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High Element Gold Nanorod Plasmonic Sensing Array for Harsh Environment Gas Detection Grant Proposal

Brian Janiszweski
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Grant Proposal in partial fulfillment of requirements for graduation from the College of Nanoscale Science and Engineering at the State University at Albany with Honors in Nanoscale Engineering, B.S.

Brian Janiszewski

Research Advisor: Dr. Michael Carpenter

May 2013

Abstract

In order to acquire funding for scientific endeavors very specific grant proposal documents must be written and submitted. The following is an example of that. This project was very useful because my peers and I will undoubtedly have to write a grant of some type or another in our future careers.

This specific proposal is a mock grant requesting money from the National Science Foundation to fund research into a gas sensor that utilizes gold nanostructures as sensing mechanism. The research done behind this project was performed over three semesters in the lab of Dr. Michael Carpenter form the College of Nanoscale Science and Engineering. The project was funded by the department of energy and the company United Technologies.

Acknowledgements

As with any accomplishment, one person never completes it solely themselves. I would like to acknowledge many people for helping me complete this project and supporting me throughout. First, my family who has always supported me and been there whenever I needed them. My friends here at the university and elsewhere that have always kept me sane, as well as entertained. My peers in the undergraduate program at the college of nanoscale science and engineering, although we did not realize what we were getting ourselves into, we got through it together. Those who work in the Carpenter research lab, who have helped me throughout three years of learning and scientific investigation, especially Dr. Nicholas Joy. If he had not been there none of this would have been remotely possible. Finally, Dr. Carpenter who has not only been a great advisor and but a great life mentor as well.

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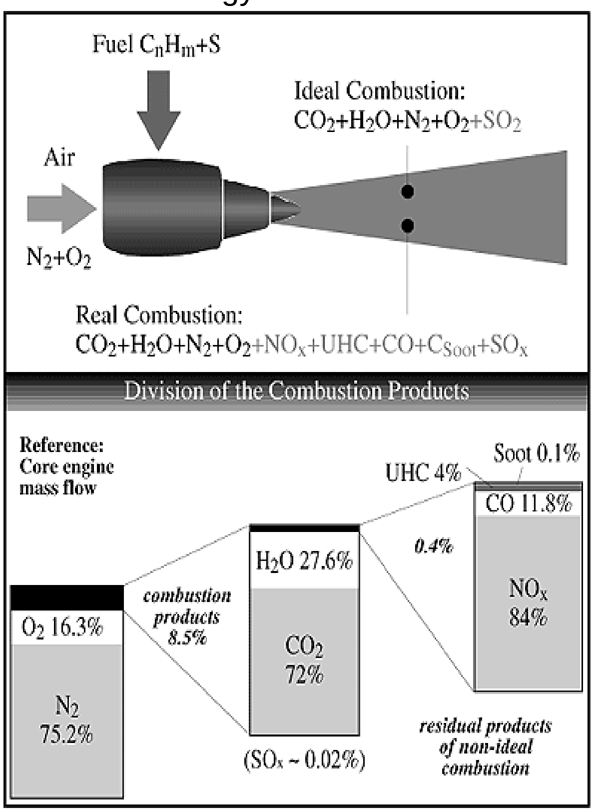
Duration: 6/15/13-6/15/14
Requested Amount: $150,000
Project Investigator: Brian Janiszewski
College of Nanoscale Science and Engineering

Project Summary

Due to new regulations, jet engines are reducing the amount of volatile gases such as NO_2, CO and residual hydrocarbons in their emissions. Currently, there is no sensor platform that is sensitive enough to detect gases within the harsh environment of jet engines that also remains stable. Optical sensors offer a versatile sensing platform that can be designed to withstand harsh environments that also offer the sensitivity needed. The proposed project is to utilize the optical properties of gold-ceramic nano-composites as an all-optical harsh environment gas sensor. This is done by using materials that demonstrate surface plasmon resonance, a phenomenon in which visible light causes the collective oscillation of electrons. This absorption is extremely dependent on the surroundings of the material and geometry of the structure and changes in unique ways in the presence of different gases, thus producing a sensing response. By utilizing different structures, each with unique properties, a sensing array can be formed that can provide the sensitivity and selectivity needed in next generation sensor technology.



Although the idea of harsh environment sensors or high element sensor arrays are not novel areas of exploration, the combination suggested is unique. Little work, if any at all, has been pursued in this area on the scale proposed. This makes the intellectual merit of this project overwhelming. The opportunity here is in providing insight into the actual sensing mechanism at work. By looking at differences in the responses of different structures at the nanoscale, either in incremental structure changes as suggested in this proposal, or in future work where radical designs are considered, a greater understanding of the surface plasmon resonance phenomenon can be attained.

The broader impact of the research proposed can be found in the primary goal of the project, which is the development of sensors that can detect the volatile gases that are produced by jet engines. As the volatile gases that are emitted become more regulated, the sensor technology will need to meet this demand as the goal toward zero volatile emissions moves forward. In addition to the area of jet engines, the research proposed can have reverberating effects in all areas of industry or research in which the detection of species within harsh environments is needed as the sensing platform suggested is adaptable. This could include factory emissions, car emissions, etc.

Project Description

Objective/Significance/Rationale

The proposed project will have four objectives that will be the focus of the research. The first will be to develop a high-element sensor array design. The second goal of the project will be to demonstrate a stable sensing response in a harsh environment. The third goal of the project will be to study the sensitivity and selectivity of the different elements in the array design and the final goal of the project will be to study the optical sensing mechanism of the sensor.

The first goal of the project will be to provide a thorough and repeatable fabrication process of the sensor. This will include sensor concept through fabrication. Different nanostructures will have different absorption interactions and it is essential that these be understood when considering the types of structures wanted in an element of the sensing array. Fabrication of the sensing array will follow the same fabrication process developed by the research group with a focus on how to improve all parts of the process to create a more stable sensor. Optimization of the array and its optical response will be the next step whether it is through redesign of sensor or the optical equipment used to gather useful data.

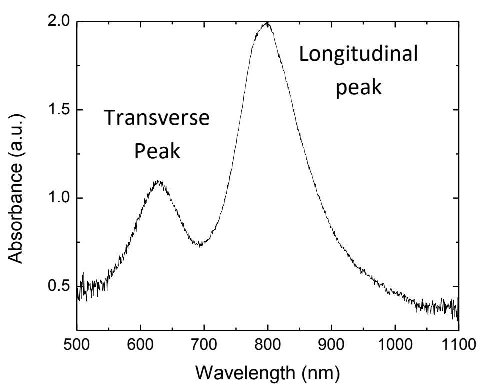
The next objective of the project will be to retrieve a stable and useful sensing response from the high element array. It is important to prove that harsh environments, which may include high temperatures and/or volatile gases, do not degrade the sensor over time and that experiments are repeatable. The conditions that the sensor will be subjected to are harsh and could possibly change the macro or microstructure of the sensor, which could result in sensing data that is misguiding, or has no meaning. Without sensing data that contains useful information, it would be ill advised and wasteful to continue working towards the next objectives of the project.

The third objective of the project is to study the sensitivity and selectivity of the sensor array. The response of the sensor is paramount to the success of the project meaning that data analysis will be a majority of the project. While data analysis techniques have already been formed within the research group, there is room for optimization of these techniques as well as new ways to accommodate the large amount of data that comes with a high element array. Methods such as figuring out the magnitude of the sensing response compared with the concentration of gas, or looking at how one structure may be selective while another is not would be examples of data analysis. While these may seem like trivial tasks at first, they can become complex when looking at 20 different structures.

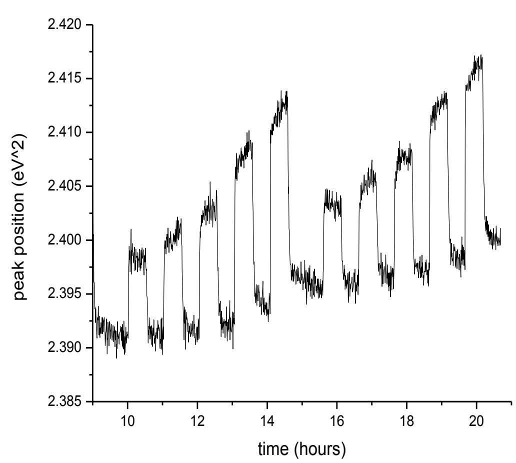
The final task of the project will to look at the fundamental physics and chemistry of optical response of the sensing material structure. Currently, the fundamental reason of the sensing response is not known. However, by using different periodic geometric structures there may be a way to distinguish what the reason, or rather, the strongest reason is for the actual optical response.

Introduction and Background

Surface plasmon resonance (SPR) is the optical excitation of valence electrons that causes them to collectively oscillate at a resonant frequency. For noble metals (Cu, Ag, Au), this resonant frequency is often near the frequency of visible light, resulting in a large amount of absorption in this part of the spectrum. For nanostructured materials, the plasmon resonance becomes localized on the structures, making it very intense compared to its geometry. The absorption is highly dependent on the shape of the nanoparticle and varies from structure to structure. For example, stimulating localized surface plasmon resonance (LSPR) in a spherical gold nanoparticle will result in absorption in the form of a single absorption peak. However, for a gold nanorod, the LSPR will manifest itself through a double-peak shape. One absorption peak corresponding to the transverse direction, and another corresponding to the longitudinal direction along the rod. An example graph of this can be seen below.

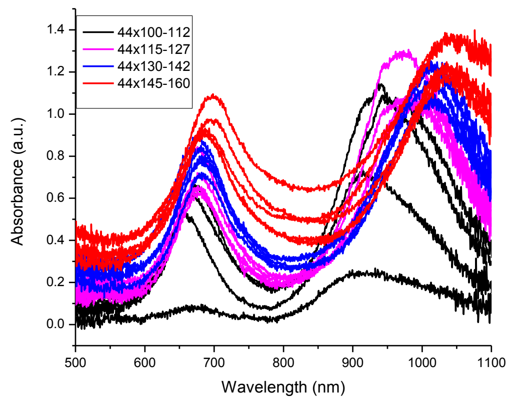


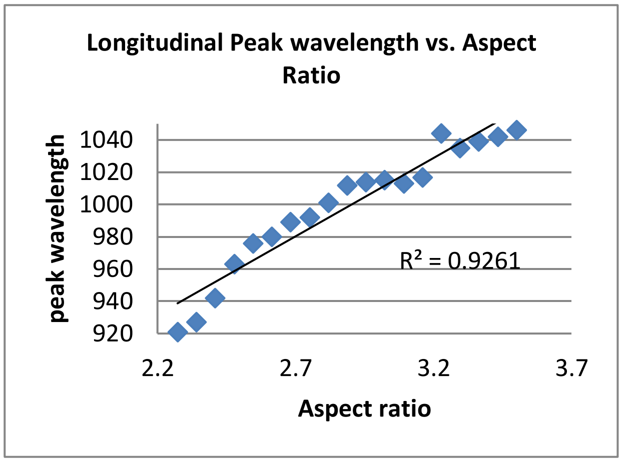
The peak absorbance wavelengths for both the transverse and longitudinal peaks are extremely dependent on changes in the environment surrounding them. This property makes these resonating nanostructures functional as sensors. The application this group is researching is to use these structures and other like it as gas sensors in harsh environments. In this case, harsh environment means high temperature (~500 °C) and in the presence of reactive gases (NO_2, CO_2, H_2). Significant progress has been made in this area by using arrays of gold nanoparticles or nanorods encapsulated in oxide materials such as cerium dioxide, titanium dioxide and yttria stabilized zirconia (YSZ). Encapsulation is accomplished by using physical vapor deposition and is used to thermally stabilize the gold nanostructures. This step is extremely important in the fabrication process because without a stable matrix, the gold nanostructures would degrade and the dual peak sensing response would be lost. Once fabricated, the peak absorbance wavelengths are monitored as a function of gas concentration at high temperature. This results in clear shifts in the peak wavelength absorbance giving rise to a sensing response. A figure of typical sensing data is shown to the right. In this figure, nanorods are being kept at 500 °C and are being exposed to an increasing concentration of hydrogen gas (200, 500, 1000, 5000, and 10,000 ppm) for one hour at a time and the peak position is tracked and plotted vs. time. One of the reasons that there is a focus on nanorods is that at equilibrium, longitudinal peak absorbance wavelength of the structure can be tuned by



changing the aspect ratio of the nanorod i.e. change the length while keeping the width constant. This allows the synthesis of nanorods that absorb at a desired wavelength.

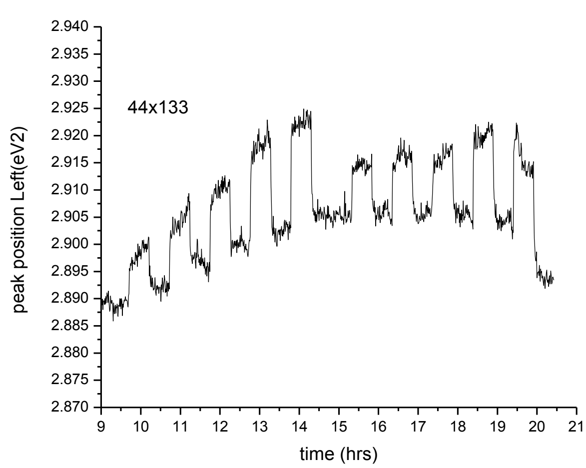
Past research has focused on one aspect ratio at a time. The purpose of this research project is to engineer a high element sensing array that will help investigate the sensing properties. Significant progress has already been made on this front as well. Samples have been fabricated that yield spectra that can be studied and monitored. An example of the type of spectra that can be attained, as well as the aspect ratio dependence it displays can be seen below.

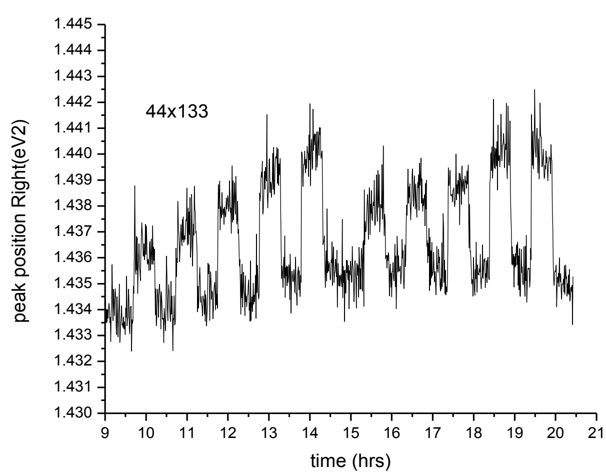


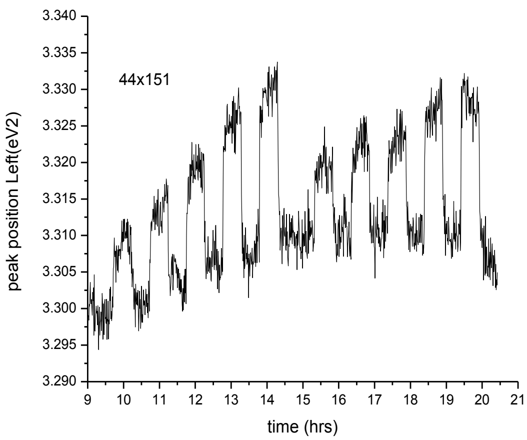


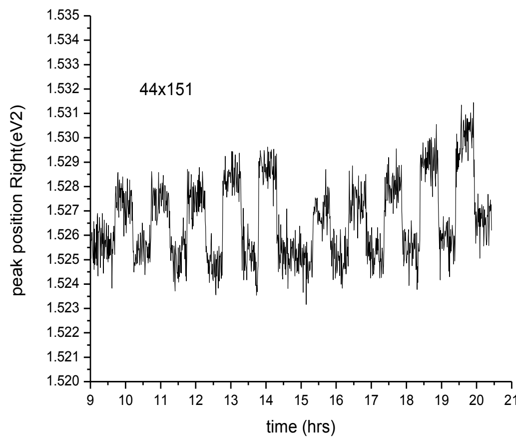
The figure on the left shows the absorption spectra of 20 different elements on the sensor array and the figure on the left shows the position of the longitudinal peak as a function of aspect ratio. One can see that as the rods go to larger aspect ratios the peak position moves father into the NIR part of the electromagnetic spectrum. There is room for improvement in this process. Sample fabrication can be completed although it far from perfect which can lead to poor absorption signals and sensing responses. Optimizing this process could eliminate heterogeneity in the signal as well lead to better sensing data.

Furthermore, sensing data has already been gathered from these preliminary samples. The data shows a clear sensing response, however experimental error as well as sample heterogeneity make this data only a preliminary test with much more work to be done. This data can be seen below for two of the elements which were exposed to hydrogen at the concentrations mentioned above.





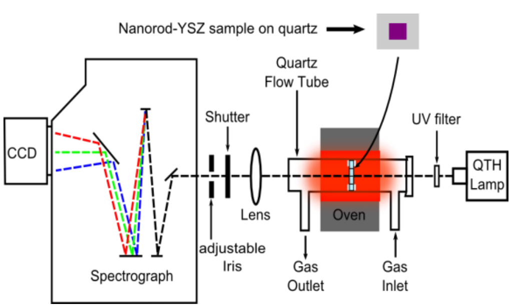




This work is promising and can be scaled up to include the sensing results of up to 20 elements as opposed to one or two. The signal to noise ratio is larger than wanted and the changes in baseline show that while a sensing response can be retrieved, the baseline is fluctuating which could be the sign of a yet to be understood phenomena. Further experiments which could be done include using principal component analysis to see how the different rod structures respond to the different gases to see if a selectivity, as well as sensitivity can be found. Finally, different geometries and structures, a study could be done on how the fundamental sensing mechanism works. For example, by creating bow tie structures, a destructive interference pattern can be made that changes the absorption signal. Another example would be a study on how an ordered array, which contains diffraction peaks, changes the absorption and sensing properties.

Statement of Work

Experiments will consist of flowtube experiments where the sample is placed in a furnace that is brought to high temperature and exposed to different gases. The peak of the absorption spectrum is monitored with time and the change in this peak absorption spectra is the sensing mechanism.



The figure at the right shows a schematic of experimental setup. Light enters a quartz flowtube and the absorption is monitored by a CCD camera which is hooked into a computer where data can be monitored and stored. The primary work of the experimenter will be data analysis in which the response will be analyzed. Statistical methods are the primary means by which the data is analyzed. As the concept of a high element array will bring in ten to twenty times the amount of work that a typical sensing experiment would bring in, a decent amount of time will be dedicated to analyzing the response. However, sample fabrication and design will be a part of this as well.

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Biographical Sketch

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A. PROFESSIONAL PREPARATION

College/University	Major	Degree & Year
University at Albany	Nanoscale Engineering	B.S. 2013

B. ACADEMIC/PROFESSIONAL APPOINTMENTS
Research Fellow, National Institute of Standards and Technology 2012
Research Assistant, Research Foundation, University at Albany 2011
Research Intern, College of Nanoscale Science and Engineering 2010

C. PUBLICATIONS
N. A. Joy, B. K. Janiszewski, S. Novak, T. W. Johnson, S. Oh, A. Raghunathan, J. Hartley, M. A. Carpenter. Thermal Stability of Gold Nanorods for High-Temperature Plasmonic Sensing, Journal of Physical Chemistry C, Submitted February 2013

D. SYNERGISTIC ACTIVITIES
Example 1: Volunteering at the Children's Museum of Science and Technology (CMOST)

COLLABORATORS AND OTHER AFFILIATIONS
Collaborators over The Last 48 Months:
Timothy Johnson, University of Minnesota- Modeling the optical absorption of gold nanorods
Sang-Hyun Oh, University of Minnesota- Modeling the optical absorption of gold nanorods

Graduate and Postdoctoral Advisors
Dr. Michael Carpenter, College of Nanoscale Science and Engineering, University at Albany

Thesis Advisor and Postgraduate Scholar Sponsors over the Last Five Years:
Graduate Students: Phillip Rogers, Nicholas Joy, Gnanprakash Dharmalingham, Selim Unal, College of Nanoscale Science and Engineering
Total Number of Graduate Students advised:4

Budget: College of Nanoscale Science and Engineering

Sponsor:Department of Energy		High Element Gold Nanorod Plasmonic Sensing Array for Harsh Environment Gas Detection			
Project Investigator:Brian Janiszewski		Co- Project Investigator :			
Period of Time: 1 YRS					
YEAR 1					
Salaries	**% Effort**	**Annual Salary**	**Total Cost**	**Requested Funding**	**Cost Share**
Total RF Paid Employees			**$0**	**$0**	**$0**
Graduate Students	**FTE**				
Name: Brian Janiszewski	**100%**	**$21,840.00**	$21,840.00	$21,840	$0
Name: Gnanaprakash Dharmalingham	**100%**	**$21,840.00**	$21,840.00	$21,840	$0
Total Graduate Students	200%		**$43,680**	**$43,680**	**$0**
Summer					
			$0	$0	$0
			$0	$0	$0
Total Summer Salaries	0%		**$0**	**$0**	**$0**
Total Salaries			$43,680	$43,680	$0
Fringe Benefits	**Rate %**	**$ Base**			
State Employees	50.81%	$0	$0	$0	$0
RF Employees *	45.00%	$0	$0	$0	$0
Graduate Students *	16.00%	$43,680	$6,989	$6,989	$0
Summer	17.00%	$0	$0	$0	$0
Total Fringe Benefits			**$6,989**	**$6,989**	**$0**
Total Salaries and Fringe Benefits			**$50,669**	**$50,669**	**$0**
Other Direct Costs - Attach Details for any item listed below					
Equipment			$20,000	$20,000	$0
*Tuition			$27,800	$27,800	$0
Travel			$2,500	$2,500	$0
Materials & Supplies			$12,000	$12,000	$0
Publications				$0	$0
Total Other Direct Costs			**$62,300**	**$62,300**	**$0**
TOTAL DIRECT COSTS			**$112,969**	**$112,969**	**$0**

Facilities and Administrative Expense	Rate %	Base MTDC			
Does not incl:equip, install,tuit	53.00%	$65,169	**$34,539**	**$34,539**	**$0.00**
Total Estimated Project Cost			**$147,508**	**$147,508**	**$0**

Budget Justification

The majority of the budget will go towards the salary, tuition and overhead included for graduate students. In this case, it is believed two is necessary to handle this work because of the amount of data that needs to analyzed. The amount of data that comes in from a single experiment currently can be handled by one student, however as the project moves forward the amount will increase by ten to twenty times this so more time will need to be spent either analyzing or forming ways to analyze data. It will also provide a higher throughput of experiments, which will allow for faster optimization of the sensor design, fabrication and use. In addition to sensing experiments, characterization time and studies into how the fundamental sensing mechanism will be a second task. These types of objectives are not achievable by one student; at least two students will be needed for this task.

The second largest part of the budget will be the funds allocated toward using the Vistec electron-beam lithography tool in the 300 mm cleanroom within the College of Nanoscale Science and Engineering. This tool is key in the fabrication of a high element array. It is the ability of this tool that provide us with nanoscale features that are uniform across the pattern, which makes the proposed research possible. Time on this tool, although expensive, is worth it due to its resolution.

Of the $20,000 asked for under equipment, about $15,000 of this is for the electron beam system. $5000 of this will be for supplies such as gas cylinders, substrates such as silicon wafers, quartz, spectroscopy equipment, chemicals such as acetone, isopropyl alcohol etc. Also included in these supplies will be the materials needed to fabricate the samples as well, as there are steps that include sputtering targets. Without this money, the samples could not be fabricated and tests could not be performed.

Finally, $2,500 is allocated towards publishing fees for scientific journals, travel expenses for conferences where the project is presented, as well as the conference fees themselves.