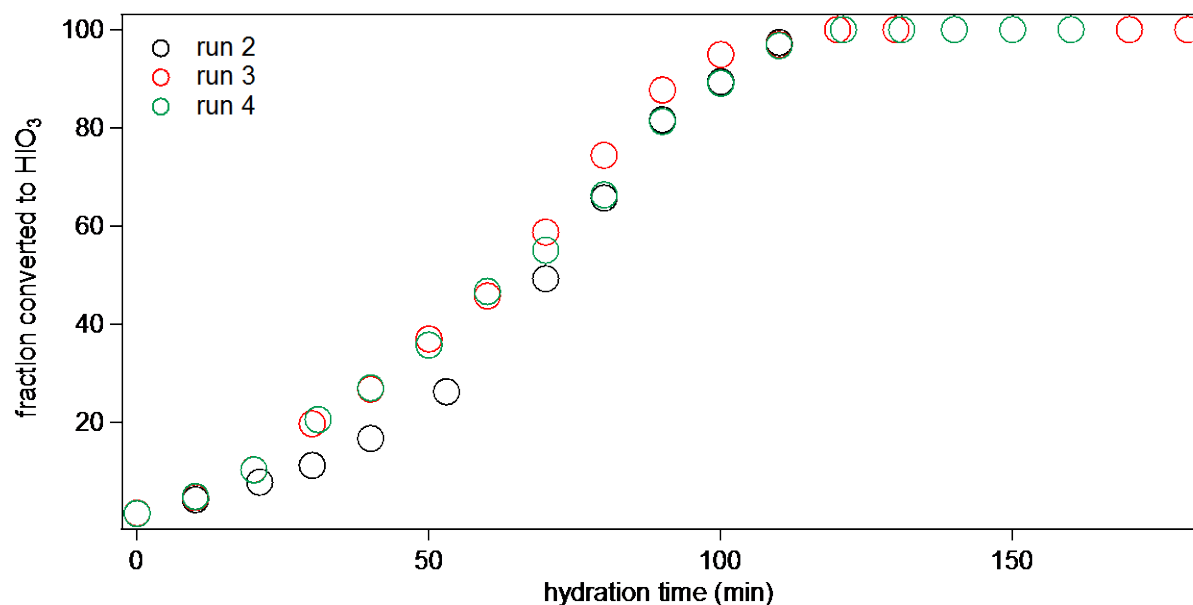
**Figure 7.** (Top, left) SEM image of a fragment from a drop-casted film. (top, right) spin coated film deposited at a rate of 500 rpm with 5 coatings. Films were casted from a  $\text{HI}_3\text{O}_8$  suspension sonicated in denatured ethanol and deposited at  $\sim 2\%$  relative humidity.

This effort has improved our understanding and knowledge in fabricating films from iodine (V) oxide particle suspensions utilizing sonication and casting techniques. Such information is critical towards our understandings of how to construct a three dimensional film composed of nanoaluminum and iodine (V) oxide with controllable properties such as % TMD, thickness, particle size distribution, particle orientation of which all are known to influence the chemical reactivity of the material. Future work will explore in greater detail the origins of single layers at high spin rates *versus* multiple layers at low spin rates. Also, suspension fluids that are more resistant to oxidation by the oxidizer particle will be pursued to improve the shelf life of this process. Formulations will be optimized to improve dispersion, fluid flow and particle retention during the spin casting process in order to provide a uniform deposited structure. Particle size effects will be investigated to determine their influence on the final deposited structure such as thickness, %TMD, layering and particle orientation given the deposition method. In addition, alternative methods for depositing 3-dimensional films will be investigated such as ink printing. Finally, oxidizer based films will be doped with fuels or deposited as fuel-oxidizer films and tested for their reactivity.

#### *Hydration Mechanism for $\text{HI}_3\text{O}_8 \rightarrow \text{HIO}_3$*

Previous efforts by our group investigating the hydration mechanism of  $\text{I}_2\text{O}_5 \rightarrow \text{HI}_3\text{O}_8$  reflected that the hydration mechanism proceeded through a nucleation and growth process followed by a diffusion limited phase [5]. However, hydration profiles for the second hydration step,  $\text{HI}_3\text{O}_8 \rightarrow \text{HIO}_3$ , appear to follow a different mechanism not limited by diffusion. In the summer of 2015 we along with a Cadet from the USAF Academy initiated a study investigating this second hydration step as a function of particle size and relative humidity given that these parameters are highly influential on the rate of hydration. Cadet Kyle Russell began initial studies into particle size effects and relative humidity on the hydration rate and profile for the conversion of  $\text{HI}_3\text{O}_8 \rightarrow \text{HIO}_3$ . Figure 8 plots of the  $\text{HI}_3\text{O}_8$  particles converted to  $\text{HIO}_3$  as a function of hydration time in an 80% relative humidity environment for 20  $\mu\text{m}$  diameter particles. Although Cadet Russell's tenure was short ( $\sim 3$  weeks) he has continued a collaboration with our group constructing an apparatus to

finish this work at the Air Force Academy which entails investigating the hydration rate of three different particle sizes at three different relative humidity levels.



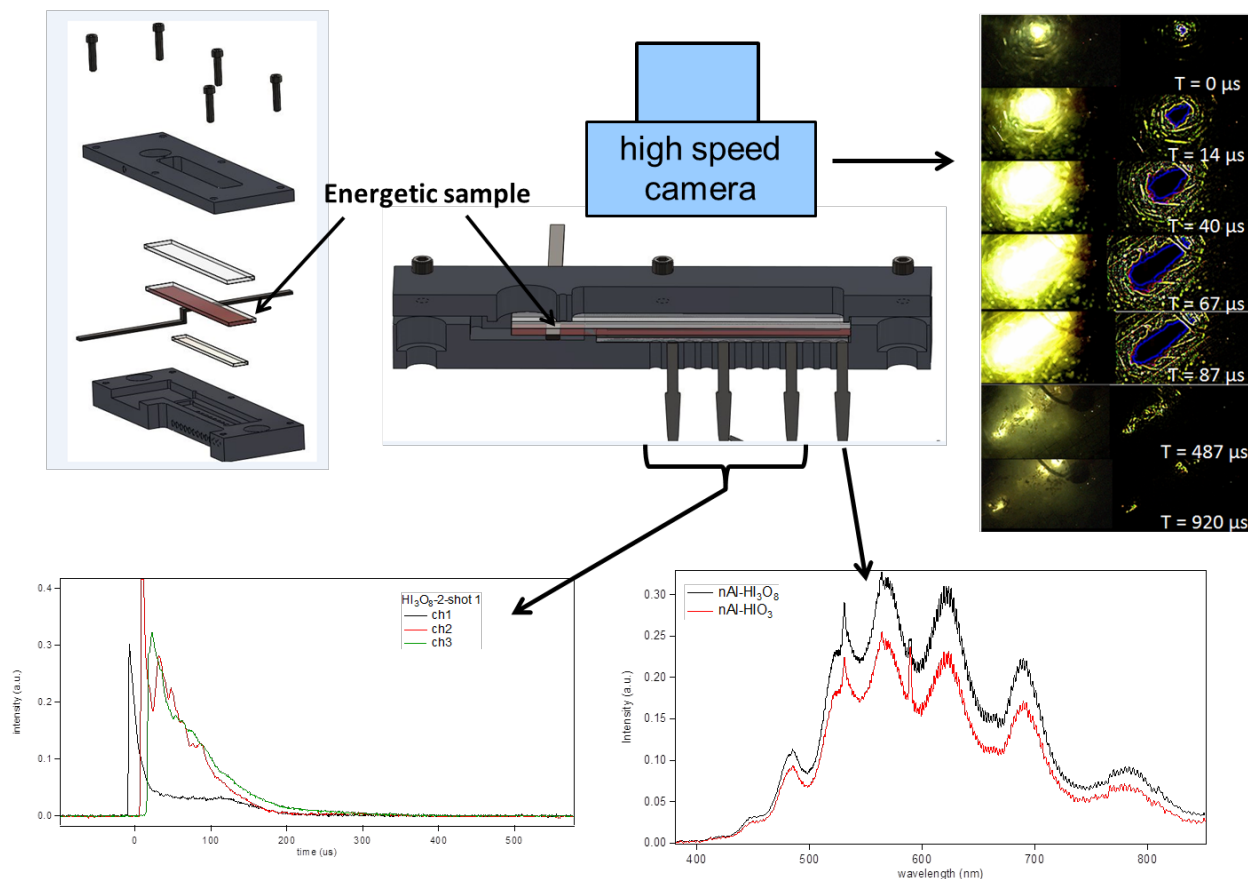
**Figure 8.** Plot of the hydration fraction as a function of time for three collected runs for 20  $\mu\text{m}$  particles of  $\text{HI}_3\text{O}_8$  at 80% relative humidity.

This knowledge is critical in determining the stability of the two different hydrates ( $\text{HI}_3\text{O}_8$  and  $\text{HIO}_3$ ) especially if one state is preferred over the other in an energetic mixture due to desired performance or safety properties (electrostatic discharge, friction & impact). The initial effort for this work has been recorded in a technical memorandum [7].

### *Nanoparticle Materials Combustion*

We are continuing to examine and develop various tools for the purposes of studying in-situ reactivity of nanoparticle composites at the sub-gram scale. Currently, such tools are being employed in the study of highly reactive composites containing crystalline iodates and nano-aluminum (nAl). A diagram of the current set-up for this chemical dynamic measurement is presented in Figure 9. In general, commercially available nAl and iodates are processed in a way such that a high degree of intermixing and particle size reduction is achieved. Test samples can then be examined in the form of a film or powder in the test fixture shown in Figure 9, top left & middle of image. Energetic samples are assembled for reactivity testing in such a way that the combustion zone of the material propagates along a plane where optical fibers can collect light from the emitting reaction above and record the time of arrival (TOA) of the light front/wave and thus one can deduce the “burn” velocity. In conjunction with the TOA measurements, a high-speed camera is following this wave front from above and recording similar behavior as the optical probes. At the end of the fixture sits one optical fiber connected to a spectrometer, which records a spectrum from the reaction zone for that particular sample run collecting information about the chemical species presence during combustion. Another in-situ tool that is coming online is a bomb calorimetry-pressurization apparatus that allows us to monitor the energy released ( $\Delta H_{\text{rxn}}$ ) and the pressurization rate for the ignited material in the form of a powder. Efforts to evaluate these in-

## Assembly and In-situ Testing of Energetic Samples



**Figure 9.** Schematic of the assembly for the testing of nanoenergetic composite materials.

situ methods on newly formulated nanocomposites containing nAl with different types of iodates ( $\text{HIO}_3$ ,  $\text{HI}_3\text{O}_8$ ,  $\text{NaIO}_3$  &  $\text{NH}_4\text{IO}_3$ ) will be presented in an upcoming JANNAF conference in December 2015 in Salt Lake City [8].

### Equation of State (EoS) for Iodine (V) Oxides

Two out of three EoS measurements are complete for the iodine (V) oxide water system in a collaboration with Livermore National Laboratory. The results of these tests have already been included in a thermochemical code utilized by the department of defense and energy in a program called Cheetah 8.0. We are working on generating the last state, the anhydride, at a high purity level (>98%) to complete testing on all three states of iodine (V) oxide. Such efforts will improve the efficiency of combustion modeling systems that utilize this oxidizer in its various states.

*Future Efforts: Evaporation of new materials and chemical reactivity testing of newly formulated nanocomposite materials with TPR/MS.*

In conjunction with our efforts in the helium droplet assembly of energetic materials and nanoparticle combustion, we will begin investigating the evaporation properties of various

oxidizers for use in future experimentation. Our interests have recently focused on various iodine oxides ( $\text{I}_2\text{O}_5$ ,  $\text{NaIO}_3$ ,  $\text{NaI}_3\text{O}_8$ , etc.) and metal oxides ( $\text{CuO}$ ,  $\text{CuO}_2$ , etc.). The evaporation of oxidizers presents a challenge in that under evaporation conditions (high vacuum, high temperature) the oxidizers tend to decompose. Our preliminary mass spectrometry measurements of non-equilibrium sublimation products suggest that sodium iodate goes into the gas phase intact. According to the experiments of others,  $\text{CuO}$  should also be possible to evaporate molecularly, however, our initial results appear only to produce oxygen and copper atoms upon heating. We plan on adjusting evaporation conditions to try to find a regime that will produce intact molecular vapor of these oxidizers.

In-situ chemical reactivity studies will also be investigated with temperature programmed reactivity (TPR) and mass spectroscopy. TPR provides a means to which one can rapidly heat up a sample and measure weight loss and species released during a reaction such as combustion. Results from the TPR experiments can be compared to emission spectroscopy data collected during the combustion of samples in the previous mentioned in-situ method. The combination of these techniques could provide valuable insight to the chemical mechanisms governing these nanoenergetic systems.

## References:

1. M.D. Grapes, T. LaGrange, L.H. Friedman, B.W. Reed, G.H. Campbell, T.P. Weihs “Combining nanocalorimetry and dynamic transmission electron microscopy for in situ characterization of materials processes under rapid heating and cooling” *Review of Scientific Instruments*, 85 (8), 084902 (2014)
2. S.B. Emery, Y. Xin, C.J. Ridge, R.J. Buszek, J.A. Boatz, J.M. Boyle, B.K. Little, C.M. Lindsay “Unusual behavior in magnesium-copper cluster matter produced by helium droplet mediated deposition” *The Journal of Chemical Physics*, 142, 084307 (2015)
3. M.P. Casaletto, A. Longo, A. Martorana, A. Prestianni, A.M. Venezia “XPS study of supported gold catalysts: the role of  $\text{Au}^0$  and  $\text{Au}^{+\delta}$  species as active sites” *Surface and Interface Analysis*, 38 (4), 215-218 (2006)
4. K. Qian, B.C. Sweeny, A.C. Johnston-Peck, W. Niu, J.O. Graham, J.S. DuChene, J. Qiu, Y-C Wang, M.H. Engelhard, D. Su, E.A. Stach, and W.D. Wei “Surface Plasmon-Driven Water Reduction: Gold Nanoparticle Size Matters” *Journal of the American Chemical Society*, 136 (28), 9842-9845 (2014)
5. B.K. Little, S.B. Emery, J.C. Nittinger, R.C. Fantasia, and C.M. Lindsay “Physiochemical Characterization of Iodine (V) oxide, Part I: Hydration Rates” *Propellants, Explosives, Pyrotechnics*, 40 (4), 595-603 (2015)
6. B.K. Little, S.B. Emery, and C.M. Lindsay “Physiochemical Characterization of Iodine (V) oxide, Part II: Morphology and Crystal Structure of Particulate Films” *Crystals*, accepted for publication Oct 2015
7. K. Russell, B.K. Little, C.M. Lindsay “Exploration of the Hydration Mechanism of  $\text{HI}_3\text{O}_8 \rightarrow \text{HIO}_3$ ” AFRL/RWME Tech Memorandum 15-XX: CRSP Project 2015 (*in preparation*)
8. B.K. Little, J.T. Langhals, L.M. Martinez, E.J. Welle, and C.M. Lindsay “Chemical Dynamics of Aluminum-iodate Composites” *Proceedings of the Joint Army Navy NASA*

*Air Force, 39<sup>th</sup> Propellant and Explosives Development and Characterization Meeting,*  
Dec (2015)

## Appendix A: In-house Activities, Energetic Core-Shell Nanoparticles

| <b>Personnel:</b> | <u>Name</u> | <u>Degree</u> | <u>Discipline</u> | <u>Involvement</u> |
|-------------------|-------------|---------------|-------------------|--------------------|
|-------------------|-------------|---------------|-------------------|--------------------|

*Air Force Employees:*

|                    |       |           |          |
|--------------------|-------|-----------|----------|
| C. Michael Lindsay | Ph.D. | Chemistry | PI (30%) |
|--------------------|-------|-----------|----------|

*On Site Contractors:*

|                            |       |                 |            |
|----------------------------|-------|-----------------|------------|
| Brian Little               | Ph.D. | Materials Chem. | S&E (50%)  |
| Claron Ridge (NRC Postdoc) | Ph.D. | Physical Chem.  | S&E (100%) |

**Visitors:**

- None this year

**Collaborations:**

- Dr. Jerry Boatz, AFRL/RZSP – *Ab initio* calculations of nanoparticle structure, energetic, and reactivity
- Dr. Robert Hinde, Dept of Chemistry, Univ. of Tennessee – Surface Impact Simulations of Doped Helium Droplets
- Dr. Yan Xin, National High Magnetic Field Lab – STEM of Cu/Mg core-shell clusters
- Dr. Jason Boyle, Dublin School, Dublin, NH – Deposition of Cu/Mg core-shell clusters
- Alexander Orlov, SUNY Stony Brook/Brookhaven National Lab – TEM and catalysis investigation of gold clusters
- Dr. Joe Zaug and Dr. Sorin Bastea, Lawrence Livermore National Laboratory – Equations of state of iodine oxide materials
- Dr. Wei David Wei, Univ. of Florida – Photocatalytic study of Au clusters on oxide supports
- Dr. Olivier Pierron, Georgia Tech – Mechanical properties of cluster films

**Publications:**

**Peer Reviewed Journal Articles (3):**

1. B.K. Little, S.B. Emery, and C.M. Lindsay, “Physiochemical Characterization of Iodine (V) Oxide Part II: Morphology and Crystal Structure of Particulate Films,” *Crystals* (accepted, 2015)
2. S.B. Emery, Y. Xin, C.J. Ridge, R.J. Buszek, J.A. Boatz, J.M. Boyle, B.K. Little, and C. M. Lindsay “Unusual behavior in magnesium-copper cluster matter produced by helium droplet mediated deposition,” *J. Chem. Phys.*, 142, 084307 (2015)
3. B.K. Little, S.B. Emery, J.C. Nittinger, R.C. Fantasia, and C.M. Lindsay “Physiochemical Characterization of Iodine (V) Oxide Part 1: Hydration Rates,” *Prop., Expl., Pyro.*, 40(4), 595-603 (2015)

**Conference Proceedings (1):**

1. C.M. Lindsay and M.E. Fajardo, “The Quest for Greater Chemical Energy Storage in Energetic Materials: Grounding Expectations.” *AIP Conf. Proc.* (accepted, 2015).

**Conference Presentations (7):**

1. C. Ridge, S. Emery, K. Rider, and C.M. Lindsay, “Cluster Films by Helium Droplet Mediated Cluster Assembly: Growth and Characterization” *HeSSSMe*, Madrid, Spain, 11 Oct 2014. (invited talk)
2. C. Ridge, S. Emery, K. Rider, and C.M. Lindsay, “Cluster Films by Helium Droplet Mediated Cluster Assembly: Growth and Characterization” SUNY Stony Brook, 5 Nov 2014. (invited talk)
3. C.M. Lindsay and M.E. Fajardo, “The Quest for Greater Chemical Energy Storage in Energetic Materials: Grounding Expectations.” *APS -Shock Compression of Condensed Matter* Meeting, 14-19 June, 2015. (invited talk)
4. C. Ridge, S. Emery, K. Rider, and C.M. Lindsay, “Helium Droplet Mediated Cluster Film Assembly: Growth and Characterization” *250<sup>th</sup>ACS Meeting, Session: Physical Chemistry of clusters and Nanoparticles*, Boston, MA, 18 Aug 2015. (talk)
5. C. Ridge, S. Emery, K. Rider, and C.M. Lindsay, “Helium Droplet Mediated Cluster Film Assembly: Growth and Characterization” *AFRL/RW Science Fair*, Ft. Walton Beach, FL, 30 Sept 2015. (talk)
6. B.K. Little, J. Langhals, E.J. Welle, and C.M. Lindsay “Chemical Dynamics of Iodine Oxide Films” *AFRL/RW Science Fair*, Ft. Walton Beach, FL, 30 Sept 2015. (poster)
7. *Invited* - PACIFICHEM Dec 2015, C. Ridge, S. Emery, K. Rider, and C.M. Lindsay, “Cluster Films by Helium Droplet Mediated Cluster Assembly: Growth and Characterization” (talk)

**Invention Disclosures and Patents Granted:**

- N/A

**Professional Activities:**

- Dr. C. Michael Lindsay – Technical Advisor to 60+ member AFRL/RWME
- Dr. C. Michael Lindsay - Mentor/Advisor to NRC Postdoc
- Dr. Brian Little and Dr. C. Michael Lindsay – Session Chairs, Biennial APS Conference on Shock Compression of Condensed Matter
- Dr. C. Michael Lindsay and served as peer-reviewer for misc. journal articles of outside researchers.
- Dr. C. Michael Lindsay – ~100 hours of STEM outreach activities in local community

**Honors Received:**

- C. Michael Lindsay, USAF S&E Award – Research Management, AFRL Munitions Directorate (2015)
- Dr. Claron Ridge and Dr. Brian Little – Energetic Materials Chemistry & Mechanics Team awarded AFMC Scientific Team of the Year (2015)

**Extended Scientific Visits:**

- None

**Technology Transitions:**

- None

## **DISTRIBUTION LIST**

AFRL-RW-EG-TR-2016-036

\*Defense Technical Info Center  
8725 John J. Kingman Rd Ste 0944  
Fort Belvoir VA 22060-6218

AFRL/RWME (1)  
AFRL/RWORR (STINFO Office) (1)