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14. ABSTRACT
We propose to purchase several small equipment to facilitate the investigation of our current ARO project on quantification of ignition properties of porous Si based energetics. Over the past year, we have successfully synthesized a range of nanostructured porous Si and tested their ignition and heat release properties. As a next step, more accurate and quantitative measurements are needed to help us understand the relationship between the nanostructures of porous Si and their ignition and combustion properties. Initially, we proposed to purchase of a

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Report Title

Final Report: Purchasing Equipment to Enhance the Study of Porous Si Based Energetics

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We propose to purchase several small equipment to facilitate the investigation of our current ARO project on quantification of ignition properties of porous Si based energetics. Over the past year, we have successfully synthesized a range of nanostructured porous Si and tested their ignition and heat release properties. As a next step, more accurate and quantitative measurements are needed to help us understand the relationship between the nanostructures of porous Si and their ignition and combustion properties. Initially, we proposed to purchase of a glove box for much better controlled synthesis of porous Si, a bomb calorimeter for heat of combustion measurement, an oxygen mass flow controller for precise gas control, a balance for precise sample mass measurement, and a flash unit and a spectroradiometer for flash ignition experiment. With the budget, we did purchased the bomb calorimeter as planned. However, our differential Scanning Calorimetry system (TGA/DSC, LABSYS evo, shown in Fig. 5.) broke in the summer so that we asked permission to spend most of the remaining funding to pay for the repair service from Setaram. Then we used the remaining funding bought a centrifuge with accessories that has significantly enhanced our abilities in material synthesis.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u> <u>Paper</u>

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u> <u>Paper</u>

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. "Si/Fe2O3 core/shell Nanoparticles for Enhanced Ignition Properties", S.D. Huang, S.L. Deng, Y. Jiang, J.H. Zhao and X. L. Zheng, in preparation.
2. "Flash Ignition of Si Nanoparticles: Effects of Particle Size and Packing Porosity", S.D. Huang, V. S. Parimi, S.L. Deng and X. L. Zheng, in preparation.

Number of Presentations: 2.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

<u>Received</u> <u>Book Chapter</u>

TOTAL:

Patents Submitted

Patents Awarded

Awards

- 2016, Resonate Awards that honor outstanding achievement in renewable energy and sustainability-focused science and technology.

Graduate Students

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

With the equipment budget of $22200. We were able to make three major progress.

1. We purchased the bomb calorimeter that allows us to measure the heat of combustion of small samples including pyrotechnic mixtures.
2. We paid the service fee to fix the problems with our differential Scanning Calorimetry system (TGA/DSC, LABSYS evo.)
3. We bought a centrifuge with accessories that has significantly enhanced our abilities in material synthesis.

Technology Transfer

Final Report:

Purchasing Equipment to Enhance the Study of Porous Si Based Energetics

Xiaolin Zheng
Department of Mechanical Engineering,
Stanford University, Stanford, CA 94305

Grant No.: W911NF-16-1-0075

Submitted to: Department of the Army

Report coverage: 03/01/2016 to 08/31/2016

Abstract

We propose to purchase several small equipment to facilitate the investigation of our current ARO project on quantification of ignition properties of porous Si based energetics. Over the past year, we have successfully synthesized a range of nanostructured porous Si and tested their ignition and heat release properties. As a next step, more accurate and quantitative measurements are needed to help us understand the relationship between the nanostructures of porous Si and their ignition and combustion properties. Initially, we proposed to purchase of a glove box for much better controlled synthesis of porous Si, a bomb calorimeter for heat of combustion measurement, an oxygen mass flow controller for precise gas control, a balance for precise sample mass measurement, and a flash unit and a spectroradiometer for flash ignition experiment. The addition of those equipment would greatly enhance our capability for our project, from synthesis, to measurement and characterization. With the budget, we did purchased the bomb calorimeter as planned. However, our differential Scanning Calorimetry system (TGA/DSC, LABSYS evo, shown in Fig. 5.) broke in the summer so that we asked permission to spend most of the remaining funding to pay for the repair service from Setaram. Then we used the remaining funding bought a centrifuge with accessories that has significantly enhanced our abilities in material synthesis.

Technical Description

Motivation

We propose to purchase several small equipment to facilitate the investigation of our current ARO project on quantification of ignition properties of porous Si based energetics. The scientific research objective of our project is to quantitatively determine the ignition temperature and minimum ignition energy of porous Si based energetic materials and to correlate those ignition properties with the physical microstructures of porous Si and the chemical compositions of the oxidizers. Over the past year, we have successfully synthesized a range of nanostructured porous Si and tested their ignition and heat release properties. As a next step, more accurate and quantitative measurements are needed to help us understand the relationship between the nanostructures of porous Si and their ignition and combustion properties.

Equipment and Service Planned and Obtained

We proposed to purchase of a glove box for much better controlled synthesis of porous Si, a bomb calorimeter for heat of combustion measurement, an oxygen mass flow controller for precise gas control, a balance for precise sample mass measurement, and a flash unit and a spectroradiometer for flash ignition experiment. The addition of those equipment will greatly enhance our capability for our project, from synthesis, to measurement and characterization. With the budget, we did purchased the bomb calorimeter as planned. However, our differential Scanning Calorimetry system (TGA/DSC, LABSYS evo, shown in Fig. 5.) broke in the summer so that we asked permission to spend most of the remaining funding to pay for the repair service from Setaram. Then we used the remaining funding bought a centrifuge with accessories that has significantly enhanced our abilities in material synthesis.

Equipment Setup

1. Bomb Calorimeter

We have purchased the 6725 Semi-Micro calorimeter to measure the heat of combustion of small samples including pyrotechnic mixtures, as shown in Fig. 1. Since the heat of reaction is a primary parameter when evaluating energetic materials, the purchased bomb calorimeter enables us to accurately measure the heat of reaction of diverse energetic materials under controlled gas environment and pressure. The heat of reaction provides complementary information to our current control volume pressure vessel measurements in terms of evaluating the combustion efficiency of energetic materials. The current system includes a small oxygen bomb pressure vessel (22 mL) that can be used to measure the heat release from samples as small as 25 mg and heat release as low as 220 J. The high sensitivity of this bomb calorimeter makes it ideal for analyzing highly reactive nanoenergetic formulations, since it allows for safely testing small quantity of samples. The instrument also has large upper limits for the heat release 5,021 J for explosive, gas producing mixtures, and 10,042 J for non-explosive, non-gas generating samples, making it useful for testing a broad range of energetic materials.

Figure 1. The bomb calorimeter for heat release measurements.

We have utilized the bomb calorimeter to investigate the effect of porous Si (p-Si)/sodium perchlorate (NaClO4) on the heat release of B/CuO. The heat of reaction of p-Si/NaClO4 mixture , B/CuO mixture, and a mixture of these two samples (B/CuO+p-Si/NaClO4) were measured with the bomb calorimeter, as shown in Fig. 2. The heat of reaction of each composition mixture was reported, and the estimated heat of reaction of the B/CuO+p-Si/NaClO4 mixture was obtained by considering the weighted sum of the individual mixtures. The results show that the addition of p-Si/NaClO4 increases the heat release of B/CuO not only due to the larger heat of reaction of p-Si/NaClO4 but also due to synergic effects.

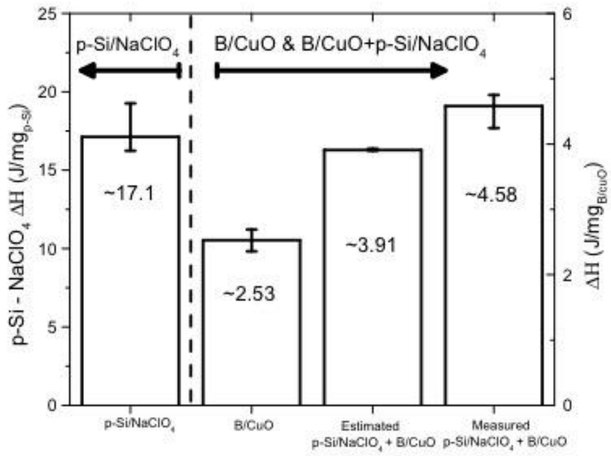

Figure 2. Normalized heat of reaction of p-Si/NaClO4 shown on the left, and B/CuO and B/CuO + p-Si/NaClO4 shown on the right. Values on the graph are averages with error

bars representing the standard deviations. The estimated values are obtained by summing the total heat release from B/CuO and p-Si/NaClO4 samples over the mass of B/CuO sample. All of tests are conducted at atmosphere pressure and room temperature.

2. Centrifuge, Rotor, and Adapters

We have purchased the Sorvall ST 16, 120V centrifuge together with a HIGHCONIC II-6X100ML rotor, and six 50 mL adapters, as shown in Fig. 3. This equipment was purchased together with the adapters to facilitate the synthesis of Si based energetic nanomaterials. For example, to synthesize Si/Fe_2O_3 core/shell nanoparticles for interfacial contact enhancement and thus better ignition properties, multiple surface treatment and electroless plating steps are needed. During these steps, products after surface treatment and coating need to be separated from the solution and rinsed off residues. The traditional separation methods such as leveraging the gravitational force or utilizing filter paper are not feasible for the current project, since the Si nanoparticles can suspend in the solution for very long time and are difficult to be collected from the filter paper. The purchased Sorvall ST 16, 120V centrifuge system has a wide range of rotation speeds, with the highest speed of 10350 rpm. With the 50 mL adapter, separating a large batch of extremely fine particles from the solution becomes tractable. With the centrifuge, separating nano and micro sized particles from the solution is significantly facilitated, resulting in shorter processing time, higher purity and larger yield.

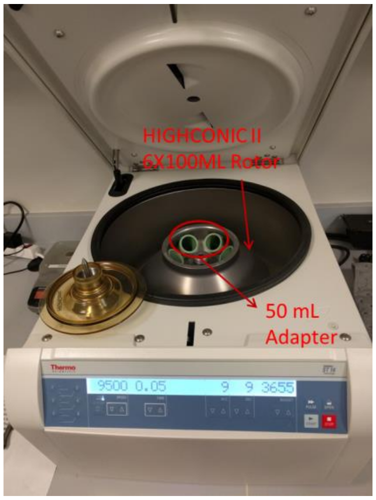

Figure 3. The centrifuge system utilized for the synthesis of Si based energetic nanoparticles.

We have successfully utilized the centrifuge system to facilitate the synthesis of Si/Fe core/shell nanoparticles. As shown in Fig. 4, Si nanoparticles are coated with Fe and become magnetic.

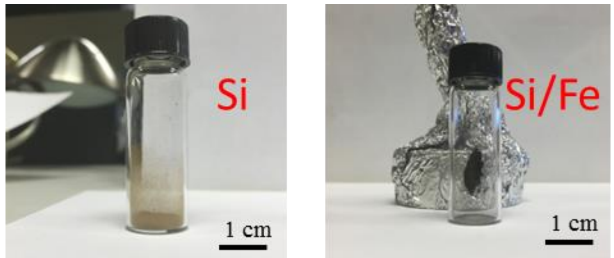

Figure 4. Si nanoparticles coated with Fe and become magnetic.

3. Service for Setaram TGA/DSC Labsys Evo

We previously purchased the simultaneous Thermogravimetric Analysis and Differential Scanning Calorimetry system (TGA/DSC, LABSYS evo, shown in Fig. 5.) and utilized it to characterize the heat flow and mass change while heating up energetic materials with controlled heating rates. This system is one of the key equipment for ignition and heat release quantifications. However, the TGA/DSC thermal analyzer displaced an error message of "real-time treatment failure time has occurred" during one of our earlier experiments, and this error prevented us from conducting further experiments due to the termination of communications between the thermal analyzer and computer. A repair service from Setaram was requested to resolve this issue.


Figure 5. The TGA/DSC experimental system.

The service was successful, for the CPU module was replaced to solve the communication issue. In addition, the service representative provided operational maintenance trainings to the postdoctoral scholar and graduate students, who have been actively utilizing the equipment. Currently, the TGA/DSC system is in good working condition.

Effect on Research and Education

Effect on Research

The thermal characterization and centrifuge equipment has already started to impact our research capabilities on energetic materials as discussed above. These instruments will enable fast, high-purity, and high-yield synthesis of nanoenergetics and facilitate thermal analysis of these materials, which in turn provides guidance to further improve the synthesis procedure for enhanced ignition and combustion properties. They are critical to achieve our research goals related to the DOD: studying the ignition and combustion properties of nanoenergetics, and understanding the surface properties of nanocatalysts.

Effect on Undergraduate and Graduate Education

The bomb calorimeter, centrifuge, and thermal analyzer and mass spectrometer systems will be used to train and educate our graduate students on the state-of-the-art thermal analysis methods and their applications in energetic materials, combustion and propulsion in general. These instruments have been located in the High Temperature Gasdynamics Laboratory (HTGL), one of the leading laboratories on combustion, propulsion, advanced diagnostics, plasma science, and material processing research in the world. The HTGL currently has 7 faculty members, over 50 Ph.D. students and about 50 M.S. students, and many of our research efforts are of interest to the DOD. The HTGL students can access these instruments after proper training and qualification from one of my graduate students.

These instruments will also impact the education of undergraduate students at Stanford. We offer Combustion course that is open to both graduate and undergraduate students, and bomb calorimetry is introduced in the course as the standard method to measure the adiabatic flame temperature of combustible mixtures. Therefore, students can have better understanding of the design principle by personally observing the system and conducting experiments with proper supervision. In addition, Professor Xiaolin Zheng actively supports the Summer Undergraduate Research Institute (SURI) program, which provides summer internship for undergraduates. All the undergraduate students engaging in HTGL research will have the opportunity to access these instruments after going through a similar training and qualification process. Therefore, the positive impact of these instruments on education will be broad and significant.

Useful Life of Equipment

The useful life of the bomb calorimeter, centrifuge system, and thermal analyzer is estimated to be about ten to fifteen years.

Bibliography

1. "Si/Fe_2O_3 core/shell Nanoparticles for Enhanced Ignition Properties", S.D. Huang, S.L. Deng, Y. Jiang, J.H. Zhao and X. L. Zheng, in preparation.
2. "Flash Ignition of Si Nanoparticles: Effects of Particle Size and Packing Porosity", S.D. Huang, V. S. Parimi, S.L. Deng and X. L. Zheng, in preparation.
3. "Enhancing Ignition and Combustion of Micron-sized Aluminum by Adding Porous Silicon", V. S. Parimi, S.D. Huang and X. L. Zheng, Proc. Combust. Inst. 36, DOI:10.1016/j.proci.2016.06.185 (2016).