Defense Threat Reduction Agency
8725 John J. Kingman Road, MS-6201
Fort Belvoir, VA 22060-6201

USSTRATCOM CENTER FOR COMBATING WMD

DTRA-TR-14-32

TECHNICAL REPORT

Multifunctional Core-Shell and Nano-channel Design for Nano-sized Thermo-sensor

Distribution Statement A. Approved for public release; distribution is unlimited.

April 2015

HDTRA1-10-1-0002

Jie Lian and Qingkai Yu

Prepared by:
Rensselaer Polytechnic Institute
110 8th St.
Troy, NY 12180

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
00-04-2015

2. REPORT TYPE
Technical

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE
Multifunctional Core-Shell and Nano-channel Design for Nano-sized Thermo-sensor

5a. CONTRACT NUMBER
HDTRA1-10-1-0002

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Jie Lian (Rensselaer)
Qingkai Yu (Texas)

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Rensselaer Polytechnic Institute
110 8th St.
Troy, NY 12180

Texas State University
601 University Dr
San Marcos, TX 78666

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Defense Threat Reduction Agency
8725 John J. Kingman Road STOP 6201
Fort Belvoir, VA 22060

10. SPONSOR/MONITOR'S ACRONYM(S)
DTRA

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
DTRA-TR-14-32

12. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution Statement A. Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This project aimed at novel nano-sized thermal sensors that can measure temperature and retrieve thermal history of the biological agents experienced during the testing of agent-defeat weapons. Thermal response of Au-based core/shell nanostructures and thin film upon rapid temperature change was studied and their potential as dynamic nanothermometers was explored. The fund ($557,586) mainly supported a PhD student and 2 postdoc fellows at Rensselaer Polytechnic Institute and Texas State University. The knowledge gained under the support of this project was disseminated through journal publications and conference presentations. The project produced 10 publications in peer-reviewed journals.

15. SUBJECT TERMS
Dyamic Nanothermometers   Core-shell Nanostructure   Thermal-induced dewetting   Thermal sensor

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
					Suhithi Peiris
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	SAR	13	**19b. TELEPHONE NUMBER** *(include area code)*
Unclassified	Unclassified	Unclassified			703-767-4732

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

CONVERSION TABLE

Conversion Factors for U.S. Customary to metric (SI) units of measurement.

MULTIPLY → BY → TO GET

TO GET ← BY ← DIVIDE

angstrom	1.000 000 x E -10	meters (m)
atmosphere (normal)	1.013 25 x E +2	kilo pascal (kPa)
bar	1.000 000 x E +2	kilo pascal (kPa)
barn	1.000 000 x E -28	meter^2 (m^2)
British thermal unit (thermochemical)	1.054 350 x E +3	joule (J)
calorie (thermochemical)	4.184 000	joule (J)
cal (thermochemical/cm^2)	4.184 000 x E -2	mega joule/m^2 (MJ/m^2)
curie	3.700 000 x E +1	*giga bacquerel (GBq)
degree (angle)	1.745 329 x E -2	radian (rad)
degree Fahrenheit	$t_k = (t^o f + 459.67)/1.8$	degree kelvin (K)
electron volt	1.602 19 x E -19	joule (J)
erg	1.000 000 x E -7	joule (J)
erg/second	1.000 000 x E -7	watt (W)
foot	3.048 000 x E -1	meter (m)
foot-pound-force	1.355 818	joule (J)
gallon (U.S. liquid)	3.785 412 x E -3	meter^3 (m^3)
inch	2.540 000 x E -2	meter (m)
jerk	1.000 000 x E +9	joule (J)
joule/kilogram (J/kg) radiation dose absorbed	1.000 000	Gray (Gy)
kilotons	4.183	terajoules
kip (1000 lbf)	4.448 222 x E +3	newton (N)
kip/inch^2 (ksi)	6.894 757 x E +3	kilo pascal (kPa)
ktap	1.000 000 x E +2	newton-second/m^2 (N-s/m^2)
micron	1.000 000 x E -6	meter (m)
mil	2.540 000 x E -5	meter (m)
mile (international)	1.609 344 x E +3	meter (m)
ounce	2.834 952 x E -2	kilogram (kg)
pound-force (lbs avoirdupois)	4.448 222	newton (N)
pound-force inch	1.129 848 x E -1	newton-meter (N-m)
pound-force/inch	1.751 268 x E +2	newton/meter (N/m)
pound-force/foot^2	4.788 026 x E -2	kilo pascal (kPa)
pound-force/inch^2 (psi)	6.894 757	kilo pascal (kPa)
pound-mass (lbm avoirdupois)	4.535 924 x E -1	kilogram (kg)
pound-mass-foot^2 (moment of inertia)	4.214 011 x E -2	kilogram-meter^2 (kg-m^2)
pound-mass/foot^3	1.601 846 x E +1	kilogram-meter^3 (kg/m^3)
rad (radiation dose absorbed)	1.000 000 x E -2	**Gray (Gy)
roentgen	2.579 760 x E -4	coulomb/kilogram (C/kg)
shake	1.000 000 x E -8	second (s)
slug	1.459 390 x E +1	kilogram (kg)
torr (mm Hg, 0^0 C)	1.333 22 x E -1	kilo pascal (kPa)

*The bacquerel (Bq) is the SI unit of radioactivity; 1 Bq = 1 event/s.

**The Gray (GY) is the SI unit of absorbed radiation.

Final Report (Feb. 15, 2010 ~ Feb. 14, 2014)

DTRA Basic Research Grant HDTRA1-10-1-0002

Multifunctional Core-Shell and Nano-channel Design for Nano-sized Thermo-sensor

PI: Jie Lian, Associate Professor, Department of Mechanical, Aerospace & Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180

Co-PI: Qingkai Yu, Assistant Professor, Ingram School of Engineering, Texas State University, San Marcos, TX 78666

(1) Objective:

The objective of the proposed research aims at the development of novel nano-sized thermal sensors based on a multifunctional core/shell and nano-channel design that can be used to measure temperature and retaining thermal history of the biological agents experienced during the testing of agent-defeat weapons. The effective temperature sensing is important for many military-related activities including environmental sensing in a highly explosive event. We will focus on fundamental understanding of the dynamic behaviors of core/shell nanostructures, nanoparticles and nano-channels in a rapid temperature transition environment, which will provide a basis for the scientific design of a novel nano-sized thermal sensor with a fast response within μs time frame.

(2) Scope

This project is under the scope of Basic and Applied Sciences Directorate and the JSTO and Nano-sized Thermo-sensor Materials (Topic C: Thrust 1)

(3) Work scope

During last several years, extensive efforts have been carried out at both Rensselaer Polytechnic Institute and Texas State University for materials design, laboratory equipment setup, experimental testing and scientific principle exploration. These efforts are base on clearly-defined tasks for each team as identified at the statement of work. Specifically, Rensselaer team (Prof. Jie Lian and his team) focused on the establishment of using surface plasma resonance (SPR) of the morphological changes for the ultrathin Au film and SiO_2/Au core/shell nanostructures as effective sensing mechanisms to capture the thermal history. The team led by Dr. Qingkai Yu at Texas State focused on the scientific principle exploration of filling dynamics inside nano-channel geometry and laser annealing of the core/shell structure developed at RPI to explore the response of the nano-sensors under extreme fast heat events.

(4) Accomplishments Achieved upon the support of the DTRA project

(1) Ultrathin Au-thin film based Nano-thermal sensor

Au-based nanostructure in thin film geometry was explored as potential nano-sized dynamic thermal sensors. The Au ultrathin films with different thicknesses varying from 1 to 5 nm were prepared by thermal vaporation on silica substrates, and the film morphology was characterized by atomic force microscopy and scanning electron microscopy. We have performed the thermal shock of Au ultrathin films using a tube furnace within the temperature regime from 200 oC to 700 oC and the duration varies from 3s up to 180 s. The morphological change of the Au-film upon thermal treatment was characterized using AFM, SEM and XRD, and their optical responses (localized surface plasmon absorption and surface enhanced Raman spectroscopy) were investigated by UV-vis-IR photospectrometer and Raman spectroscopy.

The localized surface plasmon absorption of the Au film is very sensitive to thermal annealing variation as a result of thermally dewetting induced morphological changes. The absorption bands display consistent blue shift and narrow in the FWHM. The correlations among the absorption band, FWHM, thermal shock temperature and duration were established. The effects of thicknesses on the temperature sensitivity were investigated, which allow us to design various nano-sized dynamic sensors for desired temperature regimes. Based on the systematic structural investigation and optical characterization, we have established the correlation between the absorption band, FWHM and the morphological characteristics such as particle size, shape, interparticle spacing and fraction of open dewetting area. A simplified model was derived to correlate the change of the absorption band with the temperature and duration, which allow to predict the thermal profile sensor materials experienced during a thermal event. The thermal history model was also experimentally validated. The effects of thickness of Au films on the activation energy and kinetics of thermal-dewetting were explored, allowing design of different Au film-based nanosensors with controlled sensitivity at different temperature regimes.

These results were published in numerous publications including Journal of Physical Chemistry C 116 (2012) 9000; Journal of Physical Chemistry C 117 (2013) 3366-3373; and Journal of Nanoparticle Research 16 (2014) 2273.

(2) Silica/Au core shell nanostructures for ultrafast dynamic nano-thermometers

Significant advancement was achieved in developing a core/shell nanostructure as ultrafast dynamic nano-thermometers with extreme sensitivity and fast response to rapid temperature variation. Particularly, silica/Au core shell nanostructures with well controlled surface morphologies were synthesized and the surface plasmon resonance properties upon thermal shock were investigated in order to explore their potentials ultrafast dynamic thermometer. The correlation between different synthesis conditions and the SPR was identified, and reproducibility of materials synthesis was evaluated. We also performed extensively thermal shock experiments within the time of 100 ms up to 2 seconds using pyroprobe and investigate the properties variation of the SiO_2/Au core shell nanostructures as a function of temperature and duration. The thermal history model was also developed based on the dynamics of the morphology changes as controlled by the thermal-dewetting, and the potential of using SPR variation upon thermal shock as effective sensing mechanisms was evaluated. A 3-D contour map was developed that allows us to establish the connection among the SPR peak shift, temperature and duration of a thermal event. These systematic investigation leads to the development of an ex-situ ultrafast dynamic nano-thermometer based on silica/Au core shell nanostructures with extremely fast response below sub-second and even 100 ms and sensitivity at low temperature of 300 ^{o}C.

(a) Synthesis of silica/Au core shell nanostructures

We have successfully synthesized silica/Au core shell nanostructures with well controlled surface morphologies and SPR properties. The surface coverage of the Au film on the silica core (600 nm in diameter) was controlled from partially to fully coverage. The various coverage of the Au film provides a unique optical signature of the nanoshell formation and growth in the appearance of the SP absorption bands. A continuous shift of the surface plasmon peak was observed from 554 nm to 915 nm (Figure 1), which provide a solid basis for designing different thermal sensor with different sensitivity and time response.

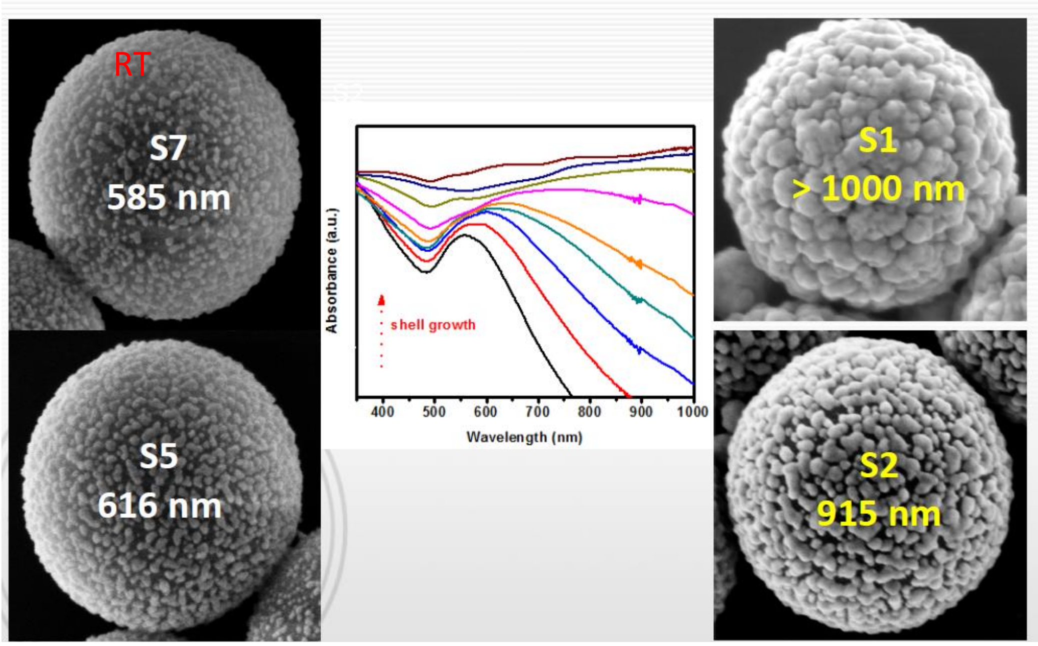

Figure 1. Silica/Au core shell nanostructures with different initial coverage of the Au nanoshell, and the corresponding surface plasmon absorption spectra as probed by UV-vis-NIR.

(b) Morphology self-organization and optical properties variation upon thermal shock

The silica/Au core shell nanostructures with different initial SP peaks were selected as the model system to explore its potential using as thermal sensor to capture a thermal event, and the morphology self-organization and optical properties variation upon thermal shock were investigated from 300 to 800 ˚C were carried out for different durations from 0.1 to 1.0 s. The silica/Au core shell nanostructures are extremely sensitive to the thermally dewetting-induced morphology self-organization, driven by the surface diffusion to reduce the surface area in order to minimize the total energy of the system. Upon thermal treatments, Au nanoshell on the silica core experienced drastic shape changes varying with thermal shock temperatures with controlled particle size, spacing and shell coverage. The drastic morphological evolutions of gold nanoshell upon thermal dewetting significantly affect the optical properties as characterized by the LSPR spectroscopy, monitoring changes in SP absorption band in the visible spectral range, behaving as a unique optical fingerprint to characterize the thermal conditions.

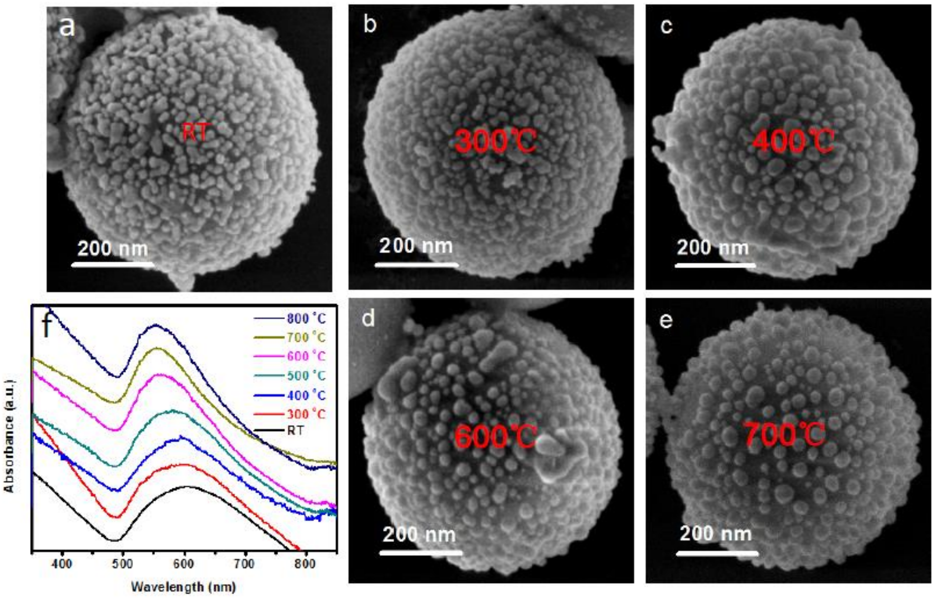

Figure 2. HR-SEM images of an incomplete gold nanoshell with the SP band locating at 602 nm wavelength prior to thermal treatments (a) and upon various thermal shock temperatures for 0.1 s: 300 ˚C (b); 400 ˚C (c); 600 ˚C (d) and 700 ˚C (e); (f) UV-vis-NIR spectra of gold nanoshells upon various thermal shock temperatures from 300 to 800 ˚C for 100 ms.

(c) 3-D contour map for characterizing thermal history

Based on the systematic investigation of the core-shell nanostructure upon thermal shock, the correlation among the surface morphology and optical properties variation as a function of thermal treatment conditions including temperature and duration can be established. A 3-D contour map was developed based on the correlation using a second order polynominal approximation to characterize the temperature and duration effects on the surface plasmon absorption peak. It can be identified that the temperature plays a dominant role in controlling the shift of the SP peak at the very short time period of 100 ms. At relatively low temperature, the silica-Au core shell nanostructure is sensitive to the thermal shock at the time scale of less than 1 second, and at high temperature, significant change occurred at a very short time frame within 300 ms, leading to distinct SP peak shift. Different 3-D contour maps were constructed for the core-shell nanostructure-based nano-thermometers with different surface coverage and initial SP properties. The thermal history (temperature and duration) of a thermal event can be retrieved based on the best estimation of two different curves intersected with two different contour maps.

In order to validate the 3-D thermal model, we have performed independent thermal shock experiments at different temperature and duration, and the corresponding surface plasmon properties were measured. The temperature and duration of the thermal sensor experienced were calculated from the 3-D thermal model, and benchmarked with the real thermal treatment conditions. An accuracy of less than 3% uncertainty in determining temperature was realized. The determination of the duration was less accurate specifically at long duration above 500 ms as the surface morphology and optical properties variation show less duration dependence at longer duration due to the extremely fast dewetting dynamics at the nano-scale.

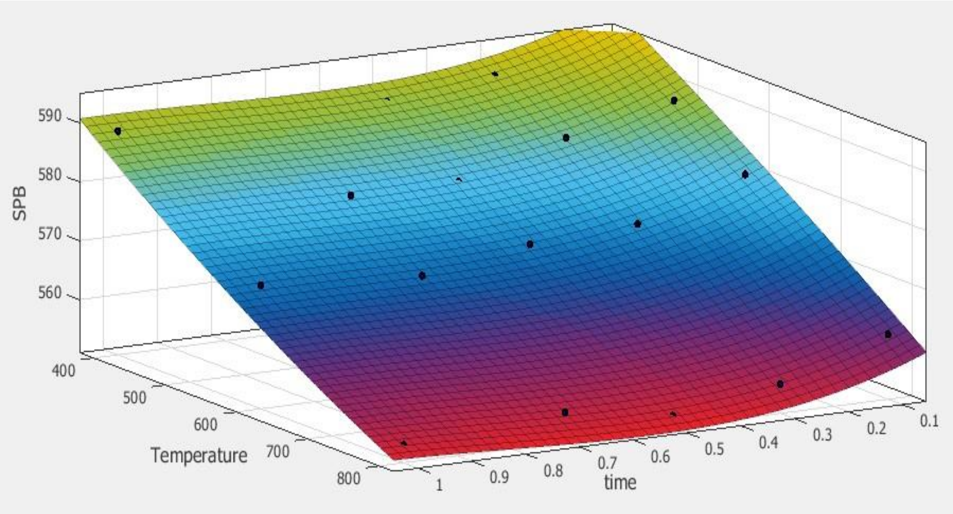

Figure 3. A 3-D thermal model of the core shell nanostructure as a thermal sensor. The duration is within 100 ms to 1 second, and temperature ranges from 400 to 800 ^{o}C.

These results of the silica/Au core shell structure were reported in a manuscript published in Advanced Functional Materials (2013, DOI: 10.1002/adfm.201303191).

(d) Feasibility evaluation of the core/shell nanostructure for real applications

A key issue for the potential application of the silica/Au core shell nanostructure for real detection is the reproducibility and sensitively in real environment. The scientific principle for temperature sensing for the core shell structure is based on the thermal dewetting-induced morphology and the associated optical properties variation. The debris of the detonation event may affect the sensitivity and applicability as sensor elements based on optical properties variation. To testify this, we have performed systematic studies to investigate the interference and impact of heterogeneous phase or impurity with the sensor elements with the focus on the reproducibility of the absorption spectra. These results indicated that the optical properties won't be affected by the second phase or impurity as it relates to the intrinsic electrical structure and electron field/nanostructure interaction. Therefore, the core shell does show potential used as sensors in a detonation event.

(e) Response of Silica/Au core shell nanostructure upon shock wave and pulsed laser annealing

To further test the time response of the core shell nanostructures in sensing thermal events, we also conducted shock tube experiments at very short time of mill-second time frame. The core shell structure survived the shock wave testing. Shift of the absorption peaks was also observed along with the microstructure evolution showing thermal-induced dewetting behavior. These results suggest that our samples are sensitive to thermal events even at an extremely fast time scale down to ms time frame.

The core-shell nanostructure was also tested by pulsed laser annealing with well controlled pulsed time from 20 ms to 100 ms and controlled laser power. Similar to the thermal treatment induced by pyroprobe, a drastic morphological evolution was observed, leading to significant variation of surface plasmon resonance. The reflectance of the surface plasmon was correlated well with the laser power, further testifying that our materials are extremely sensitive and capable of temperature sensing at a very short time frame of 20 ms. Further experiments and analysis, particularly heating transfer modeling in correlating the laser power and temperature, should be performed in order to develop the correlation among laser power, temperature, and optical properties response for accurate temperature measurements.

(3) Graphene-based materials for heat transfer media and sense materials

We also explored the potential of using the graphene-based materials (flexible graphene paper) as an effective heat transfer media and substrate to host silica/Au core shell nanostructures. The microstructure, morphology and surface plasmon properties of the silica/Au core shell nanostructures dispersed on graphene matrix were tested based on the combination of different materials characterization approaches including SEM, TEM, Raman and UV-vis-IR spectroscopy.

In addition, the graphene materials itself also display unique microstructure and vibration properties variation upon thermal shock, behaving as an additional mechanism for sensing temperature. The temperature dependence of the structural evolution of graphene oxide has been investigated by thermal shock testing using tube furnaces at different time duration varying from 3 to 180 seconds and temperature range (from room temperature up to 600 ^{o}C). X-ray diffraction analysis on the thermally-treated graphene oxide suggested an excellent correlation in the gradually-decreased lattice space of the intercalated graphite layers with temperature as a result of removal of functional groups upon thermal shock. These results indicated emerging potential of using graphene sheet as effective thermal sensor materials to capture the temperature and time variation of a thermal event. These data will be summarized into a manuscript for journal publications.

(4) Nanowire nano-thermometer

A nanowire-based nano-thermometer was developed based on the filling of metals into a nanochannel design. Particularly, different metal alloys with tunable metlingpoints were used to created nanowires in nanopores of anodic aluminium oxide by mechanical pressure injection. These nanowires inside AAO channels can behave as effective thermal sensors for temperature measurement. The sensing mechanism is based on the electrical resistance variations of nanowires upon temperature change above their melting points, leading to the breaking down of the nanowires into disconnected short nanorods due to Rayleigh instability. These results were summarized in a recent publication (Nanoscale 5 (2013) 9532).

(5) Personnel and Publications Metric

The personnel and publication metrics was summarized in the attached excel file. A detailed narrative of the metrics was elaborated below

(a) Personnel Supported

This DTRA project supported one graduate student at Rensselaer Polytechnic Institute, Mr. Hongtao Sun, and the results on Au-based nanostructure forms the basis of his doctoral thesis. Mr. Sun is expected to defend and graduate in the summer of 2014. Additionally, a post-doc research fellow (Dr. Shawn Sun) upon the support of Prof. Jie Lian’s start-up fund provided by RPI is also working extensively on this DTRA project. Leveraging with Lian’s start-up fund, the support of DTRA will have a significant impact on education and training young scientists and workforces for defense applications as well. At Texas State University, this DTRA project supported a postdoc research fellow, Dr. Zhihong Liu and summer of the co-PI Prof. Qingkai Yu. The specific work performed by these personnel is described below:

- Graduate students: Mr Hongtao Sun (Silica/Au core shell nanostructure synthesis, characterization and thermal testing); and Mr. Guoqing Xin (development of graphene-based thermal transport media as effective substrates for the nano-thermometers.
- Postdoc research fellows: Dr. Xiang Sun (partially supported by the DTRA project) focusing on the graphene-based nanostructure synthesis, thermal testing and potential exploration; Dr. Zhihong Liu (partially supported by the DTRA project) worked on the nanowire based nanothermometer and pulsed laser annealing of the silica/Au core shell nanostructures.

(b) Publications

1. G. K. Wang, X. Sun, C. S. Liu, J. Lian, “Tailored Degree of Oxidation of Graphene Oxide by Simple Chemical Reactions”, Appl. Phys. Lett., 2011, 99, 053114.

2. G. K. Wang, X. Sun, F. Y. Lu, Q. K. Yu and J. Lian, “Controlled synthesis of $MnSn(OH)_6$ graphene nanocomposites and their electrochemical properties as capacitive materials”, Journal of Solid State Chemistry 185 (2012) 172.

3. X. Sun, X. Ming, G. K. Wang, et al., “Atomic Layer Deposition of TiO2 on Graphene for Supercapacitors”, Journal of the Electrochemical Society 159 (2012) A364.

4. G. K. Wang, X. Sun, F. Y. Lu, et al., “Flexible Pillared Graphene-Paper Electrodes for High-performance Electrochemical Supercapacitors”, Small (2012) 452.

5. H. T. Sun, M. P. Yu, G. K. Wang, X. Sun and J. Lian, “Temperature-Dependent Morphology Evolution and Surface Plasmon Absorption of Ultrathin Gold Island Films” J. Phys. Chem. C 116 (2012) 9000-9008.

6. H. T. Sun, M. P. Yu, X. Sun, G. K. Wang and J. Lian, “Ultrathin Gold Island Film-based Ex-situ Nanothermometer for Effective Temperature Recording and Fast Readout”, Journal of Physics Chemistry C 117 (2013) 3366-3373.

7. D. Shao, H. T. Sun, M. P. Yu, J. Lian, S. Sawyer, “Enhanced ultraviolet (UV) emission from polyvinyl-alcohol (PVA) ZnO nanoparticles using a SiO_2-Au core/shell structure”, Nano Letters 12 (2012) 5840-5844.

8. Hongtao Sun, Xiang Sun, Mingpeng Yu, Ashish Kumar Mishra, Liping Huang, and Jie Lian, “Silica-gold core shell nnaosphere for ultrafast dynamic nanothermometer”, Advanced Functional Mateirals 2013 DOI: 10.1002/adfm.201303191.

9. Hongtao Sun, Mingpeng Yu, Xiang Sun, Gongkai Wang and Jie Lian, Ultrathin Gold Island Films for Time-dependent Temperature Sensing, Journal of Nanoparticle Research 16 (2014) 2273.

10. Peng Peng, Zhihua Su, Zhihong Liu, Qingkai Yu, Zhengdong Cheng and Jiming Bao, “Nanowire Thermometers”, Nanoscale 5 (2013) 9532.

DEPARTMENT OF DEFENSE

DEFENSE THREAT REDUCTION
AGENCY
8725 JOHN J. KINGMAN ROAD
STOP 6201
FORT BELVOIR, VA 22060
ATTN: S. PEIRIS

DEFENSE TECHNICAL
INFORMATION CENTER
8725 JOHN J. KINGMAN ROAD,
SUITE 0944
FT. BELVOIR, VA 22060-6201
ATTN: DTIC/OCA

DEPARTMENT OF DEFENSE CONTRACTORS

QUANTERION SOLUTIONS, INC.
1680 TEXAS STREET, SE
KIRTLAND AFB, NM 87117-5669
ATTN: DTRIAC